

240. Stationary Current-Voltage Curves for Complex Electrode Processes.

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By considering stationary current-voltage curves, it is shown (a) that a general relation can be deduced for the sum of the reaction, charge transfer, and transport resistances which applies to a single electrode process of any degree of complexity, (b) that the approximate concentration-dependence of the exchange current for any step in a sequence of simple consecutive reactions can be expressed by means of a single equation, and (c) that in the absence of parallel processes this equation also applies to more complex electrode processes.

THE stoichiometric number for a given step in the mechanism of an electrode process, a concept introduced by Horiuti,¹ and the dependence of the exchange current for this step upon the concentrations of species entering into the overall stoichiometric equation,² are two of the diagnostic criteria which have been developed for the elucidation of the mechanisms of electrode processes.* The general relationships upon which the use of these two criteria depends may be deduced in a number of ways, one of which involves the consideration of stationary current-voltage curves.

These relationships have been deduced by a number of workers for various special sets of circumstances. A complete review of the many contributions in this field will not be attempted here; for our present purpose, and purely by way of illustration, it suffices to draw attention to some of the cases which have been considered. Vetter,² for example, treated the case of processes for which there is a single electron-transfer step of unit stoichiometric number, in which rate-control could be exerted both by the electrode process itself and by one or more of the transport processes. Subsequently,⁸ he considered the case of a coupled sequence of different electron-transfer steps, again of unit stoichiometric number, but on this occasion he did not include non-electron transfer steps in the reaction scheme, nor did he consider the possible effect of the transport processes upon the overall rate. Parsons⁹ considered a general sequence of steps in which there is a single rate-determining step, the stoichiometric number of which is not necessarily unity, but did not consider the possibility of transport control. This treatment was modified by Bockris³ to take transport control into account.

Recently, Mauser¹⁰ has shown how many of the earlier relations can be generalised for a sequence of simple consecutive reactions, each of which may be either an electron-transfer step or an ordinary chemical reaction taking place at the electrode surface. In order to do this, he found it necessary to assume that the reaction mechanism is known, and he then established the conditions under which one or more of the unit steps can determine the overall rate of the electrode process without, however, considering the transport processes.

It was felt that his treatment could be made even more general and, therefore, it is

* For reviews of these diagnostic criteria and references see, e.g., Bockris,³ Vetter,⁴ Grahame,⁵ Gerischer,⁶ and Delahay.⁷

¹ Horiuti, *J. Res. Inst. Catalysis, Hokkaido*, 1948, **1**, 8; Horiuti and Ikusima, *Proc. Imp. Acad. Japan*, 1939, **15**, 39.

² Vetter, *Z. phys. Chem.*, 1950, **194**, 284.

³ Bockris, "Modern Aspects of Electrochemistry," Chap. IV, Butterworths, 1954; *Ann. Rev. Phys. Chem.*, 1954, **5**, 477.

⁴ Vetter, *Z. Elektrochem.*, 1955, **59**, 596.

⁵ Grahame, *Ann. Rev. Phys. Chem.*, 1955, **6**, 337.

⁶ Gerischer, *Angew. Chem.*, 1956, **68**, 20.

⁷ Delahay, *Ann. Rev. Phys. Chem.*, 1957, **8**, 229.

⁸ Vetter, *Z. Naturforsch.*, 1952, **7a**, 328.

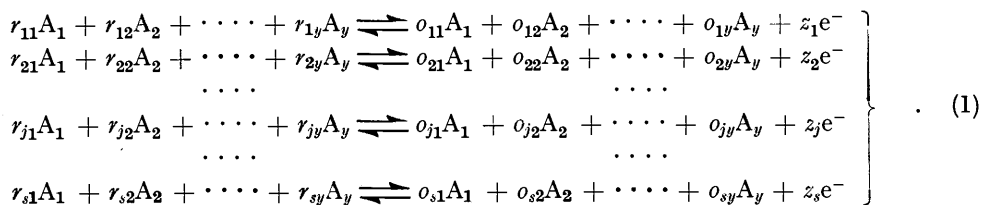
⁹ Parsons, *Trans. Faraday Soc.*, 1951, **47**, 1332.

¹⁰ Mauser, *Z. Elektrochem.*, 1958, **62**, 419.

the purpose of the present work to show (a) that a general relation for the initial slope of the current-voltage curve can be deduced which applies to a single electrode process of any degree of complexity, whatever the degree of transport control, (b) that the multiplicity of equations obtained by Mauser for the concentration dependence of the exchange velocities can be replaced by a more general equation, and (c) that this equation is not only valid for systems of simple consecutive reactions of the type considered by Mauser, but also applies to more complex processes. To simplify the problem, it will be assumed that an excess of indifferent electrolyte is present.⁸

1. THE STOICHEIOMETRIC EQUATION AND EXCHANGE VELOCITIES

The course of the electrode process will be represented by the following set of unit steps, no specific order being assumed at the outset, but there being s different unit steps in all:



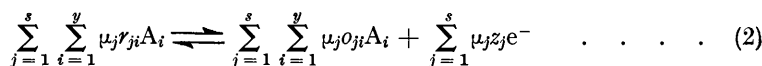
It should be noted that A_1, A_2, \dots, A_y , together represent every different type of reactant, product, and intermediate species entering into the mechanism, where these three terms will be defined below. If there are n intermediate species in a given mechanism, it will be convenient to identify them with the species A_1, A_2, \dots, A_n .

By a unit step is meant a simple step to which the law of mass action is directly applicable, so that the stoichiometric coefficients o and r are also kinetic coefficients and hence are either small positive integers or zero; they can never be negative. For this reason, and in order to avoid confusion with the commonly employed stoichiometric coefficients (denoted by ν and introduced below), o and r will be termed the kinetic coefficients while ν will simply be termed the stoichiometric coefficient. In practice, the possible values for any kinetic coefficient so defined are 0, 1, and 2.

For any unit step, say the j -th, z_j can be zero (ordinary chemical step), 1 (in the case, for example, of an electron-transfer step in a redox process) or 2, 3, etc. (e.g., incorporation of a multivalent cation into the lattice of the electrode).⁵

At first sight this notation may seem unnecessarily cumbersome, particularly since most of the kinetic coefficients appearing in the equations (1) are zero. It has been chosen for three reasons. First, these coefficients are, in fact, those which are established by experimental kinetic studies: secondly, by means of these kinetic coefficients we can define unambiguously the stoichiometric number of any given step; thirdly, this notation, or its equivalent, is necessary for the complete generality of the arguments advanced in the following sections.

The overall stoichiometric equation for the electrode process can now be formed, and the stoichiometric number of a given unit step can be defined, in the following way. Multiplying each of the equations (1) by the corresponding stoichiometric number, μ_j for the j -th unit step, and adding the s equations gives the overall stoichiometric equation:



the stoichiometric numbers being so chosen that for any intermediate species, say A_n , we have:

$$\sum_{j=1}^s \mu_j r_{jn} = \sum_{j=1}^s \mu_j o_{jn} \quad (3)$$

The usual stoichiometric coefficients, ν_{ji} for the species A_i in the j -th unit step, are obtained from expressions of the form:

$$o_{ji} - r_{ji} = \nu_{ji} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and for the same species in the overall stoichiometric equation

$$\sum_{j=1}^s \mu_j o_{ji} - \sum_{j=1}^s \mu_j r_{ji} = \sum_{j=1}^s \mu_j \nu_{ji} = \nu_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

From equation (5), if ν_i is negative then the species A_i is a reactant, but if positive it is a product. Equation (3) is based upon the usual definition of an intermediate species, $\nu_i = 0$.^{*} Hence the overall stoichiometric equation may also be written in the more usual form:

$$\sum_{i=1}^y \nu_i A_i + z e^- = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where

$$z = \sum_{j=1}^s \mu_j z_j \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and, because of the assumption of the presence of an excess of indifferent electrolyte, the Nernst equation for the equilibrium electrode potential, ϕ_o , may be expressed in the approximate form:

$$\phi_o = \phi^\circ + \frac{RT}{zF} \sum_{i=1}^y \nu_i \ln C_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

In this equation, ϕ° is the standard (concentration) electrode potential, and C_i denotes the concentration of the i -th species at electrochemical equilibrium.

The net velocity of the j -th unit step when the electrode is sustaining a current i may be written: †

$$v_j = k_{j,a} \exp(\alpha_j z_j F \phi / RT) \prod_{i=1}^y \bar{C}_i^{\nu_{ji}} - k_{j,c} \exp(-\beta_j z_j F \phi / RT) \prod_{i=1}^y \bar{C}_i^{\nu_{ji}'} \quad . \quad . \quad . \quad . \quad (9)$$

where ϕ is the potential of the working electrode, \bar{C}_i denotes the stationary concentration of A_i at the electrode surface, and α_j and β_j are the transfer coefficients. It will be assumed that α_j and β_j sum to unity, as is usually, but not necessarily,¹¹ the case, and that their values do not vary with ϕ . When $z_j = 0$ (chemical reaction), the anodic and cathodic rate constants for this unit step, $k_{j,a}$ and $k_{j,c}$, respectively, are the ordinary chemical rate constants.

From equation (9), the exchange velocity of the j -th unit step is given by:

$$\begin{aligned} v_{j0} &= k_{j,a} \exp(\alpha_j z_j F \phi_o / RT) \prod_{i=1}^y C_i^{\nu_{ji}} \\ &= k_{j,c} \exp(-\beta_j z_j F \phi_o / RT) \prod_{i=1}^y C_i^{\nu_{ji}'} \quad . \quad . \quad . \quad . \quad (10) \end{aligned}$$

* If the terms "reactant," "product," and "intermediate" are defined in this way, the use of the kinetic coefficients ν_{ji} and ν_{ji}' obviates the need for specifying whether a given species A_i is a "reduced" or "oxidised" species in the j -th unit step, etc. The stoichiometric coefficients ν_{ji} and ν_{ji}' should not be confused with those used by Mauser.¹⁰

† See, e.g., Vetter.^{2,4} The net velocity and current will be taken as positive for net anodic processes and negative for net cathodic processes.

¹¹ Audubert, *J. Phys. Radium*, 1942, **3**, 81; *Discuss. Faraday Soc.*, 1947, **1**, 72; Bonnemay, *Compt. rend.*, 1946, **222**, 793, 1222; **223**, 76; *J. Chim. phys.*, 1947, **44**, 187; Riddiford, "Surface Phenomena in Chemistry and Biology," Pergamon, London, 1958, p. 224.

and is positive. The condition for a stationary state can be expressed in the form: *

$$v_1/\mu_1 = v_2/\mu_2 = \dots = v_s/\mu_s = v \quad (11)$$

where v , the overall velocity, refers to the process symbolised by equations (2) and (6). Then

$$v = i/z\mathbf{F} \quad (12)$$

and, like the current i , is taken as positive for net anodic processes but as negative for net cathodic processes.

2. THE INITIAL SLOPE OF THE CURRENT-VOLTAGE CURVE, AND THE EXCHANGE CURRENTS

From equations (9)–(12), the ratio of the net velocity of the j -th unit step to the exchange velocity of that step is given by:

$$\frac{v_j}{v_{j0}} = \frac{\mu_j i}{z\mathbf{F}v_{j0}} = \exp(\alpha_j z_j \eta \mathbf{F}/RT) \prod_{i=1}^y \left(\frac{\bar{C}_i}{C_i}\right)^{r_{ji}} - \exp(-\beta_j z_j \eta \mathbf{F}/RT) \prod_{i=1}^y \left(\frac{\bar{C}_i}{C_i}\right)^{o_{ji}} \quad (13)$$

where

$$\eta = \phi - \phi_s \quad (14)$$

is the overpotential; η is positive for net anodic processes. Differentiating equation (13) with respect to ϕ gives:

$$\begin{aligned} \frac{\mu_j}{z\mathbf{F}v_{j0}} \cdot \frac{\partial i}{\partial \phi} &= \exp(\alpha_j z_j \eta \mathbf{F}/RT) \prod_{i=1}^y \left(\frac{\bar{C}_i}{C_i}\right)^{r_{ji}} \left\{ \alpha_j z_j \mathbf{F}/RT + \sum_{i=1}^y r_{ji} \frac{\partial \ln \bar{C}_i}{\partial \phi} \right\} \\ &- \exp(-\beta_j z_j \eta \mathbf{F}/RT) \prod_{i=1}^y \left(\frac{\bar{C}_i}{C_i}\right)^{o_{ji}} \left\{ -\beta_j z_j \mathbf{F}/RT + \sum_{i=1}^y o_{ji} \frac{\partial \ln \bar{C}_i}{\partial \phi} \right\} \quad (15) \end{aligned}$$

At electrochemical equilibrium, i and η are zero, and $\bar{C}_i = C_i$, etc., so that equation (15) becomes:

$$\frac{\mu_j}{z\mathbf{F}v_{j0}} \left(\frac{\partial i}{\partial \phi}\right)_{\eta=0} = \frac{z_j \mathbf{F}}{RT} + \sum_{i=1}^y r_{ji} \left(\frac{\partial \ln \bar{C}_i}{\partial \phi}\right)_{\eta=0} - \sum_{i=1}^y o_{ji} \left(\frac{\partial \ln \bar{C}_i}{\partial \phi}\right)_{\eta=0} \quad (16)$$

From equations (5) and (7), multiplying each of the s equations (16) by the corresponding stoichiometric number and then adding, we obtain:

$$\left(\frac{\partial i}{\partial \phi}\right)_{\eta=0} \sum_{j=1}^s \frac{\mu_j^2}{z\mathbf{F}v_{j0}} = \frac{z\mathbf{F}}{RT} - \sum_{i=1}^y v_i \left(\frac{\partial \ln \bar{C}_i}{\partial \phi}\right)_{\eta=0} \quad (17)$$

For the transport of the i -th reactant or product species to or from the electrode surface

$$\bar{C}_i/C_i = 1 - i/i_{\text{lim},i} \quad (18)$$

where $i_{\text{lim},i}$ is the transport limiting current for the given species,¹² and is reckoned positive for reactant species. From equation (18),

$$\left(\frac{\partial \ln \bar{C}_i}{\partial \phi}\right)_{\eta=0} = -\frac{1}{i_{\text{lim},i}} \left(\frac{\partial i}{\partial \phi}\right)_{\eta=0} \quad (19)$$

* Mauser¹⁰ expresses the condition, incorrectly, as $v_1\mu_1 = v_2\mu_2 = \dots = v_s\mu_s = v$.

¹² Agar and Bowden, *Proc. Roy. Soc.*, 1938, A, 169, 206.

Introducing the equations (19) into (17) gives finally:

$$\left(\frac{\partial \phi}{\partial i}\right)_{\eta=0} = \left(\frac{\partial \eta}{\partial i}\right)_{\eta=0} = \frac{RT}{zF} \left(\sum_{j=1}^s \frac{\mu_j^2}{zFv_{j0}} - \sum_{i=1}^y \frac{v_i}{i_{lim,i}} \right) \cdot \cdot \cdot \cdot \quad (20)$$

and it should be noted that this equation is valid whatever the degree of complexity of the electrode process; indeed, if one takes into account current views concerning the influence of the structure of the electrical double layer upon the rates of processes taking place at an electrode surface in the absence of specific adsorption,¹³ it is a simple matter to show that the same equation will hold whether an excess of supporting electrolyte is present or not.*

On the right-hand side of equation (20), the term $(RT/zF)\sum\mu_j^2/zFv_{j0}$ taken over all unit steps for which $z_j \neq 0$ is a measure of the charge transfer resistance; similarly, $(RT/zF)\sum\mu_k^2/zFv_{k0}$ ($z_k = 0$) and $-(RT/zF)\sum v_i/i_{lim,i}$, respectively, are measures of the reaction resistance and transport resistance.² It will be observed that the ratio $v_i/i_{lim,i}$ is negative for all A_i .

The limiting transport currents are accurately calculable in certain cases.¹⁴ In other cases, it is often possible to measure at least one of the limiting currents, when the remainder can be calculated. In such cases, however, it is important to show that the limiting current so found is, in fact, due to transport control and not the result of a slow stage in the reaction mechanism.† This is readily done by applying the usual diagnostic criteria for transport control,¹⁵ or by studying a process known to be subject to transport control in a system having the same transport characteristics as the one under investigation.^{15, 16}

Thus, the sum of the charge transfer and reaction resistances may be determined from the initial slope of the current-voltage curve, provided that this sum is not very small in comparison with the transport resistance.‡

Finally, it is instructive to consider the relation between the exchange velocity of a unit step and the corresponding exchange current.§ Parsons⁹ studied the case when there is a single rate-determining step, say the j -th, and obtained the following equation (expressed in the present notation):

$$(\partial\eta/\partial i)_{\eta=0} = RT\mu_j/zFi_{j0}$$

in which i_{j0} is the exchange current for the j -th unit step. For this particular case, equation (20) reduces to:

$$(\partial\eta/\partial i)_{\eta=0} = RT\mu_j^2/z^2F^2v_{j0}$$

which is identical with Parsons's expression provided that i_{j0} is defined as follows:

$$i_{j0} = zFv_{j0}/\mu_j \quad \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (21)$$

An alternative definition

$$i_{j0} = z_j F v_{j0}$$

has been used by some workers, possibly because they do not favour the concept of an

* Cases in which the degree of surface coverage is potential dependent will be considered elsewhere.

† See, e.g., Fig. 1 in ref. 10.

‡ If it is, one must resort to other methods. See, e.g., Gerischer⁶ and Delahay.⁷

§ The common practice of referring to the exchange current of an electrode process is misleading.

¹³ Frumkin, *Z. Elektrochem.*, 1955, **59**, 807; Breiter, Kleinerman, and Delahay, *J. Amer. Chem. Soc.*, 1958, **80**, 5111.

¹⁴ Levich, *Acta Physicochim. U.R.S.S.*, 1942, **17**, 257; *Zhur. fiz. Khim.*, 1944, **18**, 335; *Discuss. Faraday Soc.*, 1947, **1**, 37; Koutyetskii and Levich, *Doklady Akad. Nauk S.S.S.R.*, 1957, **117**, 441; Gregory and Riddiford, *J.*, 1956, 3756.

¹⁵ Bircumshaw and Riddiford, *Quart. Rev.*, 1952, **6**, 157.

¹⁶ Ibl, *Chimia*, 1955, **9**, 135.

exchange current for unit steps which do not involve electron transfer ($z_j = 0$). This view is more logical, but less convenient, than that implied by equation (21), and the latter will be retained as the general definition in the following sections.* Equation (20) may then be written in the form:

$$\left(\frac{\partial \phi}{\partial i}\right)_{\eta=0} = \frac{RT}{zF} \left(\sum_{j=1}^s \frac{\mu_j}{i_{j0}} - \sum_{i=1}^y \frac{\nu_i}{i_{\text{lim},i}} \right) \cdot \cdot \cdot \cdot \cdot \quad (20a)$$

3. DEPENDENCE OF EXCHANGE CURRENTS UPON CONCENTRATION

From equations (10) and (21), taking logarithms and introducing equation (8), we have

$$\begin{aligned} \ln i_{j0} &= \ln (k_{j,a} z^{\mu_j}) + \alpha_j z_j F \phi^0 / RT + \sum_{i=1}^y (r_{ji} + \alpha_j z_j \nu_i / z) \ln C_i \\ &= \ln (k_{j,c} z^{\mu_j}) - \beta_j z_j F \phi^0 / RT + \sum_{i=1}^y (o_{ji} - \beta_j z_j \nu_i / z) \ln C_i \quad \cdot \cdot \quad (22) \end{aligned}$$

If the concentrations of all reactant and product species are kept constant except one, say C_m , then from equation (22),

$$\begin{aligned} (\partial \ln i_{j0} / \partial \ln C_m)_{(m)} &= \sum_{i=1}^y (r_{ji} + \alpha_j z_j \nu_i / z) (\partial \ln C_i / \partial \ln C_m)_{(m)} \\ &= \sum_{i=1}^y (o_{ji} - \beta_j z_j \nu_i / z) (\partial \ln C_i / \partial \ln C_m)_{(m)} \quad \cdot \cdot \quad (23) \end{aligned}$$

[where the subscript (m) indicates that the concentrations of all reactant and product species except the m -th are kept constant. The concentrations of the intermediates will, of course, vary]. We suppose that there are n intermediate species, A_1, A_2, \dots, A_n ($\nu_i = 0$), and that A_{n+1}, \dots, A_y , are the reactant and product species ($\nu_i \neq 0$), when

$$\begin{aligned} (\partial \ln C_i / \partial \ln C_m)_{(m)} &= 1, \quad \text{for } i = m, \\ &= 0, \quad \text{for } i \neq m, 1, 2, \dots, n. \end{aligned}$$

Then equation (23) may be written:

$$\begin{aligned} (\partial \ln i_{j0} / \partial \ln C_m)_{(m)} &= r_{jm} + \alpha_j z_j \nu_m / z + \sum_{i=1}^n r_{ji} (\partial \ln C_i / \partial \ln C_m)_{(m)} \\ &= o_{jm} - \beta_j z_j \nu_m / z + \sum_{i=1}^n o_{ji} (\partial \ln C_i / \partial \ln C_m)_{(m)} \quad \cdot \quad (24) \end{aligned}$$

and it is by the application of modifications of this equation to experimental data for the variation of a given exchange current with the concentration of a reactant or product species (or with the equilibrium potential of the electrode) that the mechanisms of a number of electrode processes have been diagnosed.⁴

The modifications result from the elimination of the terms involving the concentrations of the intermediate species. Mauser,¹⁰ for example, considered the case of a mechanism comprising n simple consecutive reactions in which any A_i of the $n - 1$ intermediates A_1, A_2, \dots, A_{n-1} , appears only on the right-hand side of the i -th step and on the left-hand

* Clearly, the two definitions are different even for unit steps involving electron transfer since, in general, $z/\mu_j \neq z_j$ (see equation 7).

side of the $(i + 1)$ -th step. It follows that there is not more than one intermediate on each side of a given unit step. For this case, equation (24) becomes:

$$\begin{aligned} (\partial \ln i_{jo} / \partial \ln C_m)_{(m)} &= r_{jm} + \alpha_j z_j \nu_m / z + r_{j(j-1)} (\partial \ln C_{j-1} / \partial \ln C_m)_{(m)} \\ &= o_{jm} - \beta_j z_j \nu_m / z + o_{jj} (\partial \ln C_j / \partial \ln C_m)_{(m)} \quad . \quad (25) \end{aligned}$$

$(\partial \ln C_{j-1} / \partial \ln C_m)_{(m)}$ may be found from the $j - 1$ equations of form (25) for the steps which precede the j -th; multiplying each such equation by the corresponding stoichiometric number and adding gives:

$$\mu_{j-1} o_{(j-1)(j-1)} \left(\frac{\partial \ln C_{j-1}}{\partial \ln C_m} \right)_{(m)} = - \sum_{k=1}^{j-1} \mu_k \nu_{km} + \frac{\nu_m}{z} \sum_{k=1}^{j-1} \mu_k z_k \quad . \quad (26)$$

Similarly, from the steps $j + 1$ to n

$$\mu_{j+1} r_{(j+1)j} \left(\frac{\partial \ln C_j}{\partial \ln C_m} \right)_{(m)} = \sum_{k=j+1}^n \mu_k \nu_{km} - \frac{\nu_m}{z} \sum_{k=j+1}^n \mu_k z_k \quad . \quad (27)$$

Introducing these equations into equation (25), we find:

$$\begin{aligned} (\partial \ln i_{jo} / \partial \ln C_m)_{(m)} &= r_{jm} + \alpha_j z_j \nu_m / z - \frac{1}{\mu_j} \sum_{k=1}^{j-1} \mu_k \nu_{km} + \frac{\nu_m}{\mu_j z} \sum_{k=1}^{j-1} \mu_k z_k \\ &= o_{jm} - \beta_j z_j \nu_m / z + \frac{1}{\mu_j} \sum_{k=j+1}^n \mu_k \nu_{km} - \frac{\nu_m}{\mu_j z} \sum_{k=j+1}^n \mu_k z_k \quad . \quad (28) \end{aligned}$$

which is the general equation from which equations (51) to (58) in Mauser's article are readily obtainable, *i.e.*, the use of the stoichiometric coefficients o and r obviates the necessity for a multiplicity of equations. There is no need to specify that A_m is a reactant species, for example, nor is there any need to specify where it enters into the mechanism. The essential difference is that, whereas Mauser's considerations are based upon a given mechanism, the present argument can be applied, with obvious reservations, to any mechanism for a system comprising simple consecutive reactions, *i.e.*, it can be used for diagnostic purposes.

Other equations have been developed for diagnostic purposes. For example, in the case of a mechanism in which there is but one electron-transfer step in a sequence of simple consecutive reactions, say the j -th, Vetter¹⁷ derived the following equation:

$$(\partial \ln i_o / \partial \ln \phi_o)_{(m)} = \frac{F}{RT} \left(\alpha + \frac{z_{m,r}}{\nu_m |z} \right) = \frac{F}{RT} \left(-\beta + \frac{z_{m,o}}{\nu_m |z} \right) \quad . \quad (29)$$

for the case when all reactant and product species except the m -th are maintained at constant concentration, and

$$(\partial \ln i_o / \partial \ln C_m)_{(m,n)} = z_{m,r} - \nu_m z_{n,r} / \nu_n = z_{m,o} - \nu_m z_{n,o} / \nu_n \quad . \quad (30)$$

for the case when all reactant and product species are maintained at constant concentration except the m -th and n -th species, one of which is a reactant and the other a product. The concentrations of these two species are varied in such a manner that the equilibrium

¹⁷ Vetter, *Z. Elektrochem.*, 1951, **55**, 123.

potential remains unchanged. From equation (28), it is readily seen that for the case of mechanism comprising a single electron-transfer step Vetter's z terms are given by

$$z_{m,r} = r_{jm} - \frac{1}{\mu_j} \sum_{k=1}^{j-1} \mu_k \nu_{km} \quad \dots \quad (31)$$

and

$$z_{m,o} = o_{jm} + \frac{1}{\mu_j} \sum_{k=j+1}^n \mu_k \nu_{km} \quad \dots \quad (32)$$

It is of particular interest to note that Vetter's equation (30) is also valid for the case of a sequence of simple consecutive reactions in which there are two or more electron-transfer steps, a fact that could be of much assistance as a further diagnostic criterion.

4. TYPES OF MECHANISM FOR ELECTRODE PROCESSES

More than one process may take place at the surface of an electrode, for example, the simultaneous discharge of a metal cation species and of hydrogen ion at the dropping-mercury electrode at high cathodic potentials. Even if the changes occurring at the electrode surface are uniquely represented by one stoichiometric equation, however, it is still conceivable that two or more parallel processes are occurring at the surface, where by the term parallel is understood the case of reactions using the same reactants and forming the same products but proceeding by distinct routes involving completely different intermediate species.

Excluding the case of parallel processes, it is instructive to consider the possible ways in which the unit steps of the reaction route may be coupled together by means of the intermediate species or, and this amounts to the same thing, to consider the possible types of unit step. For this purpose, one need only take into account the number of different types of intermediate species entering into a given unit step; the reactant and product species are of no importance so far as the question of coupling is concerned.

The simplest form of coupling is that which Mauser¹⁰ has termed the case of simple consecutive reactions, discussed in Section 3; it might be described more conveniently as 1 to 1 coupling. The sequence begins with a unit step in which there are no intermediate species on the left-hand side, and only one intermediate species on the right-hand side. This can be described as a 0 : 1 unit step. The sequence finishes with a unit step in which one intermediate species appears on the left-hand side, but none on the other side, *i.e.* a 1 : 0 step. The remaining unit steps of the sequence can be described as 1 : 1 steps.

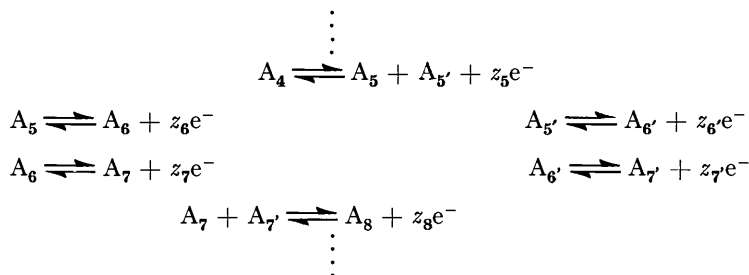
Because of the usual kinetic restrictions on the molecularity of a unit step, the possible types of alternative steps are very limited. It will be assumed that the molecularity of any unit step cannot exceed two, whichever direction is considered. On this assumption, the starting step or steps are limited to two types, 0 : 1 and 0 : 2; similarly, the final step or steps are restricted to the types 1 : 0 and 2 : 0. For the remaining unit steps of the mechanism there are four possibilities, the 1 : 1 type discussed above, 1 : 2, 2 : 1, and 2 : 2.

Any intermediate participating in the reaction mechanism must satisfy the general requirement shown in equation (3). In consequence, it will be seen that an equation of the same form as (28) is applicable to any of the eight types of unit step listed above, with but one exception (see below). All that is necessary is that equation (28) should be re-written in the form:

$$\begin{aligned} \left(\frac{\partial \ln i_{jo}}{\partial \ln C_m} \right)_{(m)} &= r_{jm} + \frac{\alpha_j z_j \nu_m}{z} - \frac{1}{\mu_j} \sum_q \mu_q \nu_{qm} + \frac{\nu_m}{\mu_j z} \sum_q \mu_q z_q \\ &= o_{jm} - \frac{\beta_j z_j \nu_m}{z} + \frac{1}{\mu_j} \sum_p \mu_p \nu_{pm} - \frac{\nu_m}{\mu_j z} \sum_p \mu_p z_p \quad \dots \quad (33) \end{aligned}$$

where the summation q is taken over all the unit steps which give rise to the one or two intermediate species on the left-hand side of the j -th unit step, and p is taken over all the unit steps generated by the intermediate species formed in the j -th unit step. Thus, if there is one unit step which uniquely determines the rate of the electrode process, by itself the fact that the logarithm of the magnitude of the exchange current varies linearly with the logarithm of the magnitude of the concentration of a reactant or product species A_m can give no indication as to the complexity of the mechanism. On the other hand, the very generality of equation (33) means that it can be applied to a single electrode process of any degree of complexity.

This equation cannot be applied, however, to a 1 : 1 step in certain improbable, but not inconceivable, circumstances. This is illustrated by the following scheme in which a set of unit steps (from which all reactants and products have been omitted) form a closed loop:



The loop shown is formed from four 1 : 1 steps, preceded by a 1 : 2 step and followed by a 2 : 1 step. Irrespective of the number of 1 : 1 steps in either arm of the loop, which could also be preceded or followed by a 2 : 2 step, it will be seen that equation (33) cannot be applied to any 1 : 1 step in such a loop. On the other hand, no single 1 : 1 unit step in a closed loop can be uniquely rate-determining, although two 1 : 1 steps, one in each arm of the loop, could jointly determine the rate.

In conclusion, it will also readily be seen that provided one generalises Mauser's¹⁰ anodic and cathodic slopes * in the form:

$$A_j^a = \frac{1}{\mu_j} \sum_q \mu_q z_q + \alpha_j z_j \qquad A_j^c = \frac{1}{\mu_j} \sum_p \mu_p z_p + \beta_j z_j$$

where the summations p and q have the same significance as in equation (33), all his conclusions concerning 1 to 1 coupling are applicable to single-electrode processes of complex form. In particular, two 1 : 1 steps, one in each arm of a closed loop, can only jointly determine the overall rate if they have exactly the same Tafel slope.

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* Mauser's anodic slope, A_j^a , is related to b_a , the anodic Tafel slope corresponding to rate control by the j -th unit step, as follows:

$$b_a \cdot A_j^a = 2.303RT/F.$$

Similarly, for the cathodic case,

$$-b_c \cdot A_j^c = 2.303RT/F.$$