THE STUDY OF THE MECHANISM OF AN ELECTRODE REACTION BY FIRST- AND SECOND-ORDER TECHNIQUES

A THEORETICAL APPROACH

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(Received 22nd December 1983; in revised form 6th February 1984)

ABSTRACT

The theoretical expressions for the faradaic admittance and the faradaic demodulation voltage are rewritten, introducing the thermodynamic restrictions proposed by Reinmuth in 1972 and without any specification of the mechanism of the electrode reaction.

The result is applied to general first-order kinetics of the type CECEC…etc. A treatment is also given in the case that one or more of the steps are of a higher order. Although the overall rate equation becomes extremely complex in such a case, it is shown that the expressions describing the faradaic admittance and the faradaic demodulation voltage are relative simple.

From some numerical examples it is made clear that, in general, by these methods discrimination between possible mechanisms can be realized on the basis of the potential dependences of the overall rate constant, operational transfer coefficient, irreversibility quotient and demodulation voltage. This work is believed to provide a framework for future quantitative studies of electrode reactions. Some ideas about its possible further elaboration are given.

(I) INTRODUCTION

In many cases, the mathematical description of the rate of redox processes at an electrode/solution interface was and still is based on the assumption of the validity of the well-known Butler–Volmer equation relating the faradaic current j_F to the interfacial potential E and the interfacial concentrations c_O and c_R by the relationship

$$j_F = -nFk_{sh}\left[c_O \exp(-\alpha\phi) - c_R \exp(1-\alpha)\phi\right] \tag{1}$$

with

$$\phi = (nF/RT)[E - E^\circ] \tag{2}$$

Many different techniques have been developed to determine the kinetic parameters k_{sh} ("standard" heterogeneous rate constant) and α (cathodic transfer coefficient) for a large number of mainly inorganic electrode reactions in various media. From

the collection of these data made by Tanaka and Tamamushi [1], one may easily obtain the impression that k_{sh} and α values are just characteristics of the system, although in some cases a physico-chemical background could be indicated, e.g. the catalyzing effect of adsorbing anions [2–4] and the more general effect of the potential across the double layer described by Frumkin [5]. However, quite often the results from different techniques or even those obtained for the same redox system by different investigators are inconsistent and, although experimental artefacts were not always recognized, these inconsistencies have inspired a number of authors to voice doubts about the general validity of the Butler–Volmer equation.

The simplest example is the case of charge transfer proceeding via a linear sequence of single-electron transfer steps. Remarkably enough, the theory of this mechanism had been given attention long ago by Vetter [6], Hurd [7], Hush and Blackledge [8] and Mohilner [9], among others. Yet it was only during the last decade that this type of mechanism was quantitatively shown to apply to the reduction of several divalent metal ions at mercury, e.g. Zn^{2+} [8,10–13], Ni^{2+} [14], Mn^{2+} [15], Cu^{2+} [16] and Cd^{2+} [8,17]. The techniques employed in these studies were relaxation techniques of different orders: the large-amplitude galvanostatic pulse method [10,12,14–16], the ac impedance method [17] and the faradaic rectification method [11]. All the studies have in common that reliable results appear to have been obtained by collecting very precise data over a very wide range of the mean electrode potential.

However, it should not be ignored that the consistency of the data with the two-electron transfer model was established only by virtue of one or more assumptions that cannot be proved experimentally. This was most clearly emphasized in a theoretical study by Reinmuth [18], who considered the information that can be obtained from relaxation experiments of different orders, if no explicit rate equation is postulated a priori; in other words, if neither the potential dependence nor the order of the charge-transfer reaction in c_O and c_R is specified. The most important conclusion was reached that it is not possible to establish unambiguously the prevalence of e.g. a first-order rate equation from data obtained using a single technique, be it zero, first, second or higher order. On the other hand, it has also been stated that inconsistencies can be expected between second-order kinetic parameters and the corresponding quantities obtained from first-order results, in the case that the rate equation is not first order in c_O or c_R. So, the combination of the two approaches is thought to be useful, if not indispensable, for making really unambiguous decisions about reaction mechanisms.

Reinmuth's reasoning being quite general, it is the aim of the present paper to work out a more explicit discussion of this matter, with reference to the ac impedance method as it has long been performed in our laboratory [19], and its combination with the recently developed second-order demodulation method [20]. The collection of fourteen relatively simple mechanisms for two-electron reductions tabulated by Bongenaar et al. [17] will serve as a starting point, but an attempt will be made to generalize their implications as much as possible.

(II) THEORY

In order to have more comprehensible expressions we will restrict ourselves initially to the simple linear overall stoichiometry inherent in a reaction of the type $O + n\,e^- \rightleftarrows R$. The implications of a more complex reaction will be discussed afterwards. For the same reason, throughout the text we will assume that we are dealing with so-called dc reversible reactions, for which the Nernst equation applies to the interfacial mean concentrations $\bar{c}_O$ and $\bar{c}_R$, most conveniently expressed by

$$\bar{c}_O D_O^{1/2} / \bar{c}_R D_R^{1/2} = [D_O/D_R]^{1/2} \exp(\phi) = \exp(\zeta) \tag{3}$$

where D_O and D_R are the respective diffusion coefficients.

The discussions will be devoted to reaction mechanisms which may consist of several partial reaction steps of different types (electron transfer, dismutation, coupled chemical steps, or even adsorption), but always with unstable intermediates, which means that the existence of coupled homogeneous reactions is excluded.

Apart from the reaction mechanism, the current–potential characteristic may also be influenced by the potential dependence of the electrical double layer. Effects of this nature are also considered separately. Throughout it is assumed that double layer charging is not affected by the presence of the electroactive species; in other words the interfacial admittance Y is composed of the double layer capacity of the supporting electrolyte in parallel with the faradaic admittance [19,21]. Likewise, demodulation by the interface gives rise to the separate "demodulation voltage sources" S_F and S_c as we described recently [20].

(II.1) General expressions for faradaic admittance and demodulation voltage source under dc reversible conditions

If all intermediates are unstable, the faradaic current j_F will be a function of the three independent principal variables ϕ, c_O and c_R. Consequently the Taylor expansion, used to derive expressions for the first- and higher-order current–voltage relationship, contains three first-order and six second-order partial derivatives; in the notation we introduced previously [22],

$$\tilde{F} = (\partial j_F/\partial \phi)_{c_O,c_R} \quad \tilde{O} = (\partial j_F/\partial c_O)_{\phi,c_R} \quad \tilde{R} = \partial j_F/\partial c_R)_{\phi,c_O} \tag{4}$$

$$\widetilde{FF} = (\partial \tilde{F}/\partial \phi)_{c_O,c_R} \quad \widetilde{OF} = (\partial \tilde{O}/\partial \phi)_{c_O,c_R} \quad \widetilde{RF} = (\partial \tilde{R}/\partial \phi)_{c_O,c_R} \tag{5}$$
$$= (\partial \tilde{F}/\partial c_O)_{\phi,c_R} \qquad = (\partial \tilde{F}/\partial c_R)_{\phi,c_O}$$

$$\widetilde{OO} = (\partial \tilde{O}/\partial c_O)_{\phi,c_R} \quad \widetilde{OR} = (\partial \tilde{O}/\partial c_R)_{\phi,c_O} \quad \widetilde{RR} = (\partial \tilde{R}/\partial c_R)_{\phi,c_O} \tag{6}$$
$$= (\partial \tilde{R}/\partial c_O)_{\phi,c_R}$$

With linear diffusion as the model for mass transfer the complex faradaic

admittance Y_F is found to obey the expression [19,22]:

$$Y_F = Y_F' + iY_F'' = \left(\frac{nF}{RT}\right)\tilde{F}\frac{p^2 + p + ip}{(p+1)^2 + 1}$$ (7)

with

$$p = \frac{(2\omega)^{1/2}}{\lambda} = \frac{(2\omega)^{1/2}nF}{\tilde{R}D_R^{-1/2} - \tilde{O}D_O^{-1/2}}$$ (8)

where ω is the angular frequency. Note that $(nF/RT)\tilde{F} = R_{ct}^{-1}$, the reciprocal of the charge-transfer resistance in the Randles equivalent circuit [21].

For the amplitude $[S_F]$ of the faradaic demodulation voltage source we recently derived an expression which, for the present purpose, is transformed into a more convenient quantity S_F^*, expressed by

$$S_F^* = [S_F]\frac{RT}{nF}\left(\frac{2\omega_H C_d}{j_A}\right)^2$$

$$= \frac{(p_H + 1)^2 + 1}{(p_H + 1)^2 + (a_H + 1)^2}\left\{-\frac{\widetilde{FF}}{2\tilde{F}} + \frac{\chi_f'}{\lambda}\frac{p_H + 2}{(p_H + 1)^2 + 1} + \frac{\chi_c'\tilde{F}}{\lambda^2}\frac{1}{(p_H + 1)^2 + 1}\right\}$$ (9)

where $p_H = (2\omega_H)^{1/2}/\lambda$ as in eqn. (8) with ω_H the high frequency; $a_H = p_H/(R_{ct}\omega_H C_d)$, and

$$\chi_f' = (\partial\lambda/\partial\phi) = (nF)^{-1}\left[\widetilde{RF}D_R^{-1/2} - \widetilde{OF}D_O^{-1/2}\right]$$ (10)

$$\chi_c' = (nF)^{-2}\left[-\widetilde{RR}D_R^{-1} + 2\widetilde{OR}D_O^{-1/2}D_R^{-1/2} - \widetilde{OO}D_O^{-1}\right]$$ (11)

The conclusion from eqn. (9) is that the demodulation effect is governed by the first-order parameter p_H and three parameters comprising combinations of first- and second-order partial derivatives. All the parameters are in principle dependent on the mean dc electrode potential, i.e. on the quantities ϕ or ζ defined in eqns. (2) and (3). S_F^* is dependent on the high frequency ω_H via the presence of the dimensionless parameter p_H.

In order to put the potential and frequency dependencies in a more intelligible form, use can be made of the relationships between the partial derivatives following from thermodynamic restrictions as derived by Reinmuth [18]. It can easily be recognized that Reinmuth's considerations hold for fluctuations around the dc current, potential and surface concentrations under dc reversible conditions, as well as in the case of fluctuations around the equilibrium state. Therefore we have

$$\tilde{O}\bar{c}_O = -\tilde{R}\bar{c}_R = -\tilde{F}$$ (12)

$$OF\bar{c}_O = \tfrac{1}{2}\left[\tilde{F} - \widetilde{FF} - \widetilde{OO}\bar{c}_O^2\right]$$ (13)

$$\widetilde{RF}\bar{c}_R = \tfrac{1}{2}\left[\tilde{F} + \widetilde{FF} + \widetilde{RR}\bar{c}_R^2\right] \tag{14}$$

$$\widetilde{OR}\bar{c}_O\bar{c}_R = -\tfrac{1}{2}\left[\widetilde{OO}\bar{c}_O^2 + \widetilde{RR}\bar{c}_R^2\right] \tag{15}$$

With these relationships, the expression for S_F^* can be rewritten in several completely equivalent forms, depending on the partial derivatives eliminated. The following version appears to be the most attractive:

$$S_F^* = \frac{\dfrac{1}{2}\dfrac{\exp(\zeta)-1}{\exp(\zeta)+1}(p_H+2) - \dfrac{\widetilde{FF}}{2\tilde{F}}(p_H^2+p_H) + \dfrac{\widetilde{RR}\bar{c}_R^2\exp(\zeta)+\widetilde{OO}\bar{c}_O^2}{2\tilde{F}\left[\exp(\zeta)+1\right]}p_H}{(p_H+1)^2+(a_H+1)^2} \tag{16}$$

in which use has also been made of eqn. (3). So, the *three terms* determining S_F^* in eqn. (9) have been rearranged to obtain three terms, but containing only *two second-order quantities* instead of three. Comparing with Reinmuth's notations [18], we see that

$$\widetilde{FF}/\tilde{F} = 1 - 2\alpha \tag{17}$$

and

$$\frac{\widetilde{RR}\bar{c}_R^2\exp(\zeta)+\widetilde{OO}\bar{c}_O^2}{\tilde{F}\left[\exp(\zeta)+1\right]} = \frac{(\nu_R^*-1)\exp(\zeta)+(1-\nu_O^*)}{\exp(\zeta)+1} \tag{18}$$

where α is to be considered as an *operational transfer coefficient*, and ν_R^* and ν_O^* as *operational stoichiometric coefficients*. As long as a rate equation has not been specified, however, the meaning and thus the usefulness of these quantities remains unclear.

The relationship between the first-order derivatives, eqn. (12), can also be used to simplify eqn. (7) for the faradaic admittance to the well-known expression [19]

$$Y_F = Y_F' + iY_F'' = \frac{\omega^{1/2}}{2\sigma}\frac{(p+1)+i}{(p+1)^2+1} \tag{19}$$

where

$$\sigma = \frac{RT}{n^2F^22^{1/2}}\left[\left(\bar{c}_O D_O^{1/2}\right)^{-1} + \left(\bar{c}_R D_R^{1/2}\right)^{-1}\right] \tag{20}$$

(II.2) Separability of the parameters

Consideration of eqns. (16)–(20) leads to the conclusion that from measurements of S_F^* at fixed potential and varied frequency the values of $p' = p_H\omega_H^{-1/2}$ and the quantities defined in eqns. (17) and (18) can be determined. From Y_F only p' can be obtained, which may be useful as a check. Repeating this at different potentials enables us to examine the potential dependence of α and to find the values of ν_R^* and ν_O^*, provided that these quantities are constants.

The latter condition, however, is not always met, as will be discussed in the following sections.

(III) EXPLICIT APPLICATIONS

In our previous paper [20] we discussed the shape and further characteristics of demodulation polarograms assuming the validity of the Butler–Volmer rate equation. The corresponding expression for S_F^* was given in eqn. (29) of Part IV. It was shown that S_F^* is an S-shaped function of the dc potential with limiting values of $+\frac{1}{2}$ at $\zeta \gg 0$ and $-\frac{1}{2}$ at $\xi \ll 0$.

Here the discussion will be extended to other rate equations.

(III.1) First-order kinetics

If a reaction mechanism can be represented by an overall rate equation of the form

$$j_F = -nF[k_f c_O - k_b c_R] = -nFk_f(E)[c_O - c_R \exp(\phi)] \tag{21}$$

the reaction is still first order in c_O and c_R. The third term in eqn. (16) equals zero, or, to put it differently, in eqn. (18) $\nu_R^* = \nu_O^* = 1$.

Eqn. (21) applies to mechanisms consisting of an arbitrary number of consecutive linear reactions, either of the type $O + e^- \rightleftarrows Y$, $Y + e^- \rightleftarrows R$ (Y being an intermediate), or of the type $O \rightleftarrows O_1$, $Y_1 \rightleftarrows Y_2$ (i.e. heterogeneous reactions without charge transfer). The overall forward rate constant is related to the individual forward rate constants k_i and the individual equilibrium constants K_i by [6,7,11,17]

$$k_f^{-1}(E) = \sum_{i=1}^{m} k_i^{-1} \prod_{j=0}^{i-1} K_j \qquad (K_O = 1) \tag{22}$$

The question is then, whether the potential dependence of $k_f(E)$ can be predicted on the basis of theoretical principles. The experimental facts collected thus far strongly suggest that each elementary single-electron transfer reaction would conform to the Butler–Volmer model with a transfer coefficient equal to 0.5. For example, in the studies of the two-step reactions mentioned earlier [8,10–17] this follows from the change of α from ca. 0.75 at positive potentials to ca. 0.25 at negative potentials, these values being in agreement with the predictions of Devanathan [23] for the two-step mechanism. A multi-step mechanism with n electron-transfer reactions would generally lead to

$$k_f^{-1}(E) = \sum_{i=1}^{n} k_{s,i}^{-1} \exp\left(\frac{i - 0.5}{n}\phi\right) \tag{23}$$

in which

$$k_{s,i} = k_i(E = E^\circ) \exp\left[\frac{F}{RT}\sum_{j=i}^{n}\left(E^\circ - E_j^\circ\right)\right] \tag{24}$$

Evidently several steps can be simultaneously rate-controlling, while their relative preponderance can to a large extent be chosen at will be adjusting the dc potential.

The operational transfer coefficient ranges from $\alpha = 0.5/n$ at negative potentials to $\alpha = 1 - (0.5/n)$ at positive potentials.

However, in some cases experimental results are such that these limits are exceeded, α tending to zero in the negative region [17] or to unity in the positive region [24]. It must be concluded that, in addition to charge-transfer steps, "chemical" reactions, i.e. not influenced by the interfacial potential difference, can also be more or less rate controlling. Assuming that these reactions can precede the first electron transfer, be intermediate and can follow the final electron transfer, eqn. (23) must be extended with a series of $n + 1$ terms:

$$k_f(E)^{-1} = \sum_{i=1}^{n+1} k_{c,i}^{-1} \exp\left(\frac{i-1}{n}\phi\right) + \sum_{i=1}^{n} k_{s,i}^{-1} \exp\left(\frac{i-0.5}{n}\phi\right) \tag{25}$$

with

$$k_{s,i} = k_i(E = E^\circ) \exp\left[\frac{F}{RT}\sum_{j=i}^{n}\left(E^\circ - E_j^\circ\right)\right] \times \prod_{j=i+1}^{n+1} K_{c,j} \tag{26}$$

$$k_{c,i} = k_{c,i}^\circ \exp\left[\frac{F}{RT}\sum_{j=i}^{n}\left(E^\circ - E_j^\circ\right)\right] \times \prod_{j=i}^{n+1} K_{c,j} \tag{27}$$

where k_i denotes the potential-dependent rate constant of the ith electron transfer, and $k_{c,i}^\circ$ the potential-independent rate constant of the heterogeneous chemical process preceding the ith electron transfer.

It should be stressed that this model is suggested by experimental evidence rather than by a soundly developed theory.

It will be evident that this model, summarized in the mathematical expression (25), should be clearly distinguished from the deeply elaborated and frequently quoted continuum theoretical treatments leading to a potential dependence of the apparent transfer coefficient as well. The latter potential dependence originates from electronic coupling of the charge transfer and the solvent polarization [25].

Of course, in expression (25) the chemical steps can sometimes be identified beyond all reasonable doubt, like the protonation of the intermediate O_2^- in the reduction of oxygen [26]. In some other cases, like the reductions of Cd(II) [17], Zn(II) [12] and $Fe(C_2O_4)_3^{3-}$ [24], however, one has to resort to hypotheses on slow heterogeneous dissociation of complexes or slow dehydration that might turn out to be true in the end.

At present, however, we feel that these "chemical" steps should be identified with the stochastic creation of energy-rich molecular fluctuations and/or the creation of

geometrical orientations at the electrode interface necessary for an electron to acquire a sufficiently high probability of transfer. These two processes, i.e. the "chemical" step and the electron transfer, are both supposed to proceed in both directions and also to be totally mutually independent.

It will be clear that if solvent molecules are involved in the stochastic processes mentioned above this explanation will not be very different from the idea of slow dehydration.

For an electrode reaction, the configuration after charge transfer, if succesful, will relax, thus making the reverse charge transfer improbable. A reverse charge transfer will be possible again only if the appropriate energetic and/or geometrical fluctuation arises. This reasoning can apply to any charge transfer step. If, in between two charge-transfer steps, there is more than one chemical step, e.g. a relaxation and an organization, these will be indistinguishable and will show up as one chemical step.

The above view is rather close to the explanation given by Conway et al. [27] of the low proton mobility in aqueous solutions. They were able to show by calculation that the rotation of a water molecule into an appropriate position is a much slower process than proton tunnelling and, in fact, is the rate-determining step.

Only a charge-transfer step at an electrode can be accelerated or decelerated by choosing the electrode potential, and by that choice the relative contribution of a step to the overall rate can be varied.

It is highly probable that both causes of a potential dependence of the operational transfer coefficient will in general be operative at the same time. Because the effect of a multi-step contribution is much more serious there is reason for some doubt about the feasibility of an experimental verification of continuum theories. In order to show a potential dependence of the transfer coefficient of an elementary charge-transfer step in an analysis like that advocated in this paper, an extremely high precision of the experimental data would be essential. For the time being, in eqn. (25) and the following, transfer coefficients of individual charge-transfer steps will be assumed to be potential independent.

The general trend in eqn. (25) is that the operational transfer coefficient decreases from $\alpha = 1$ in the anodic region to $\alpha = 0$ in the cathodic region. However, the relative weight of the constants $k_{c,i}$ and $k_{s,i}$, respectively, determines the feasibility of demonstrating the existence of all the steps. This is shown in Figs. 1 and 2 where the potential dependence of the relevant quantities k_f, α, $p' = p\omega^{-1/2}$ and S_F^* is represented for the case of an overall electrode reaction involving two electrons. Corresponding to the chosen sets of parameters, the rate control is governed by a typical mechanism, for example CECEC (all steps rate controlling) or cEcEc (only the two charge-transfer steps rate controlling), etc. A survey is given in Table 1.

It is important to note that closely similar mechanisms cannot always be distinguished. Among the symmetrical examples considered here, this especially applies to mechanisms with and without the intermediate C step. This means that the occurrence of such chemical steps will be hard to prove. On the other hand, it may happen that two dissimilar mechanisms incidentally lead to almost identical k_f vs. E curves. In that case, the second-order behaviour (S_F^* vs. E) enables a clear distinc-

tion to be made; for example, compare the dashed curves in Fig. 1 (E–E mechanism) with the continuous curves indicated with b in Fig. 2 (CECEC with the middle C dominating).

Due to the nature of eqn. (26), the value of p' attains a constant value equal to $(2D_O)^{1/2}/k_{c,n+1}$ at extreme anodic potentials; at the same time the operational transfer coefficient becomes equal to $\alpha = 1$. At extreme cathodic potentials we have $p' = (2D_O)^{1/2}/k_{c,1}$ and $\alpha = 0$. Consequently the values of S_F^* range between $+0.5$ in the anodic region and -0.5 in the cathodic region. The potential dependence in
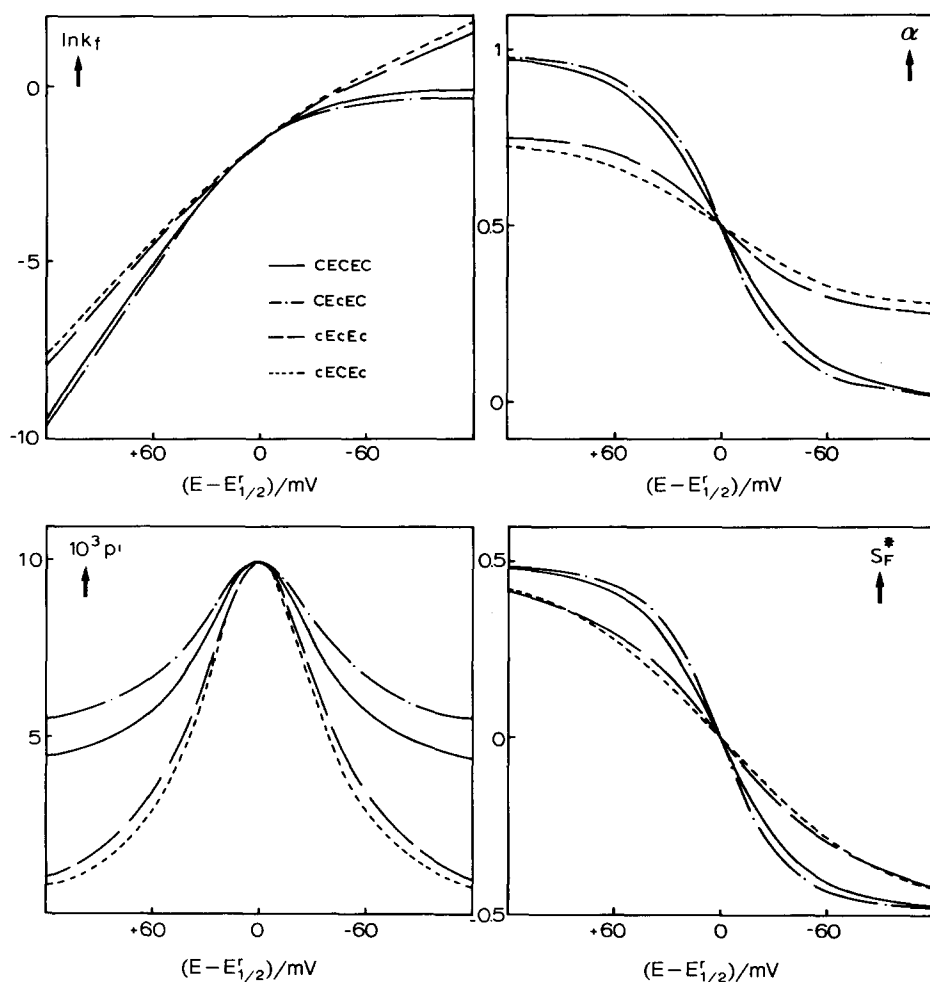

Fig. 1. Theoretical potential dependences of $\ln k_f$, α, p' and S_F^* in the case of the linear five-step mechanism for the reaction $O + 2e^- \rightleftarrows R$. Rate control by electron-transfer steps and (some) chemical steps. See Table 1. Values of other parameters: $D_O = 8 \times 10^{-6}$ cm^2 s^{-1}, $\omega_H = 2\pi \times 10^5$ s^{-1}, $C_d = 25$ μF cm^{-2}.

between those limits is sensitive to the kind of mechanism, and this sensitivity will be greater if the high frequency ω_H is increased.

A clear asymmetry in the S_F^* vs. E curve can be expected if the mechanism leads to $\alpha \neq 0.5$ at $E = E_{1/2}^r$. Experimental examples of this case will be discussed in a subsequent paper.

(III.2) Non-linear stoichiometry; "simple" rate equations

If a mechanism involves one or more higher-order reaction steps, the overall rate equation usually becomes very complex, unless it can be assumed that only one step
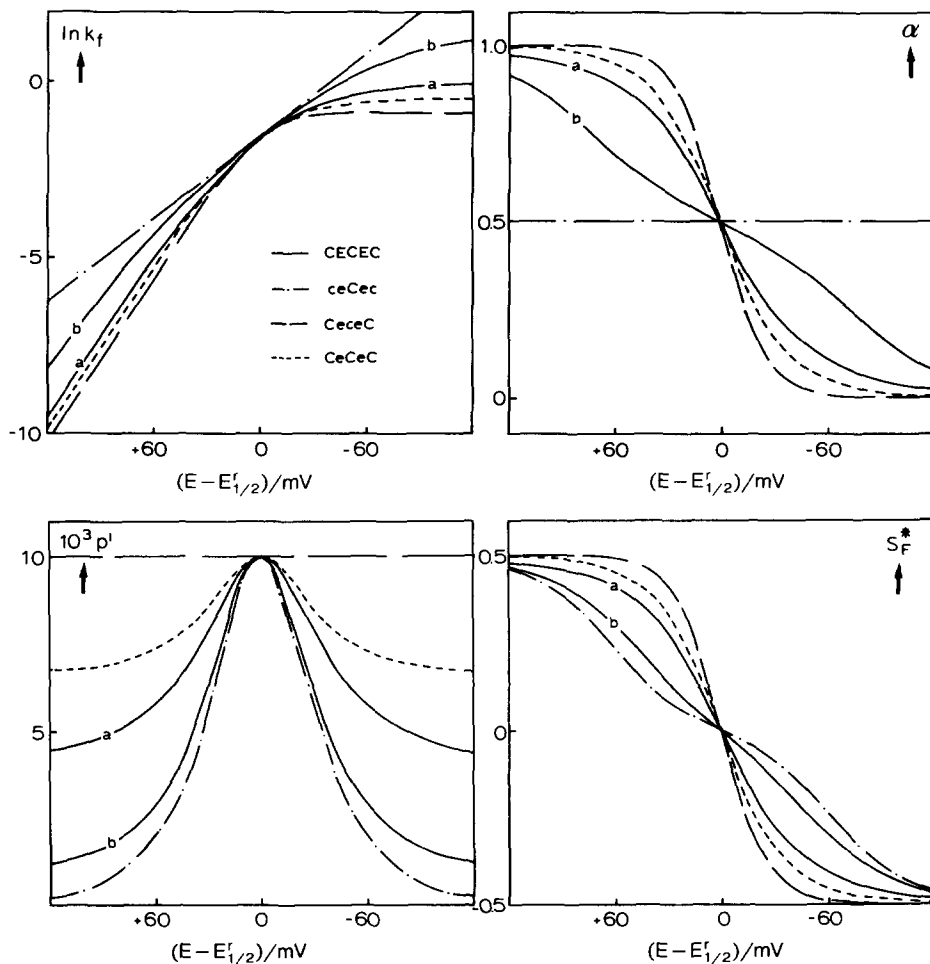

Fig. 2. Theoretical potential dependence of $\ln k_f$, α, p' and S_F^* in the case of the linear five-step mechanism for the reaction $O + 2 e^- \rightarrow R$. Rate control by chemical steps (except curves a and b). See Table 1. Other parameters as in Fig. 1.

in the whole sequence of reactions is completely rate-determining. The examples at hand in the case of $n = 2$ were discussed by Van der Pol et al. [11] and Bongenaar et al. [17]. From these treatments it can be inferred that the overall rate equation will be of the form

$$j_F = -nFk_f\left[c_O^p c_R^q - c_O^r c_R^s \exp(t\phi)\right] \tag{28}$$

where p, q, r, s are integer or non-integer numbers like 1, 2, $\frac{1}{2}$ or 0. For thermodynamic reasons the following relationship must hold:

$$p - r = s - q = t \tag{29}$$

Applying this formalism to the partial derivatives that, according to eqns. (8) and (12)–(20), determine first- and second-order behaviour, the following expressions result:

$$\tilde{F} = nFk_f t \bar{c}_O^p \bar{c}_R^q \tag{30}$$

$$p' = 2^{1/2}/\lambda = (2D_O)^{1/2}\left[1 + \exp(\zeta)\right]^{-1} k_f^{-1} t^{-1} \bar{c}_O^{(1-p)} \bar{c}_R^{(-q)} \tag{31}$$

$$\widetilde{FF}/\tilde{F} = t + 2\mathrm{d}\ln k_f/\mathrm{d}\phi = t - 2\alpha \tag{32}$$

$$\widetilde{RR}\bar{c}_R^2/\tilde{F} = q + s - 1 = 2q + t - 1 \tag{33}$$

$$\widetilde{OO}\bar{c}_O^2/\tilde{F} = 1 - p - r = 1 + t - 2p \tag{34}$$

Evidently the operational stoichiometric coefficients defined in eqn. (18) are $\nu_O^* = p + r$ and $\nu_R^* = q + s$, respectively.

The mean interfacial concentrations in the expression for p', eqn. (31), can be eliminated, e.g. in the case of Nernstian behaviour with linear diffusion by

$$\bar{c}_O = c_O^* \exp(\zeta)\left[1 + \exp(\zeta)\right]^{-1} \tag{35a}$$

$$\bar{c}_R = (D_O/D_R)^{1/2} c_O^*\left[1 + \exp(\zeta)\right]^{-1} \tag{35b}$$

TABLE 1

Values of individual rate parameters $k_{c,i}$ and $k_{s,i}$ in cm s^{-1} (see eqns. 25–27) used to calculate the theoretical potential dependence of $\ln k_f$, α, p' and S_F^* in Figs. 1 and 2 for the reaction $O + 2\,e^- \rightleftarrows R$

Type of mechanism	$k_{c,1}$	$k_{s,1}$	$k_{c,2}$	$k_{s,2}$	$k_{c,3}$
Fig. 1					
CECEC	1.0	1.0	1.0	1.0	1.0
CEcEC	0.8	0.8	1000	0.8	0.8
cEcEc	1000	0.4	1000	0.4	1000
cECEc	1000	0.6	0.6	0.6	1000
Fig. 2					
CECEC (a)	1.0	1.0	1.0	1.0	1.0
CECEC (b)	4.0	4.0	0.25	4.0	4.0
ceCec	1000	1000	0.2	1000	1000
CeceC	0.4	1000	1000	1000	0.4
CeCeC	0.6	1000	0.6	1000	0.6

Then the extrema of p' are:

if $\exp(\zeta) \gg 1$: $\quad p' = 2^{1/2} \left(c_O^* \right)^{1-p-q} D_O^{(1-q)/2} D_R^{q/2} k_f (E)^{-1} \exp[(q-1)\zeta]$

if $\exp(\zeta) \ll 1$: $\quad p' = 2^{1/2} \left(c_O^* \right)^{1-p-q} D_O^{(1-q)/2} D_R^{q/2} k_f (E)^{-1} \exp[(1-p)\zeta]$

It should be noted that p and q do not necessarily have the same value at anodic and cathodic potentials, as the rate-controlling step may be different. Accordingly, the concentration dependence may change with potential.

The potential dependence of k_f will be determined by the nature of the rate-controlling step. Direct determination of $\alpha = -\mathrm{d}\ln k_f / \mathrm{d}\phi$ is hindered by the fact that the parameter $\widetilde{FF}/\tilde{F}$, which can be obtained experimentally, contains both t and α.

An illustration of these general conclusions is presented in Fig. 3 and Table 2, where the behaviour is predicted for the mechanism which may be symbolized as CECDC:

$$O \rightleftarrows O' \qquad\qquad R_{co}$$
$$O' + e^- \rightleftarrows Y \qquad\quad R_{el}$$
$$Y \rightleftarrows Y' \qquad\qquad R_{cy}$$
$$2Y' \rightleftarrows O' + R' \qquad R_d$$
$$R' \rightleftarrows R \qquad\qquad R_{cr}$$
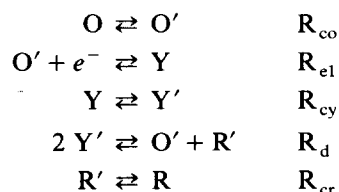
with any step rate-controlling alternately. As was done in ref. 17, the unknown concentrations of the intermediates have been eliminated by assuming that the
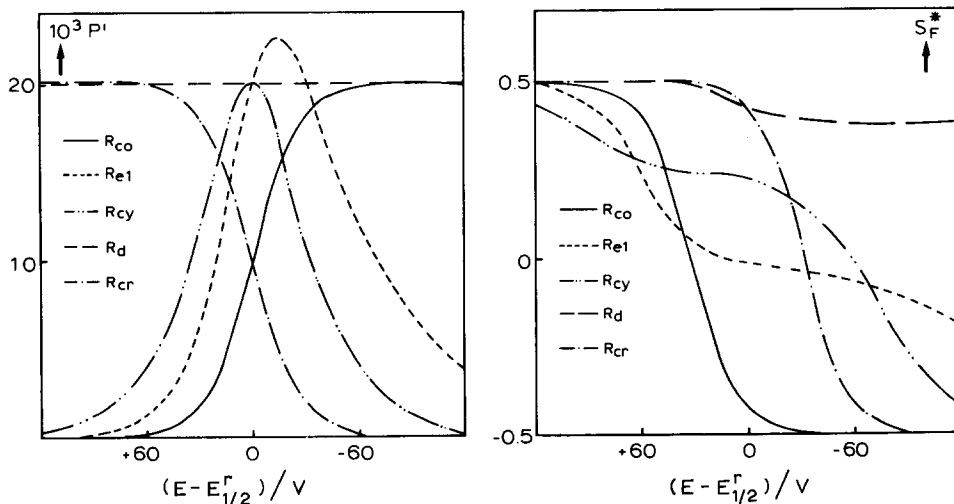

Fig. 3. Theoretical potential dependences of p' and S_F^* in the case of a non-linear five-step mechanism (see text and Table 2) for the reaction $O + 2e^- \rightarrow R$. Each curve corresponds to a case of one step being rate determining, as indicated. Value of the rate constant k_f at $E = E^\circ$: 0.2 cm s^{-1}. Other parameters as in Fig. 1.

non-controlling reactions are in virtual equilibrium. The notation in Table 2 conforms to the following set of partial rate equations:

$$(R_{co}): v_O = k_O[c_O - K_O c_{O'}] \qquad k_O \neq f(E) \qquad (36a)$$
$$K_O = k_{-O}/k_O \neq f(E)$$

$$(R_{e1}): v_1 = k_1[c_{O'} - K_1 c_Y] \qquad k_1 = k_{s1} \exp(-\tfrac{1}{2}\alpha_1\phi) \qquad (36b)$$
$$K_1 = K_1^O \exp(\tfrac{1}{2}\phi)$$
$$K_1^O = \exp[(F/RT)(E^\circ - E_1^\circ)]$$

$$(R_{cy}): v_Y = k_Y[c_Y - K_Y c_{O'}] \qquad k_Y \neq f(E) \qquad (36c)$$
$$K_Y = k_{-Y}/k_Y \neq f(E)$$

$$(R_d): v_d = k_d[(c_{Y'})^2 - K_d c_{O'} c_{R'}] \qquad k_d \neq f(E) \qquad (36d)$$
$$K_d = k_{-d}/k_d \neq f(E)$$

$$(R_{cr}): v_R = k_R[c_{R'} - K_R c_R] \qquad k_R \neq f(E) \qquad (36e)$$
$$K_R = k_{-R}/k_R \neq f(E)$$

It can be concluded that the behaviour of S_F^* especially is indicative of the non-linear mechanism. Compare, for example, the case where R_d is rate-determining in Fig. 3 with the CeceC case in Fig. 2.

The cases treated here must be considered as examples of a larger number of such types of mechanisms. The diagnostics of other examples are easily derived by analogous procedures. It is interesting to note that even a slight change in the mechanism has a drastic impact: in the case that the dismutation step R_d leads to the regeneration of O instead of O' while R_{co} is rate determining, the rate equation is determined by $p = 1$, $q = 0$, $r = \frac{1}{2}$, $s = \frac{1}{2}$ and $t = \frac{1}{2}$, cf. mechanism F1 in ref. 17.

(III.3) Non-linear stoichiometry; "complex" rate equations

From the expressions for k_f in Table 2 the conclusion must be drawn that there is no reason that in a certain potential region only one step should be rate-controlling.

TABLE 2

Expressions for $1/k_f$ and values of α, p, q, r, s and t pertaining to the five subcases (one rate-determining step) of the non-linear mechanism for the reaction $O + 2 e^- \rightleftarrows R$ represented in Fig. 3

Rate-determing step	k_f^{-1}	α	p	q	r	s	t
R_{cO}	k_0^{-1}	0	1	0	0	1	1
R_{e1}	$K_0 k_1^{-1}$	$\frac{1}{4}$	1	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
R_{cy}	$K_0 K_1 k_y^{-1}$	$\frac{1}{2}$	1	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
R_d	$K_0 K_1 K_y k_d^{-1}$	1	2	0	1	1	1
R_{cR}	$K_0 K_1 K_y K_d k_R^{-1}$	1	1	0	0	1	1

Therefore an attempt should be made to consider *as an example* the same mechanism (CECDC) allowing all steps to contribute to rate control. Assuming steady-state behaviour, i.e. no accumulation of intermediates, the procedure to be followed is the elimination of the unknown interfacial concentrations of intermediates from the set of partial rate equations (36a) to (36e), combined with the equalities

$$v_O = v_R = v_d = \tfrac{1}{2}v_Y = \tfrac{1}{2}v_1 = -j_F/2F \tag{37}$$

The resulting rate equation is rather complex, as the derivation involves the solutions of a quadratic equation in $\tfrac{1}{2}v_1$. Yet it could be used to find the partial derivatives defined in eqns. (4)–(6), which determine first- and second-order behaviour (i.e. the quantities $p' = p\omega^{-1/2}$ in eqn. (8) and S_F^* in eqn. (16)), according to their derivation by means of the Taylor expansion [22].

However, in the case of a dc reversible system an easier route can be followed, if it is realized that the partial rate equations are *explicit* functions of the concentrations of the intermediates, but *implicit* functions of the concentrations of the stable reactants c_O and c_R. This is because the concentration of each intermediate will be a function of the three independent variables c_O, c_R and E (or ϕ). Thus it is permissible to expand each expression for v_i in eqn. (36) in a Taylor series with respect to its own primary variables, and to separate the first-order part, $\Delta v_i^{(1)}$, and the second-order part, $\Delta v_i^{(2)}$, from the mean part $\overline{\Delta v_i}$. For example, for reaction R_{co} we obtain the simple result:

$$\Delta v_O^{(1)} + \Delta v_O^{(2)} = k_O\left[\Delta c_O^{(1)} + \Delta c_O^{(2)}\right] - k_O K_O\left[\Delta c_{O'}^{(1)} + \Delta c_{O'}^{(2)}\right]$$

and, since in the dc reversible case the equilibrium condition, $K_O = \bar{c}_O/\bar{c}_{O'}$, holds for the mean concentrations,

$$\Delta v_O^{(1)} + \Delta v_O^{(2)} = k_O \bar{c}_O \left\{ \frac{\Delta c_O^{(1)} + \Delta c_O^{(2)}}{\bar{c}_O} - \frac{\Delta c_{O'}^{(1)} + \Delta c_{O'}^{(2)}}{\bar{c}_{O'}} \right\} \tag{38a}$$

where $\Delta c_i^{(1)}$ is the first-order part and $\Delta c_i^{(2)}$ the second-order part of the fluctuation around $\bar{c}_i$ [22]. Similar reasoning leads to Taylor series for the other reactions:

$$\Delta v_i^{(1)} + \Delta v_1^{(2)} = k_1 \bar{c}_{O'} \left\{ \frac{\Delta c_{O'}^{(1)} + \Delta c_{O'}^{(2)}}{\bar{c}_{O'}} - \frac{\Delta c_Y^{(1)} + \Delta c_Y^{(2)}}{\bar{c}_Y} - \frac{\Delta \phi^{(1)} + \Delta \phi^{(2)}}{2} \right.$$

$$\left. - \frac{1 - 2\alpha_1}{8}\left[\Delta \phi^{(1)}\right]^2 - \frac{\alpha_1}{2}\frac{\Delta c_{O'}^{(1)}\Delta \phi^{(1)}}{\bar{c}_{O'}} - \frac{1 - \alpha_1}{2}\frac{\Delta c_Y^{(1)}\Delta \phi^{(1)}}{\bar{c}_Y} \right\} \tag{38b}$$

$$\Delta v_Y^{(1)} + \Delta v_Y^{(2)} = k_Y \bar{c}_Y \left\{ \frac{\Delta c_Y^{(1)} + \Delta c_Y^{(2)}}{\bar{c}_Y} - \frac{\Delta c_{Y'}^{(1)} + \Delta c_{Y'}^{(2)}}{\bar{c}_{Y'}} \right\} \tag{38c}$$

$$\Delta v_d^{(1)} + \Delta v_d^{(2)} = k_d \bar{c}_{Y'}^2 \left\{ 2 \frac{\Delta c_Y^{(1)} + \Delta c_Y^{(2)}}{\bar{c}_{Y'}} - \frac{\Delta c_{O'}^{(1)} + \Delta c_{O'}^{(2)}}{\bar{c}_{O'}} - \frac{\Delta c_{R'}^{(1)} + \Delta c_{R'}^{(2)}}{\bar{c}_{R'}} \right.$$

$$\left. + \left[\frac{\Delta c_{Y'}^{(1)}}{\bar{c}_{Y'}} \right]^2 - \frac{\Delta c_{O'}^{(1)} \Delta c_{R'}^{(1)}}{\bar{c}_{O'} \bar{c}_{R'}} \right\} \tag{38d}$$

$$\Delta v_R^{(1)} + \Delta v_R^{(2)} = k_R \bar{c}_{R'} \left\{ \frac{\Delta c_{R'}^{(1)} + \Delta c_{R'}^{(2)}}{\bar{c}_{R'}} - \frac{\Delta c_R^{(1)} + \Delta c_R^{(2)}}{\bar{c}_R} \right\} \tag{38e}$$

Note that only the electron-transfer reaction and the dismutation reaction give rise to additional terms in $[\Delta \phi^{(1)}]^2$, etc., due to the existence of second-order derivatives.

The next step is to realize that the steady-state relationship expressed in eqn. (37) will also hold separately for the first-order and the second-order contributions to Δv_i. Then, taking all first-order terms together, it is seen that the intermediate $\Delta c^{(1)}$'s are easily eliminated, while the terms in $\Delta c_O^{(1)}$, $\Delta c_R^{(1)}$ and $\Delta \phi^{(1)}$ remain:

$$-\frac{1}{2} \Delta v_1^{(1)} \left\{ \frac{1}{k_O \bar{c}_O} + \frac{4}{k_1 \bar{c}_{O'}} + \frac{4}{k_Y \bar{c}_Y} + \frac{1}{k_d \bar{c}_{Y'}^2} + \frac{1}{k_R \bar{c}_{R'}} \right\} = \Delta \phi^{(1)} - \frac{\Delta c_O^{(1)}}{\bar{c}_O} + \frac{\Delta c_R^{(1)}}{\bar{c}_R} \tag{39}$$

If this is compared with the *formal* first-order expansion of the faradaic current [22]:

$$\Delta j_F^{(1)} = -F \Delta v_1^{(1)} = \tilde{F} \Delta \phi^{(1)} + \tilde{O} \Delta c_O^{(1)} + \tilde{R} \Delta c_R$$

it appears that eqn. (12) holds, as it should, and that the partial derivative $\tilde{F}$ can be expressed simply by:

$$\tilde{F} = 2 F \bar{c}_O k_{ff} \tag{40}$$

and consequently $p' = p \omega^{-1/2}$ (see eqn. (8)) is of the form

$$p' = (2 D_O)^{1/2} [1 + \exp \zeta]^{-1} k_{ff}^{-1} \tag{41}$$

where k_{ff} can be considered as *a "formal" rate constant* given by

$$\frac{1}{k_{ff}} = \frac{1}{k_O} + \frac{4 K_O}{k_1} + \frac{4 K_O K_1}{k_Y} + \frac{K_O}{k_D K_D K_R \bar{c}_R} + \frac{\bar{c}_O}{k_R K_R \bar{c}_R} \tag{42}$$

The potential dependence of the five terms in eqn. (42) is readily inferred from eqns. (35) and (36); the result is:

$$\frac{1}{k_{ff}} = \frac{1}{k_O} + \frac{\exp(\frac{1}{2} \alpha_1 \phi)}{k_{s1}} + \frac{\exp(\frac{1}{2} \phi)}{k_{sY}} + \frac{1 + (D_O/D_R)^{1/2} \exp(\phi)}{k_{sd} c_O^*} + \frac{\exp(\phi)}{k_{-R}} \tag{43}$$

Note that the fourth term corresponding to the dismutation step is a sum of two terms, so that the whole series contains the terms in 0ϕ, $\frac{1}{2}\alpha_1\phi$, $\frac{1}{2}\phi$ and ϕ.

The elaboration of the second-order part is more tedious but feasible. First, the

same calculation is made as was done for eqn. (39), leading to

$$-\frac{1}{2}\Delta v_1^{(2)}\left\{\frac{1}{k_O\bar{c}_O} + \frac{4}{k_1\bar{c}_{O'}} + \frac{4}{k_Y\bar{c}_Y} + \frac{1}{k_d\bar{c}_Y^2} + \frac{1}{k_R\bar{c}_{R'}}\right\} = \Delta\phi^{(2)} - \frac{\Delta c_O^{(2)}}{\bar{c}_O} + \frac{\Delta c_R^{(2)}}{\bar{c}_R}$$

$$+ \frac{1-2\alpha_1}{4}\left[\Delta\phi^{(1)}\right]^2 + \alpha_1\frac{\Delta c_O^{(1)}\Delta\phi^{(1)}}{\bar{c}_{O'}} + (1-\alpha_1)\frac{\Delta c_Y^{(1)}\Delta\phi^{(1)}}{\bar{c}_Y} - \left[\frac{\Delta c_Y^{(1)}}{\bar{c}_{Y'}}\right]^2 + \frac{\Delta c_O^{(1)}\Delta c_R^{(1)}}{\bar{c}_{O'}\bar{c}_{R'}}$$

$$(44)$$

If this is compared with the *formal* second-order expansion of the faradaic current [22], taking into account eqn. (12):

$$\Delta j_F^{(2)} = -F\Delta v_1^{(2)} = \tilde{F}\left[\Delta\phi^{(2)} - \frac{\Delta c_O^{(2)}}{\bar{c}_O} + \frac{\Delta c_R^{(2)}}{\bar{c}_R}\right] + \tfrac{1}{2}\widetilde{FF}\left[\Delta\phi^{(1)}\right]^2 + \widetilde{OF}\Delta c_O^{(1)}\Delta\phi^{(1)}$$

$$+ \widetilde{RF}\Delta c_R^{(1)}\Delta\phi^{(1)} + \tfrac{1}{2}\widetilde{OO}\left[\Delta c_O^{(1)}\right]^2 + \widetilde{OR}\Delta c_O^{(1)}\Delta c_R^{(1)} + \tfrac{1}{2}\widetilde{RR}\left[\Delta c_R^{(1)}\right]^2 \qquad (45)$$

we see that the series of quadratic and cross-product terms in eqn. (44) must be identical to the series of quadratic and cross-product terms in eqn. (45). Therefore the explicit meaning of the second-order partial derivatives $\widetilde{FF} = \partial^2 j_F/\partial\phi^2$, etc. [22], can be found after substitution of the appropriate relationships in terms of Δc_O, Δc_R and $\Delta\phi$ for $\Delta c_O^{(1)}$, $\Delta c_y^{(1)}$, $\Delta c_Y^{(1)}$ and $\Delta c_R^{(1)}$. These relationships can be derived by some manipulation from the combination of eqns. (38) with eqn. (39); e.g. from (38a) and (39), with the abbreviation used in eqn. (42)

$$\frac{\Delta c_O^{(1)}}{\bar{c}_{O'}} = \frac{k_{ff}}{k_O}\left[\Delta\phi^{(1)} - \frac{\Delta c_O^{(1)}}{\bar{c}_O} + \frac{\Delta c_R^{(1)}}{\bar{c}_R}\right]$$

The other expressions needed are obtained by combining eqns. (38c), (38d) and (38e) with (39). The final results of the operation are the explicit expressions for $\widetilde{FF}/\tilde{F}$, $\widetilde{OO}\bar{c}_O^2/\tilde{F}$ and $\widetilde{RR}\bar{c}_R^2/\tilde{F}$, that are tabulated in Table 3. The other partial derivatives $\widetilde{OF}$, $\widetilde{RF}$ and $\widetilde{OR}$ are found to obey eqns. (13), (14) and (15), respectively.

TABLE 3

Explicit expressions for the second-order partial derivatives occurring in eqn. (16) for the general CECDC mechanism, cf. eqns. (36)

$$\frac{1}{2}\frac{\widetilde{FF}}{\tilde{F}} = -\tfrac{1}{4} + (1-\alpha_1)\tilde{B} + \tilde{A} - \tfrac{1}{2}(\tilde{A} - \tilde{D} - \tilde{E})^2 - \tilde{A}\tilde{E}$$

$$\frac{1}{2}\frac{\widetilde{OO}\bar{c}_O^2}{\tilde{F}} = \tilde{A} - \tilde{D} - (\tilde{A} + \tilde{B} + \tilde{C})^2 - \tilde{A}\tilde{E}$$

$$\frac{1}{2}\frac{\widetilde{RR}\bar{c}_R^2}{\tilde{F}} = \tilde{A} - (\tilde{A} + \tilde{B} + \tilde{C})^2 - \tilde{A}\tilde{E}$$

$\tilde{A} = k_{ff}/k_O \qquad \tilde{B} = k_{ff}(2K_0/k_1) \qquad \tilde{C} = k_{ff}(2K_0K_1/k_Y)$
$\tilde{D} = k_{ff}/(K_O/k_dK_dK_R\bar{c}_R) \qquad \tilde{E} = k_{ff}(\bar{c}_O/k_RK_R\bar{c}_R)$
$\tilde{A} + 2\tilde{B} + 2\tilde{C} + \tilde{D} + \tilde{E} = 1$

The most important conclusions from the derivations are the following. The experimental quantity p', to be obtained as a function of potential from ac admittances, will not show up the quadratic nature of the mechanism due to the dismutation step, unless p' vs. ϕ curves are determined at varied concentration; otherwise no discrimination between a CECDC mechanism and a CECEC (with the second E fast) can possibly be made. The experimental quantity S_F^*, however, to be obtained as a function of potential from demodulation measurements, potentially reveals the quadratic nature, primarily by the presence of non-zero $\widetilde{OO}$ and $\widetilde{RR}$ values. If more than one step is rate-controlling, this will be revealed by the fact that $\widetilde{FF}/\tilde{F}$, $\widetilde{OO}\bar{c}_O^2/\tilde{F}$ and $\widetilde{RR}\bar{c}_R^2/\tilde{F}$ are (potential dependent) functions of the individual rate constants rather than constant numbers.

The consequences for kinetic studies (past and future) are obvious: if there is any reason to suppose or to suspect the presence of a non-linear intermediate reaction, the application of a second-order method is almost obligatory. On the other hand, if it is concluded that the mechanism contains only linear steps, this may have to be justified by means of the second-order response to any suitable perturbation.

(IV) POSSIBLE EXTENSIONS OF THE THEORY

The treatment in this paper may be considered as a framework for quantitative analyses of electrode reaction mechanisms in terms of consecutive steps. In view of the restrictions introduced in the beginning of section (II), we wish to make some remarks that may be relevant to practical situations, without, however, going into details.

(i) Non-specific double-layer effects, i.e the Frumkin corrections are easily accounted for by stating that the transfer of the reactant O to the reaction plane in the double layer is a fast reaction preceding the whole sequence [13]. Therefore any expression for k_f^{-1}, e.g. eqns. (22), (25) and (42), has to be multiplied by the equilibrium constant of this reaction, i.e. the reciprocal of the Boltzmann factor $\exp[-(z_O F/RT)\Phi_x]$, where Φ_x is the potential in the reaction plane. In addition it will be more correct to analyze the resulting k_f as a function of $\exp[(nF/RT)(E - \Phi_x(E) - E^\circ + \Phi_x(E^\circ))]$ instead of $\exp[(nF/RT)(E - E^\circ)]$.

(ii) Specific double-layer effects, e.g. catalysis or inhibition by adsorbed species, are more difficult to account for, and their presence could even obscure the potential dependence prescribed by the elementary model. The reason is the possible potential dependence of the amount of adsorbed catalyst or inhibitor, which has the effect that the constants $k_{s,i}$ and $k_{c,i}$ in eqns. (25)–(27) and in Table 2 may be potential dependent. Note also that the treatment in section (III.3) has to be extended since, in principle, k_O, k_Y, k_d and k_R must be allowed to depend on the potential, so that additional partial derivatives with respect to ϕ occur in eqns. (38a–3).

(iii) The theory will also be applicable to reactions of more complicated overall stoichiometry, e.g. $O_1 + O_2 + \ldots + n\, e^- \rightleftarrows R_1 + R_2 + \ldots$. Here O_1, O_2 etc. may represent different or identical species, as may R_1, R_2, etc. Probably the best way to

account for this complication is the procedure outlined in section (III.3) (also in the case of a linear reaction sequence), as the basic idea will always be the assumption of simple partial reaction steps.

(iv) If the overall rate constant is too low the reaction may be non-dc reversible, at least in part of the potential range covered. In that case the simplifying thermodynamic relationships, eqns. (12)–(15), are not applicable. We think that the implications of this may be rather serious, and that it will be necessary to think of a separate treatment. It should not be overlooked that the demodulation technique covers a very wide potential range and is therefore liable to be affected by dc-irreversibility at large polarization.

(v) Finally, two reasons for a possible fundamental non-applicability of the theory must be mentioned: (a) accumulation and subsequent adsorption or diffusion of the intermediate if it is not totally unstable; and (b) significant adsorption of the stable reactant and/or product. In both cases the interfacial processes become "coupled" via the mass-transfer processes involved, as is known already with respect to the ac admittance technique (see, for example, refs. 19 and 28). At present it is difficult to predict whether the demodulation method will also add new information to what can be learned from the first-order approach when these complications arise.

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