Chapter 6

APPENDIXES

6.1. SINGLE ELECTRON TRANSFER AT AN ELECTRODE

6.1.1. Laplace Transformation. Useful Definitions and Relationships

Laplace transformation is a convenient tool for resolving linear differential, integrodifferential, and partial derivative equations thanks to their conversion into algebraic equations in Laplace space. We will need only a limited number of definitions and relationships in the derivations below. They are summarized in Table 6.1,[1] which is to be read from left to right, or vice versa, according to the case. The variable that undergoes the transformation is named t here and will be t or τ in the following applications. In both cases, the corresponding Laplace variable is denoted s.

6.1.2. Cyclic Voltammetry of Nernstian Systems. Current– and Charge–Potential Curves

In this section we establish the equation of the forward scan current potential curve in dimensionless form (equation 1.3), justify the construction of the reverse trace depicted in Figure 1.4, and derive the charge-potential forward and reverse curves, also in dimensionless form. Linear and semi-infinite diffusion is described by means of the one-dimensional first and second Fick's laws applied to the reactant concentrations. This does not imply necessarily that their activity coefficients are unity but merely that they are constant within the diffusion layer. In this case, the activity coefficient is integrated in the diffusion coefficient. The latter is assumed to be the same for A and B (D).

The concentrations of A and B thus obey the following system of partial derivative equations, accompanied by a series of initial and

---

Elements of Molecular and Biomolecular Electrochemistry: An Electrochemical Approach to Electron Transfer Chemistry, By Jean-Michel Savéant

TABLE 6.1. Useful Laplace Transforms

Laplace Transform	Original Function
$\bar{f}(s) = \int_0^\infty f(t)\exp(-st)\,dt$	$f(t)$
$s\bar{f}(s) - f_{t=0}$	$\dfrac{\partial f}{\partial t}$
$s^2\bar{f}(s) - sf_{t=0} - \left(\dfrac{\partial f}{\partial t}\right)_{t=0}$	$\dfrac{\partial^2 f}{\partial t^2}$
$\bar{f}(s)\bar{g}(s)$	$\int_0^t f(\eta)g(t-\eta)\,d\eta = \int_0^t f(t-\eta)g(\eta)\,d\eta$
$\dfrac{1}{s}$	1
$\dfrac{1}{\sqrt{s}}$	$\dfrac{1}{\sqrt{\pi t}}$
$\dfrac{1}{s+A}$	$\exp(-At)$
$\dfrac{1}{(s+A)(s+B)(s+C)}$	$\dfrac{(C-B)\exp(-At) + (A-C)\exp(-Bt) + (B-A)\exp(-Ct)}{-(B-A)(C-B)(A-C)}$
$\dfrac{Ps^2 + Qs + R}{s[(s+A)^2 + B^2]}$	$\dfrac{R}{A^2+B^2} + \left(P - \dfrac{R}{A^2+B^2}\right)\exp(-At)\cos(Bt) + \dfrac{1}{B}\left(Q - AP - \dfrac{AR}{A^2+B^2}\right)\exp(-At)\sin(Bt)$

boundary conditions:

$$\frac{\partial C_A}{\partial t} = D\frac{\partial^2 C_A}{\partial x^2} \qquad \frac{\partial C_B}{\partial t} = D\frac{\partial^2 C_B}{\partial x^2}$$

$$t = 0, x \geq 0 \quad \text{and} \quad x = \infty, t \geq 0: \qquad C_A = C^0, \quad C_B = 0$$

$$x = 0, t \geq 0: \qquad \frac{\partial C_A}{\partial x} + \frac{\partial C_B}{\partial x} = 0 \quad \text{(conservation of fluxes)}$$

$$C_A = C_B \exp\left[\frac{F}{\mathcal{R}T}(E - E^0)\right] \quad \text{(Nernst's law)}$$

where the electrode potential depends on time according to

$$0 \leq t \leq t_R: \qquad E = E_i - vt$$

$$t_R \leq t \leq 2t_R: \qquad E = E_f + v(t - t_R) = 2E_f - E_i + vt$$

The current is related to the fluxes of A and B according to

$$\frac{i}{FS} = D\left(\frac{\partial C_{\mathrm{A}}}{\partial x}\right)_{x=0} = -D\left(\frac{\partial C_{\mathrm{B}}}{\partial x}\right)_{x=0}$$

and the charge passed is defined as $Q_e = \int_0^t i(\eta)\,d\eta$. Since the cathodic currents are counted as positive, Q_e quantifies the amount of negative charge passed from the electrode to the solution at time t.

It is useful to introduce normalized variables, functions, and parameters so as to obtain a dimensionless formulation, resolve the problem at this level, and finally, come back to the real experimental quantities. This strategy allows one to find out, here and in more complicated cases, the minimal number of parameters that are actually governing the electrochemical responses. We thus introduce the following normalized variables:

$$\textit{time}: \tau = \frac{Fv}{\mathcal{R}T}t, \quad \tau_R = \frac{E_i - E_f}{v} = u_i - u_f$$

$$\textit{potential}: \xi = -\frac{F}{\mathcal{R}T}(E - E^0), \quad u_i = \frac{F}{\mathcal{R}T}(E_i - E^0), \quad u_f = \frac{F}{\mathcal{R}T}(E_f - E^0)$$

$$\text{(in practice, } u_i \gg 0 \,\text{and}\, u_f \ll 0\text{)}$$

$$\textit{space}: y = x\sqrt{\frac{Fv}{RTD}}, \quad \text{concentrations}: \quad a = \frac{C_{\mathrm{A}}}{C^0}, \quad b = \frac{C_{\mathrm{B}}}{C^0}$$

$$\textit{current}: \psi = \frac{i}{FSC^0\sqrt{D}\sqrt{\dfrac{Fv}{\mathcal{R}T}}}$$

$$\textit{charge}: q_e = \frac{Q_e\left(\dfrac{Fv}{\mathcal{R}T}\right)^{1/2}}{FSC^0\sqrt{D}}$$

The set of equations above thus becomes

$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} \qquad \frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2}$$

$$\tau = 0,\, y \geq 0 \text{ and } y = \infty, \tau \geq 0: \qquad a = 1, \quad b = 0$$

$$y = 0, \tau \geq 0: \qquad a = b\exp(-\xi), \quad \frac{\partial a}{\partial y} + \frac{\partial b}{\partial y} = 0$$

where ξ and τ are related by

$$0 \leq \tau \leq \tau_R: \qquad \xi = \xi_c = -u_i + \tau$$

$$\tau_R \leq \tau \leq 2\tau_R: \quad \xi = \xi_a = -2u_f + u_i - \tau = -u_f - (\tau - \tau_R)$$

The dimensionless current is given by

$$\psi = \left(\frac{\partial a}{\partial y}\right)_{y=0} = -\left(\frac{\partial b}{\partial y}\right)_{y=0}$$

and the dimensionless charge by $q_e = \int_0^\tau \psi(\eta)\, d\eta$. Laplace transformation is particularly expedient to handle the two partial derivative equations. We thus obtain, taking the initial conditions into account,

$$s\bar{a} - 1 = \frac{\partial^2 \bar{a}}{\partial y^2}$$

$$s\bar{b} = \frac{\partial^2 \bar{b}}{\partial y^2}$$

Integration of these two second-order constant-coefficient differential equations, taking into account the second $y = 0$ boundary condition, leads to

$$\begin{aligned}\bar{a} = \frac{1}{s} &+ \left[\bar{a}_{y=0} - \frac{1}{\sqrt{s}}\left(\frac{\partial \bar{a}}{\partial y}\right)_{y=0} - \frac{1}{s}\right]\frac{\exp(-\sqrt{s}y)}{2}\\ &+ \left[\bar{a}_{y=0} + \frac{1}{\sqrt{s}}\left(\frac{\partial \bar{a}}{\partial y}\right)_{y=0} - \frac{1}{s}\right]\frac{\exp(\sqrt{s}y)}{2}\\ \bar{b} = &\left[\bar{b}_{y=0} - \frac{1}{\sqrt{s}}\left(\frac{\partial \bar{b}}{\partial y}\right)_{y=0}\right]\frac{\exp(-\sqrt{s}y)}{2}\\ &+ \left[\bar{b}_{y=0} + \frac{1}{\sqrt{s}}\left(\frac{\partial \bar{b}}{\partial y}\right)_{y=0}\right]\frac{\exp(\sqrt{s}y)}{2}\end{aligned}$$

The coefficient of the term in $\exp(\sqrt{s}y)$, which tends toward infinite with y, must be nil in both equations since for $y = \infty$, $\bar{a}$ and $\bar{b}$ remain finite (equal to $1/s$ and 0, respectively). It follows that

$$\bar{a}_{y=0} = \frac{1}{s} - \frac{\bar{\psi}}{\sqrt{s}} \quad \text{and} \quad \bar{b}_{y=0} = \frac{\bar{\psi}}{\sqrt{s}} \tag{6.1}$$

Coming back to the original space, we obtain integral relationships linking, in dimensionless terms, the concentrations at the electrode surface to the current:

$$(a)_{y=0} = 1 - \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau - \eta}} d\eta \tag{6.2}$$

$$(b)_{y=0} = \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau - \eta}} d\eta \tag{6.3}$$

Adding up these two equations leads to $(a)_{y=0} + (b)_{y=0} = 1$, which expresses the fact that the sum of the concentrations at the surface is equal to the concentration of A introduced in the solution.

The integral relationships above are valid for any transient technique other than cyclic voltammetry, since at this stage of the derivation, the fact that the potential is a linear function of time has not yet been introduced. It is also valid in the case where charge transfer is not fast and together with diffusion, kinetically governs the electrochemical response. In the present case, the linear relationship between potential and time comes into play through Nernst's law, leading to

$$(a)_{y=0} = \frac{\exp(-\xi)}{1+\exp(-\xi)} \qquad (b)_{y=0} = \frac{1}{1+\exp(-\xi)}$$

Thus, over the entire voltammogram,

$$\frac{1}{\sqrt{\pi}}\int_0^{\tau} \frac{\psi(\eta)}{\sqrt{\xi-\eta}}\,d\eta = \frac{1}{1+\exp(-\xi)}$$

During the first part of the scan, $\xi = \xi_c = -u_i + \tau$, and therefore

$$\frac{1}{\sqrt{\pi}}\int_{-u_i}^{\xi} \frac{\psi(\eta)}{\sqrt{\xi-\eta}}\,d\eta = \frac{1}{1+\exp(-\xi)} \tag{6.4}$$

$u_i \rightarrow \infty$ as the starting potential is made more and more positive compared to the standard potential, thus finally leading to equation (1.5).

During the second part of the scan, we may decompose the interval of integration in two portions:

$$\frac{1}{\sqrt{\pi}}\int_0^{\tau_R} \frac{\psi_c(\eta)}{\sqrt{\tau-\eta}}\,d\eta + \frac{1}{\sqrt{\pi}}\int_{\tau_R}^{\tau} \frac{\psi_a(\eta)}{\sqrt{\tau-\eta}}\,d\eta = \frac{1}{1+\exp(-\xi_a)}$$

where ψ_c and ψ_a stands for the forward and reverse current traces, noting that ξ on the right-hand side represents the potential during the second part of the scan ($\xi = \xi_a = -u_f + \tau - \tau_R$). The preceding equation may be recast as follows:

$$\frac{1}{\sqrt{\pi}}\int_0^{\tau} \frac{\psi_c(\eta)}{\sqrt{\tau-\eta}}\,d\eta + \frac{1}{\sqrt{\pi}}\int_{\tau_R}^{\tau} \frac{[\psi_a(\eta)-\psi_c(\eta)]}{\sqrt{\tau-\eta}}\,d\eta = \frac{1}{1+\exp(-\xi_a)}$$

The first term of the left-hand side relates to the first part of the scan and its prolongation during the second part of the scan. Thus,

$$\frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi_c(\eta)}{\sqrt{\tau-\eta}}d\eta = \frac{1}{1+\exp(-\xi_c)} = \frac{1}{1+\exp(2u_f+\xi_a)}$$

Thus, if the inversion potential is far beyond the standard potential, meaning that $2u_f + \xi_a \rightarrow -\infty$,

$$\frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi_c(\eta)}{\sqrt{\tau-\eta}}d\eta = 1$$

and thus

$$\frac{1}{\sqrt{\pi}}\int_{\infty}^{\xi_a}\frac{[\psi_a(\eta)-\psi_c(\eta)]}{\sqrt{\xi_a-\eta}}d\eta = -\frac{1}{1+\exp(\xi_a)}$$

Comparing this equation with the equation characterizing the forward scan,

$$\frac{1}{\sqrt{\pi}}\int_{-u_i}^{\xi}\frac{\psi(\eta)}{\sqrt{\xi-\eta}}d\eta = \frac{1}{1+\exp(-\xi)}$$

shows that the anodic and cathodic traces are superimposed exactly after transformations depicted in Figure 1.4 have been performed.

The charge passed is obtained, in dimensionless form, by integrating ψ over the 0–τ interval leading to the normalized charge–time (or –potential) curves in Figure 6.1a. Figure 6.1b shows that the charge passed during the reverse scan can be deduced from the charge passed during the forward scan in exactly the same manner as for the current (Figure 1.4).

A particularly important conclusion concerns the actual charge: At any point of the scan the charge passed, Q_e, is proportional to the concentration and *inversely proportional* to the square root of the scan rate as results from the equation

$$Q_e = FSC^0\sqrt{\frac{RTD}{Fv}}q_e$$

whereas the current is *proportional* to the square root of the scan rate.

6.1.3. Double-Layer Charging in Cyclic Voltammetry. Oscillating and Nonoscillating Behavior

During the *forward scan*, the Laplace expression of equation (1.10) is written

$$L_a s^2 \bar{i}_C + \Delta R_u s \bar{i}_C + \frac{\bar{i}_C}{C_d} = \frac{v}{s}$$

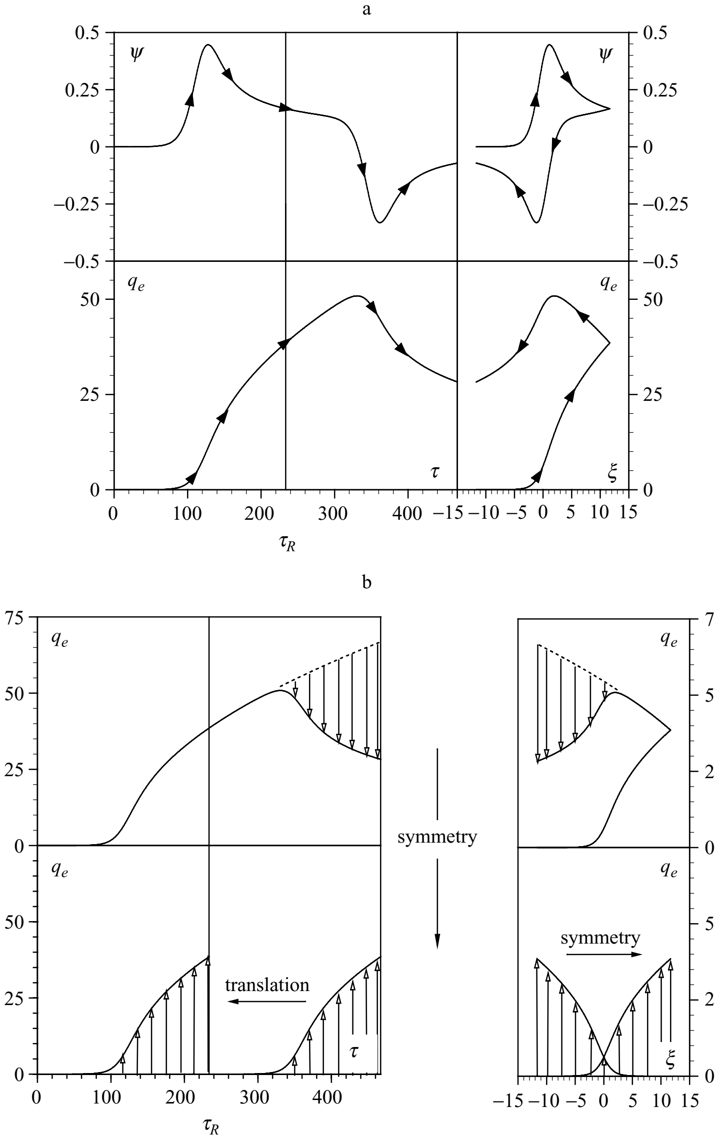


FIGURE 6.1. a: Dimensionless current (ψ) and charge passed (q_e) in the cyclic voltammetry of a Nernstian system. b: Construction of the reverse trace from the forward trace.

leading to

$$\bar{i}_C = \frac{C_d v}{C_d L_a s\left(s^2 + \frac{\Delta R_u}{L_a}s + \frac{1}{C_d L_a}\right)}$$

that is, with the definitions of ω and ρ_u given in the text:

$$\bar{i}_C = \frac{C_d v \omega^2}{s(s^2 + 2\rho_u \omega s + \omega^2)} = \frac{C_d v \omega^2}{s[(s + \rho_u \omega)^2 + \omega^2(1 - \rho_u^2)]}$$

The oscillatory or nonoscillatory behavior of i_C depends on the roots of the second-order trinomial in the denominator of the right-hand member being real or imaginary. These conditions are achieved when $\Delta R_u > \Delta R_u^c$ and $\Delta R_u < \Delta R_u^c$, respectively, where the critical value, ΔR_u^c, corresponding to the transitions between the two regimes is given by $\Delta R_u^c = 2\sqrt{L_a/C_d}$, or introducing $\rho_u = \Delta R_u/\Delta R_u^c$, by $\rho_u = 1$. We also introduce $\omega = 1/\sqrt{C_d L_a}$. There are thus three different cases:

1. $\Delta R_u > \Delta R_u^c (\rho_u > 1)$:

$$\bar{i}_C = \frac{C_d v \omega^2}{s[s + \omega(\rho_u + \sqrt{\rho_u^2 - 1})][s + \omega(\rho_u - \sqrt{\rho_u^2 - 1})]}$$

leading to

$$i_C = C_d v \left\{ 1 + \frac{\rho_u - \sqrt{\rho_u^2 - 1}}{2\sqrt{\rho_u^2 - 1}} \exp\left[-\omega(\rho_u + \sqrt{\rho_u^2 - 1})t\right] - \frac{\rho_u + \sqrt{\rho_u^2 - 1}}{2\sqrt{\rho_u^2 - 1}} \exp\left[-\omega(\rho_u - \sqrt{\rho_u^2 - 1})t\right] \right\}$$

We note, in passing, that when $\rho_u \to \infty$ (i.e., when $\Delta R_u \gg \Delta R_u^c$),

$$i_C = C_d v \left[1 - \exp\left(-\frac{\omega}{2\rho_u} t\right)\right] = C_d v \left[1 - \exp\left(-\frac{t}{\Delta R_u C_d}\right)\right]$$

the same double-layer charging curve as when no positive feedback compensation of the ohmic drop is attempted (equation 1.8), simply by replacing the total resistance R_u by the remaining uncompensated resistance ΔR_u.

2. $\Delta R_u = \Delta R_u^c \quad (\rho_u = 1)$:

$$\bar{i}_C = \frac{C_d v \omega^2}{s(s + \omega)^2}$$

leading to

$$i_C = C_d v[1 - \exp(-\omega t) - \omega t \exp(-\omega t)]$$

3. $\Delta R_u < \Delta R_u^c \quad (\rho_u < 1)$:

$$\bar{i}_C = \frac{C_d v \omega^2}{s(s^2 + 2\rho_u \omega s + \omega^2)} = \frac{C_d v \omega^2}{s[(s + \rho_u \omega)^2 + \omega^2(1 - \rho_u^2)]}$$

leading to

$$i_C = C_d v \Bigg[1 - \exp(-\rho_u \omega t) \cos(\omega \sqrt{1 - \rho_u^2 t}) \\ - \frac{\rho_u}{\sqrt{1 - \rho_u^2}} \exp(-\rho_u \omega t) \sin(\omega \sqrt{1 - \rho_u^2 t}) \Bigg]$$

typical of damped oscillations. Sustained oscillations are obtained when $\rho = 0$. Then

$$i_C = C_d v(1 - \cos \omega t).$$

ω thus appears as their pulsation, their period being $2\pi/\omega$.

During the *reverse scan*, the Laplace transformation is based on t–t_R as the time variable. Equation (1.10) then becomes

$$L_a(s^2 \bar{i}_C - sC_d v) + \Delta R_u(s\bar{i}_C - C_d v) + \frac{\bar{i}_C}{C_d} = -\frac{v}{s}$$

taking due account of the new initial conditions: namely, that $i_C = C_d v$ for t–$t_R = 0$. Thus, introducing the same parameters ω and ρ_u yields

$$\bar{i}_C = -C_d v \frac{-s^2 - 2\rho_u \omega s + \omega^2}{s(s^2 + 2\rho_u \omega s + \omega^2)} = C_d v \left[\frac{1}{s} - \frac{2\omega^2}{s(s^2 + 2\rho_u \omega s + \omega^2)} \right]$$

The equations of the reverse traces are thus derived straightforwardly from those of the forward scan in the same three cases:

1. $\Delta R_u > \Delta R_u^c (\rho_u > 1)$:

$$i_C = C_d v \Bigg\{ -1 - 2\frac{\rho_u - \sqrt{\rho_u^2 - 1}}{2\sqrt{\rho_u^2 - 1}} \exp\left[-\omega\left(\rho_u + \sqrt{\rho_u^2 - 1} \right)(t - t_R) \right] \\ + 2\frac{\rho_u + \sqrt{\rho_u^2 - 1}}{2\sqrt{\rho_u^2 - 1}} \exp\left[-\omega\left(\rho_u - \sqrt{\rho_u^2 - 1} \right)(t - t_R) \right] \Bigg\}$$

We note, in passing, that when $\rho_u \to \infty$ (i.e., $\Delta R_u \gg \Delta R_u^c$),

$$i_C = C_d v \left[-1 + 2\exp\left(-\frac{\omega}{2\rho_u} t \right) \right] = C_d v \left[-1 + 2\exp\left(-\frac{t}{\Delta R_u C_d} \right) \right]$$

the same double-layer charging curve as when no positive feedback compensation of the ohmic drop is attempted [equation (1.9)].

2. $\Delta R_u = \Delta R_u^c(\rho_u = 1)$:

$$i_C = C_d v\{-1 + 2\exp[-\omega(t - t_R)] + 2\omega t \exp[-\omega(t - t_R)]\}$$

3. $\Delta R_u < \Delta R_u^c(\rho_u < 1)$:

$$i_C = C_d v\left\{-1 + 2\exp[-\rho_u \omega t](t - t_R)\cos\left[\omega\sqrt{1 - \rho_u^2}(t - t_R)\right]\right.$$
$$\left. + 2\frac{\rho_u}{\sqrt{1 - \rho_u^2}}\exp(-\rho_u \omega t)\sin\left[\omega\sqrt{1 - \rho_u^2}(t - t_R)\right]\right\}$$

typical of damped oscillations. Sustained oscillations are obtained when $\rho = 0$, thus corresponding to

$$i_C = C_d v(-1 + 2\cos\omega t)$$

The equations of the forward and reverse traces for oscillatory and nonoscillatory behaviors are summarized in Table 6.2.

6.1.4. Effect of Ohmic Drop and Double-Layer Charging on Nernstian Cyclic Voltammograms

This section is devoted to the establishment of equations (1.12) and (1.13). In addition to the dimensionless variables used previously (Section 6.1.2), we normalize the Faradaic and double-layer charging current,

$$\psi_f = \frac{i_f}{FSC^0\sqrt{D}(Fv/\mathcal{R}T)^{1/2}} \qquad \psi_C = \frac{i_C}{FSC^0\sqrt{D}(Fv/\mathcal{R}T)^{1/2}}$$

and the two potentials, E and E':

$$\xi = -\frac{Fv}{\mathcal{R}T}(E - E^0) \qquad \xi' = -\frac{Fv}{\mathcal{R}T}(E' - E^0)$$

We may thus translate the current and potential relationships of Section 1.3.1 [equations (1.11)] into the following dimensionless equations:

$$\xi = \xi' - \rho\psi \quad \text{and} \quad \psi_C = \frac{\theta_c}{\rho}\frac{d\xi}{d\tau}$$

ρ and θ_c being defined by equations (1.13). Thus,

$$\psi_C = \frac{\theta_c}{\rho}\frac{d\xi'}{d\tau} - \theta_c\frac{d\psi}{d\tau} \quad \text{leading to} \quad \psi + \theta_c\frac{d\psi}{d\tau} = \frac{\theta_c}{\rho}\frac{d\xi'}{d\tau} + \psi_f$$

TABLE 6.2. Positive Feedback Compensation of Ohmic Drop: Equations of the Forward and Reverse Traces for Oscillatory and Nonoscillatory Behaviors[a]

$\Delta R_u > \Delta R_u^c$ $(\rho_u > 1)$	Forward scan: $i_C = C_d v\left\{1 + \dfrac{\rho_u - \sqrt{\rho_u^2 - 1}}{2\sqrt{\rho_u^2 - 1}}\exp\left[-\omega\left(\rho_u + \sqrt{\rho_u^2 - 1}\right)t\right] - \dfrac{\rho_u + \sqrt{\rho_u^2 - 1}}{2\sqrt{\rho_u^2 - 1}}\exp\left[-\omega\left(\rho_u - \sqrt{\rho_u^2 - 1}\right)t\right]\right\}$ Reverse scan: $i_C = C_d v\left\{-1 - 2\dfrac{\rho_u - \sqrt{\rho_u^2 - 1}}{2\sqrt{\rho_u^2 - 1}}\exp\left[-\omega\left(\rho_u + \sqrt{\rho_u^2 - 1}\right)(t - t_R)\right] + 2\dfrac{\rho_u + \sqrt{\rho_u^2 - 1}}{2\sqrt{\rho_u^2 - 1}}\exp\left[-\omega\left(\rho_u - \sqrt{\rho_u^2 - 1}\right)(t - t_R)\right]\right\}$ leading to equations (1.8) and (1.9) when $\rho_u \to \infty$ (i.e., $\Delta R_u \gg \Delta R_u^c$)
$\Delta R_u = \Delta R_u^c$ $(\rho_u = 1)$	Forward scan: $i_C = C_d v[1 - \exp(-\omega t) - \omega t \exp(-\omega t)]$ Reverse scan: $i_C = C_d v\{-1 + 2\exp[-\omega(t - t_R)] + 2\omega t \exp[-\omega(t - t_R)]\}$
$\Delta R_u < \Delta R_u^c$ $(\rho_u < 1)$	Forward scan: $i_C = C_d v\left\{1 - \exp(-\rho_u \omega t)\cos\left(\omega\sqrt{1 - \rho_u^2}t\right) - \dfrac{\rho_u}{\sqrt{1 - \rho_u^2}}\exp(-\rho_u \omega t)\sin\left(\omega\sqrt{1 - \rho_u^2}t\right)\right\}$ Reverse scan: $i_C = C_d v\left\{-1 + 2\exp[-\rho_u \omega t](t - t_R)\cos\left[\omega\sqrt{1 - \rho_u^2}(t - t_R)\right] + 2\dfrac{\rho_u}{\sqrt{1 - \rho_u^2}}\exp(-\rho_u \omega t)\sin\left[\omega\sqrt{1 - \rho_u^2}(t - t_R)\right]\right\}$ $\rho = 0$ (sustained oscillations): Forward scan: $i_C = C_d v[1 - \cos(\omega t)]$ Reverse scan: $i_C = C_d v[-1 + 2\cos(\omega t)]$

[a] $\omega = 1/\sqrt{C_d L_a}$, $\rho_u = \Delta R_u / \Delta R_u^c$ with $\Delta R_u^c = 2\sqrt{L_a / C_d}$.

with

$$\frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi_f(\eta)}{\sqrt{\tau-\eta}}d\eta = \frac{1}{1+\exp(-\xi)}$$

During the forward scan, $\xi' = \xi'_c = -u_i + \tau$, $d\xi'/d\tau = 1$, and thus

$$\psi_c - \frac{\theta_c}{\rho} + \theta_c\frac{d\psi_c}{d\tau} = \psi_f$$

where ψ_c stands for the cathodic current (i.e., the current during the forward scan). It follows that

$$\frac{1}{\sqrt{\pi}}\int_0^{\tau}\left(\psi - \frac{\theta_c}{\rho} + \theta_c\frac{d\psi}{d\eta}\right)\frac{d\eta}{\sqrt{\tau-\eta}} = \frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi_f(\eta)}{\sqrt{\tau-\eta}}d\eta = \frac{1}{1+\exp(-\xi)}$$

Since $\xi = -u_i + \tau - \rho\psi_c$,

$$\frac{1}{\sqrt{\pi}}\int_{-u_i}^{\xi'_c}\left(\psi_c - \frac{\theta_c}{\rho} + \theta_c\frac{d\psi_c}{d\eta}\right)\frac{d\eta}{\sqrt{\xi'_c-\eta}} = \frac{1}{1+\exp\left(-\xi'_c + \rho\psi_c\right)}$$

and in practice:

$$\frac{1}{\sqrt{\pi}}\int_{-\infty}^{\xi'_c}\left(\psi_c - \frac{\theta_c}{\rho} + \theta_c\frac{d\psi_c}{d\eta}\right)\frac{d\eta}{\sqrt{\xi'_c-\eta}} = \frac{1}{1+\exp\left(-\xi'_c + \rho\psi_c\right)}$$

[i.e., equation (1.12), where the subscript c has been dropped for simplicity.] During the reverse scan, $\xi' = \xi'_a = -u_f - (\tau - \tau_R)$, $d\xi'/d\tau = -1$ and thus

$$\psi_a + \frac{\theta_c}{\rho} + \theta_c\frac{d\psi_a}{d\tau} = \psi_f$$

where ψ_a stands for the cathodic current (i.e., the current during the reverse scan). It follows that

$$\frac{1}{\sqrt{\pi}}\int_0^{\tau_R}\left(\psi_c - \frac{\theta_c}{\rho} + \theta_c\frac{d\psi_c}{d\eta}\right)\frac{d\eta}{\sqrt{\tau-\eta}} + \frac{1}{\sqrt{\pi}}\int_{\tau_R}^{\tau}\left(\psi_a + \frac{\theta_c}{\rho} + \theta_c\frac{d\psi_a}{d\eta}\right)\frac{d\eta}{\sqrt{\tau-\eta}}$$
$$= \frac{1}{1+\exp(-\xi'_a + \rho\psi_a)}$$

The first term on the left-hand side relates to the first part of the scan:

$$\frac{1}{\sqrt{\pi}}\int_0^{\tau_R}\left(\psi_c - \frac{\theta_c}{\rho} + \theta_c\frac{d\psi_c}{d\eta}\right)\frac{d\eta}{\sqrt{\tau-\eta}} = \frac{1}{1+\exp(-u_f - \rho\psi_a)}$$

Therefore,

$$\frac{1}{\sqrt{\pi}}\int_{-u_f}^{\xi'_a}\left(\psi_a+\frac{\theta_c}{\rho}+\theta_c\frac{d\psi_a}{d\eta}\right)\frac{d\eta}{\sqrt{\tau-\eta}}=\frac{1}{1+\exp(-\xi'_a+\rho\psi_a)}-\frac{1}{1+\exp(-u_f-\rho\psi_a)}$$

which allows the computation of the reverse trace, ψ_a, once the parameter u_f, which characterized the potential of scan inversion, has been specified.

The entire cyclic voltammogram is no longer reversible according to the definition we have attached to this term so far. In other words, the symmetry and translation operations as in Figures 1.4 and 6.1 do no longer allow the superposition of the reverse and forward trace. It also appears that the midpoint between the anodic and cathodic peak potentials does not exactly coincide with the standard potential. The gap between the two potentials increases with the extent of the ohmic drop as illustrated in Figure 6.2 for typical conditions, which thus provides an estimate of the error that would result if the two potentials were regarded as equal.

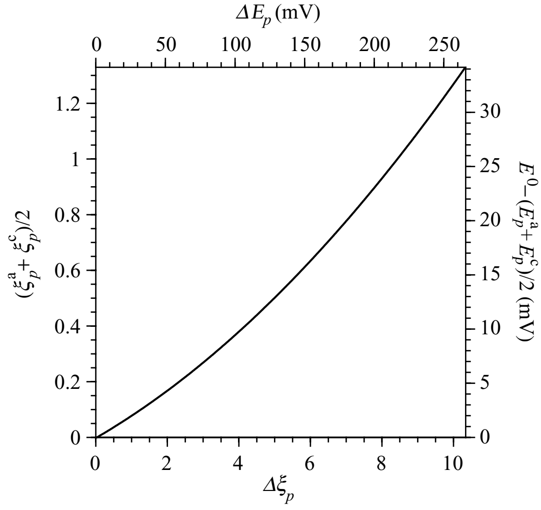


FIGURE 6.2. Difference between the midpoint between the anodic and cathodic peak potentials and the standard potential and the extent of ohmic drop (as measured by the difference between the cathodic peak potentials in the absence and presence of ohmic drop). Bottom horizontal and left-hand vertical axes: dimensionless representation. Top horizontal and right-hand vertical axes: potential differences at 25°C. Inversion of the potential scan at $\xi = 20$ (0.514 V beyond the standard potential).

6.1.5. Potential Step and Double Potential Step Chronoamperometry of Nernstian Systems

The analysis is the same as in the preceding section, as long as the relationship between potential and time has not been introduced. The same dimensionless approach may also be followed with the exception of the time variable, which may now be normalized against the inversion time t_R: $\tau = t/t_R$, leading to the following definition of the normalized current: $\psi = i\sqrt{t_R}/FSC^0\sqrt{D}$. In applying equations (6.1) to the first potential step, we take into account that in the conditions specified in Section 1.3.2, the concentration of A at the electrode surface is zero (i.e., $\bar{a}_{y=0} = 0$), or equivalently, the concentration of B at the electrode is equal to C^0 (i.e., $\bar{b}_{y=0} = 1/s$). It follows that $\bar{\psi} = 1/\sqrt{s}$ and therefore $\psi = 1/\sqrt{\pi\tau}$, thus yielding equation (1.19). During the second step, equation (6.3) leads to

$$(b)_{y=0} = \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta = \frac{1}{\sqrt{\pi}}\int_0^1 \frac{\psi_c(\eta)}{\sqrt{\tau-\eta}}d\eta + \frac{1}{\sqrt{\pi}}\int_1^\tau \frac{\psi_a(\eta)}{\sqrt{\tau-\eta}}d\eta = 0$$

and thus

$$\frac{1}{\sqrt{\pi}}\int_1^\tau \frac{\psi_c(\eta)-\psi_a(\eta)}{\sqrt{\tau-\eta}}d\eta = \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi_c(\eta)}{\sqrt{\tau-\eta}}d\eta$$

$$\frac{1}{\sqrt{\pi}}\int_0^{\tau-1} \frac{\psi_c(\eta)-\psi_a(\eta)}{\sqrt{(\tau-1)-\eta}}d\eta = 1$$

It follows that

$$\psi_a = -\frac{1}{\sqrt{\pi(\tau-1)}} + \frac{1}{\sqrt{\pi\tau}}$$

thus leading to equation (1.21).

6.1.6. Overlapping of Double-Layer Charging and Faradaic Currents in Potential Step and Double Potential Step Chronoamperometry. Oscillating and Nonoscillating Behavior

In the Laplace space, equation (1.22) is written

$$L_a s^2\bar{i} + \Delta R_u s\bar{i} + \frac{\bar{i}}{C_d} = \Delta E + \frac{\bar{i}_f}{C_d}$$

During the forward scan (Section 6.1.4),

$$\bar{i}_f = \frac{FSC^0\sqrt{D}}{\sqrt{s}}$$

leading to

$$\bar{i} = \frac{\Delta E}{L_a\left(s^2 + \dfrac{\Delta R_u}{L_a}s + \dfrac{1}{C_d L_a}\right)} + \frac{FSC^0\sqrt{D}}{C_d L_a\left(s^2 + \dfrac{\Delta R_u}{L_a}s + \dfrac{1}{C_d L_a}\right)\sqrt{s}}$$

that is, to

$$\bar{i} = C_d \Delta E \bar{f}(s) + FSC^0\sqrt{D}\frac{\bar{f}(s)}{\sqrt{s}}$$

TABLE 6.3. Double-Layer Charging and Ohmic Drop in Potential Step Chronoamperometry: Characteristic Function $\bar{f}(s)$ and $f(t)$ in the Laplace and Original Spaces[a]

$\Delta R_u > \Delta R_u^c$ $(\rho_u > 1)$	$\bar{f}(s) = \dfrac{\omega^2}{\left[s + \omega(\rho_u + \sqrt{\rho_u^2 - 1})\right]\left[s + \omega(\rho_u - \sqrt{\rho_u^2 - 1})\right]}$ $f(t) = \omega\dfrac{\exp\left[-\omega\left(\rho_u - \sqrt{\rho_u^2 - 1}\right)t\right] - \exp\left[-\omega\left(\rho_u + \sqrt{\rho_u^2 - 1}\right)t\right]}{2\sqrt{\rho_u^2 - 1}}$ when $\rho_u \to \infty$ (i.e., $\Delta R_u \gg \Delta R_u^c$) $f(t) = \dfrac{\exp(-\Delta R_u C_d t)}{\Delta R_u C_d}$
$\Delta R_u = \Delta R_u^c$ $(\rho_u = 1)$	$\bar{f}(s) = \dfrac{\omega^2}{(s + \omega)^2}$ $f(t) = \omega^2 t \exp(-\omega t)$
$\Delta R_u < \Delta R_u^c$ $(\rho_u < 1)$	$0 < \rho_u < 1$: damped oscillations $\bar{f}(s) = \dfrac{\omega^2}{[(s + \rho_u\omega)^2 + \omega^2(1 - \rho_u^2)]}$ $f(t) = \dfrac{\omega}{\sqrt{1 - \rho_u^2}}\exp(-\rho_u\omega t)\sin(\sqrt{1 - \rho_u^2}\omega t)$ $\rho_u = 0$: sustained oscillations: $\bar{f}(s) = \dfrac{\omega^2}{s^2 + \omega^2}$ $f(t) = \omega\sin(\omega t)$

[a] $\omega = 1/\sqrt{C_d L_a}$, $\rho_u = \Delta R_u/\Delta R_u^c$ with $\Delta R_u^c = 2\sqrt{L_a/C_d}$.

or in the original space,

$$i = C_d \Delta E f(t) + \frac{FSC^0\sqrt{D}}{\sqrt{\pi}} \int_0^t f(\eta) \frac{d\eta}{\sqrt{t-\eta}} \tag{6.5}$$

The first term is the double-layer charging response, while the second is a measure of the overlap between double-layer charging and Faradaic reaction, which eventually tends toward the Faradaic response that would have been obtained if double-layer charging were absent. As to the expression of the characteristic functions $\bar{f}(s)$ and $f(t)$ in the Laplace and original spaces, respectively, with the same notations as in Section 6.1.4,

$$\Delta R_u^c = 2\sqrt{\frac{L_a}{C_d}} \qquad \rho_u = \frac{\Delta R_u}{\Delta R_u^c} \qquad \omega = \frac{1}{\sqrt{C_d L_a}}$$

three different cases must be distinguished depending on ρ_u being larger, equal, or smaller than 1. The results are summarized in Table 6.3.

Calculation of the convolution integral in equation (6.5) may be performed as depicted in Section 2.2.8, leading to the results displayed in Figure 1.12.

6.1.7. Solvent Reorganization in Marcus–Hush Model

For the sake of simplicity, we first compute the free-energy changes, ΔG_{I} and ΔG_{II}, in the case where the *reaction site is far enough from the electrode surface for image effects to be neglected.* At any stage of the first charging process, the number of charge borne by the reactant is

$$z(v) = z_{\mathrm{A}} + v(z - z_{\mathrm{A}}) \qquad (0 \le v \le 1)$$

and the electrical potential at a distance r from the center of the A equivalent sphere is

$$\varphi(v) = \frac{e_0}{4\pi\varepsilon_0}\frac{z(v)}{\varepsilon_S r}$$

where ε_0 is the vacuum permitivity, e_0 the electron charge, and ε_S the solvent static dielectric constant. The potential, $\varphi'_{\mathrm{A}}(v)$, to be considered in the computation of

$$\Delta G_I = e_0 \int_0^1 \varphi'_{\mathrm{A}}(v)(z - z_{\mathrm{A}})\, dv$$

is obtained for $r = a_{\mathrm{A}}$ (where a_{A} is the reactant radius), after subtraction of the self-potential of A[2,3]:

$$\varphi'_{\mathrm{A}}(v) = \left(\frac{e_0}{4\pi\varepsilon_0}\frac{z(v)}{\varepsilon_S a_{\mathrm{A}}} - \frac{e_0}{4\pi\varepsilon_0}\frac{z(v)}{a_{\mathrm{A}}}\right) = \frac{e_0}{4\pi\varepsilon_0}\frac{z(v)}{a_{\mathrm{A}}}\left(\frac{1}{\varepsilon_S} - 1\right)$$

Thus,

$$\Delta G_I = \frac{e_0^2}{4\pi\varepsilon_0 a_{\mathrm{A}}}\left(\frac{1}{\varepsilon_S} - 1\right)\left[z_{\mathrm{A}}(z - z_{\mathrm{A}}) + \frac{(z - z_{\mathrm{A}})^2}{2}\right]$$

During the second step, the charge number varies as

$$z(v) = z + v(z_{\mathrm{A}} - z) \qquad (0 \le v \le 1)$$

The potential at a distance r from the center of A is now the sum of its value at the end of the first step [i.e., $(e_0/4\pi\varepsilon_0)(z/\varepsilon_S r)$] and of its variation in a medium that responds only via the optical dielectric constant, ε_{op} (square of the refractive index). Altogether,

$$\varphi(v) = \frac{e_0}{4\pi\varepsilon_0}\left(\frac{z}{\varepsilon_S r} + \frac{v(z_{\mathrm{A}} - z)}{\varepsilon_{op} r}\right)$$

The potential, $\varphi'_A(v)$, to be considered in the computation of ΔG_{II}, is finally obtained, for $r = a_{\mathrm{A}}$, after subtraction of the appropriate self-potentials:

$$\varphi'_{\mathrm{A}}(v) = \frac{e_0}{4\pi\varepsilon_0}\left[\frac{z}{a_{\mathrm{A}}}\left(\frac{1}{\varepsilon_S} - 1\right) + \frac{v(z_{\mathrm{A}} - z)}{a_{\mathrm{A}}}\left(\frac{1}{\varepsilon_{op}} - 1\right)\right]$$

leading to

$$\Delta G_{II} = \frac{e_0^2}{4\pi\varepsilon_0 a_{\mathrm{A}}}\left[\left(\frac{1}{\varepsilon_S} - 1\right)z(z_{\mathrm{A}} - z) + \left(\frac{1}{\varepsilon_{op}} - 1\right)\frac{(z - z_{\mathrm{A}})^2}{2}\right]$$

Overall,

$$\Delta G_I + \Delta G_{II} = \lambda_0(z_{\mathrm{A}} - z)^2$$

with

$$\lambda_0^{el} = \frac{e_0^2}{4\pi\varepsilon_0}\frac{1}{2a_{\mathrm{A}}}\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_S}\right)$$

In the case of a *homogeneous electron transfer between two molecules*,

$$\mathrm{A}^{z_{\mathrm{A}}} + \mathrm{D}^{z_{\mathrm{D}}} \rightleftharpoons \mathrm{A}^{z_{\mathrm{A}}-1} + \mathrm{D}^{z_{\mathrm{D}}+1}$$

the presence of two reacting ions must be taken into account in the expression of the electrical potentials, and the charging process must be achieved on both species. Thus, during step I, the numbers of charge borne by the reactants are

$$z_{\mathrm{a\,or\,d}}(v) = z_{\mathrm{A\,or\,D}} + v(z_{\mathrm{a\,or\,d}} - z_{\mathrm{A\,or\,D}})$$

The z's with lowercase subscripts designate the current values of the charge number for the acceptor and donor, respectively, while the z's with uppercase subscripts designate the values of the charge number for the acceptor and donor in the initial state, respectively. The electrical potential at any point of the space is

$$\varphi(v) = \frac{e_0}{4\pi\varepsilon_0}\left[\frac{z_{\mathrm{a}}(v)}{\varepsilon_S r_{\mathrm{a}}} + \frac{z_{\mathrm{d}}(v)}{\varepsilon_S r_{\mathrm{d}}}\right]$$

where r_{a} and r_{d} are the distances to the centers of A and D. At the surface of each ion, the potential minus the self-potential are

$$\varphi'_{\mathrm{a}}(v) = \frac{e_0}{4\pi\varepsilon_0}\left[\frac{z_{\mathrm{a}}(v)}{a_{\mathrm{A}}}\left(\frac{1}{\varepsilon_S} - 1\right) + \frac{z_{\mathrm{d}}(v)}{r_d\varepsilon_S}\right]$$

where r_{d} now represents the distance between the center of D and any point at the surface of A:

$$\varphi'_{\mathrm{d}}(v) = \frac{e_0}{4\pi\varepsilon_0}\left[\frac{z_{\mathrm{d}}(v)}{a_{\mathrm{D}}}\left(\frac{1}{\varepsilon_S} - 1\right) + \frac{z_{\mathrm{a}}(v)}{r_{\mathrm{a}}\varepsilon_S}\right]$$

where r_{a} now represents the distance between the center of A and any point at the surface of D. Averaging these expressions over the surface of each reactant, one obtains

$$\bar{\varphi}'_{\mathrm{a}}(v) = \frac{e_0}{4\pi\varepsilon_0}\left[\frac{z_{\mathrm{a}}(v)}{a_{\mathrm{A}}}\left(\frac{1}{\varepsilon_S} - 1\right) + \frac{z_{\mathrm{d}}(v)}{d\varepsilon_S}\right]$$

$$\bar{\varphi}'_{\mathrm{d}}(v) = \frac{e_0}{4\pi\varepsilon_0}\left[\frac{z_{\mathrm{d}}(v)}{a_{\mathrm{D}}}\left(\frac{1}{\varepsilon_S} - 1\right) + \frac{z_{\mathrm{a}}(v)}{d\varepsilon_S}\right]$$

d being the distance between the centers of the two reactants. The computation of

$$\Delta G_I = e_0\left[\int_0^1 \bar{\varphi}'_{\mathrm{a}}(v)(z_{\mathrm{a}} - z_{\mathrm{A}})dv + \int_0^1 \bar{\varphi}'_{\mathrm{d}}(v)(z_{\mathrm{d}} - z_{\mathrm{D}})\, dv\right]$$

thus leads to

$$\Delta G_I = \frac{e_0^2}{4\pi\varepsilon_0}\left\{\frac{z_{\mathrm{a}}z_{\mathrm{d}} - z_{\mathrm{A}}z_{\mathrm{D}}}{\varepsilon_S d} + \left[z_{\mathrm{A}}(z_{\mathrm{a}} - z_{\mathrm{A}}) + \frac{(z_{\mathrm{a}} - z_{\mathrm{A}})^2}{2}\right]\left(\frac{1}{\varepsilon_S} - 1\right)\frac{1}{a_{\mathrm{A}}} \right.$$
$$\left. + \left[z_{\mathrm{D}}(z_{\mathrm{d}} - z_{\mathrm{D}}) + \frac{(z_{\mathrm{d}} - z_{\mathrm{D}})^2}{2}\right]\left(\frac{1}{\varepsilon_S} - 1\right)\frac{1}{a_{\mathrm{D}}}\right\}$$

During step II, the numbers of charge borne by the reactants are

$$z_{\mathrm{a\,or\,d}}(v) = z_{\mathrm{a\,or\,d}} + v(z_{\mathrm{A\,or\,D}} - z_{\mathrm{a\,or\,d}})$$

The potential at any point at a distance r_{a} from the center of A and r_{d} from the center of D is the sum of its value at the end of step I:

$$\frac{e_0}{4\pi\varepsilon_0}\left(\frac{z_{\mathrm{a}}}{\varepsilon_S r_{\mathrm{a}}} + \frac{z_{\mathrm{d}}}{\varepsilon_S r_{\mathrm{d}}}\right)$$

and of its variation in a medium that responds only via the optical dielectric constant, ε_{op} (square of the refractive index). Altogether,

$$\varphi'_{\mathrm{a\,or\,d}}(v) = \frac{e_0}{4\pi\varepsilon_0}\left[\frac{z_{\mathrm{a}}}{\varepsilon_S r_{\mathrm{a}}} + \frac{z_{\mathrm{d}}}{\varepsilon_S r_{\mathrm{d}}} + \frac{v(z_{\mathrm{A}} - z_{\mathrm{a}})}{\varepsilon_{op} r_{\mathrm{a}}} + \frac{v(z_{\mathrm{D}} - z_{\mathrm{d}})}{\varepsilon_{op} r_{\mathrm{d}}}\right]$$

After subtraction of the self-potentials and averaging over the surface of each ion, one obtains

$$\bar{\varphi}'_{\mathrm{a}}(v) = \frac{e_0}{4\pi\varepsilon_0}\left[\frac{z_{\mathrm{a}}}{a_{\mathrm{A}}}\left(\frac{1}{\varepsilon_S} - 1\right) + \frac{z_{\mathrm{d}}}{d\varepsilon_S} + \frac{v(z_{\mathrm{A}} - z_{\mathrm{a}})}{a_{\mathrm{A}}}\left(\frac{1}{\varepsilon_{op}} - 1\right) + \frac{v(z_{\mathrm{D}} - z_{\mathrm{d}})}{\varepsilon_{op} d}\right]$$
$$\bar{\varphi}'_{\mathrm{d}}(v) = \frac{e_0}{4\pi\varepsilon_0}\left[\frac{z_{\mathrm{d}}}{a_{\mathrm{D}}}\left(\frac{1}{\varepsilon_S} - 1\right) + \frac{z_{\mathrm{a}}}{d\varepsilon_S} + \frac{v(z_{\mathrm{D}} - z_{\mathrm{d}})}{a_{\mathrm{D}}}\left(\frac{1}{\varepsilon_{op}} - 1\right) + \frac{v(z_{\mathrm{A}} - z_{\mathrm{a}})}{\varepsilon_{op} d}\right]$$

Computation of

$$\Delta G_{II} = e_0\left[\int_0^1 \bar{\varphi}'_{\mathrm{a}}(v)(z_{\mathrm{A}} - z_{\mathrm{a}})\, dv + \int_0^1 \bar{\varphi}'_{\mathrm{d}}(v)(z_{\mathrm{D}} - z_{\mathrm{d}})\, dv\right]$$

thus leads to

$$\Delta G_{II} = \frac{e_0^2}{4\pi\varepsilon_0}\left\{\left[\frac{(z_A - z_a)(z_D - z_d)}{\varepsilon_{op}} - \frac{z_d(z_a - z_A) + z_a(z_d - z_D)}{\varepsilon_S}\right]\frac{1}{d}\right.$$
$$+\left[\frac{(z_a - z_A)^2}{2}\left(\frac{1}{\varepsilon_{op}} - 1\right) - z_a(z_a - z_A)\left(\frac{1}{\varepsilon_S} - 1\right)\right]\frac{1}{a_A}$$
$$\left.+\left[\frac{(z_d - z_D)^2}{2}\left(\frac{1}{\varepsilon_{op}} - 1\right) - z_d(z_d - z_D)\left(\frac{1}{\varepsilon_S} - 1\right)\right]\frac{1}{a_D}\right\}$$

Overall,

$$\Delta G_{I+II} = \frac{e_0^2}{4\pi\varepsilon_0}\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_S}\right)\left[\frac{(z_a - z_A)^2}{2a_A} + \frac{(z_d - z_D)^2}{2a_D} + \frac{(z_a - z_A)(z_d - z_D)}{d}\right]$$

Since

$$-(z_a - z_A) = (z_d - z_D) = X$$

$G_{0,A} = \lambda_0^{hom} X^2$ for the reactants, and similarly,

$G_{0,B} = \lambda_0^{hom}(1 - X)^2$ for the products, with

$$\lambda_0^{hom} = \frac{e_0^2}{4\pi\varepsilon_0}\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_S}\right)\left[\frac{1}{2a_A} + \frac{1}{2a_D} - \frac{1}{d}\right]$$

[i.e., equation (1.44)].

Similar derivations apply for the *electrochemical case* when taking the *image force effect* into account. More precisely, in the expression of the potential at the surface of the A sphere, the contribution of the electrical image of A (which bears an opposite charge and which center is located at a distance d_i from the center of A) has to be taken into account.

In the first step,

$$\bar{\varphi}'_A(v) = \frac{e_0}{4\pi\varepsilon_0}\left[\frac{z_A + v(z - z_A)}{a_A}\left(\frac{1}{\varepsilon_S} - 1\right) - \frac{z_A + v(z - z_A)}{d_i\varepsilon_S}\right]$$

$$\Delta G_I = \frac{e_0^2}{4\pi\varepsilon_0}\left[\frac{z_A(z - z_A) + \frac{1}{2}(z - z_A)^2}{a_A}\left(\frac{1}{\varepsilon_S} - 1\right) - \frac{z_A(z - z_A) + \frac{1}{2}(z - z_A)^2}{d_i\varepsilon_S}\right]$$

In the second step,

$$\bar{\varphi}'_{\mathrm{A}}(v) = \frac{e_0}{4\pi\varepsilon_0}\left[\frac{z}{a_{\mathrm{A}}}\left(\frac{1}{\varepsilon_S}-1\right) - \frac{z}{d_i\varepsilon_S} + \frac{v(z_{\mathrm{A}}-z)}{a_{\mathrm{A}}}\left(\frac{1}{\varepsilon_{op}}-1\right) - \frac{v(z_{\mathrm{A}}-z)}{\varepsilon_{op}d_i}\right]$$

$$\Delta G_{II} = \frac{e_0^2}{4\pi\varepsilon_0}\left[\frac{z(z_{\mathrm{A}}-z)}{a_{\mathrm{A}}}\left(\frac{1}{\varepsilon_S}-1\right) - \frac{z(z_{\mathrm{A}}-z)}{d_i\varepsilon_S}\right.$$

$$\left. + \frac{(z_{\mathrm{A}}-z)^2}{2a_{\mathrm{A}}}\left(\frac{1}{\varepsilon_{op}}-1\right) - \frac{(z_{\mathrm{A}}-z)^2}{2\varepsilon_{op}d_i}\right]$$

$$\Delta G_I + \Delta G_{II} = \frac{e_0^2}{4\pi\varepsilon_0}\left(\frac{1}{\varepsilon_{op}}-\frac{1}{\varepsilon_S}\right)\left(\frac{1}{2a_{\mathrm{A}}}-\frac{1}{2d_i}\right)(z-z_{\mathrm{A}})^2$$

Thus,

$$G_{0,\mathrm{A}} = \lambda_0^{el}(z-z_{\mathrm{A}})^2$$

with

$$\lambda_0^{el} = \frac{e_0^2}{4\pi\varepsilon_0}\left(\frac{1}{\varepsilon_{op}}-\frac{1}{\varepsilon_S}\right)\left[\frac{1}{2a_{\mathrm{A}}}-\frac{1}{2d_i}\right]$$

thus establishing equation (1.27).

6.1.8. Effect of the Multiplicity of Electronic States in the Electrode

The individual forward rate constant for the transfer of one electron from one electron state in the metal to the acceptor (oxidized form of the redox couple) in the solution may be expressed as

$$k_{f,j} = Z^{el}\kappa_{el,j}\exp\left(-\frac{F\Delta G^{\neq}_{f,j}}{\mathcal{R}T}\right)$$

where $\kappa_{el,j}$ is the transmission coefficient defined in equation (1.36). The individual activation free energy for the forward reaction, $\Delta G^{\neq}_{f,j}$, is related to the reorganization energy, λ_t, according to

$$\Delta G^{\neq}_{f,j} = \frac{\lambda_t}{4}\left(1-\frac{\mathbf{E}-\mathbf{E^0}}{\lambda_t}\right)^2 = \frac{1}{4\lambda_t}\left[\lambda_t - (\mathbf{E}-\mathbf{E^0})\right]^2$$

where $\mathbf{E}$ is the energy of the electron in the metal and $\mathbf{E^0}$ is its value when the electrode potential, E, is equal to the formal potential of the redox couple, E^0. The overall rate constant, k_f, is obtained after multiplication by the Fermi–Dirac probability of finding an electron with the energy **E**:

$$\frac{1}{1+\exp\left[\frac{F}{\mathcal{R}T}(\mathbf{E}-\mathbf{E}_F)\right]}$$

by integration over the entire set of electron states in the metal:

$$\frac{k_f}{k_\infty}=\frac{\displaystyle\int_{-\infty}^{\infty}\kappa_{el}(\mathbf{E})\rho(\mathbf{E})\frac{\exp\left[-\left(\frac{F}{4\mathcal{R}T\lambda_t}\right)[\lambda_t-(\mathbf{E}-\mathbf{E}^\mathbf{0})]^2\right]}{1+\exp\left[\left(\frac{F}{\mathcal{R}T}\right)(\mathbf{E}-\mathbf{E}_\mathbf{F})\right]}d\mathbf{E}}{\lim(\mathbf{E}_F-\mathbf{E}^\mathbf{0}\gg\lambda_t)\displaystyle\int_{-\infty}^{\infty}\kappa_{el}(\mathbf{E})\rho(\mathbf{E})\frac{\exp\left[-\left(\frac{F}{4\mathcal{R}T\lambda_t}\right)[\lambda_t-(\mathbf{E}-\mathbf{E}^\mathbf{0})]^2\right]}{1+\exp\left[\left(\frac{F}{\mathcal{R}T}\right)(\mathbf{E}-\mathbf{E}_\mathbf{F})\right]}d\mathbf{E}}$$

where k_∞ is the maximal rate constant and $\rho(\mathbf{E})$ is the density of states corresponding to the energy **E**.

Similarly, for the oxidation process,

$$k_{b,j}=Z^{el}\kappa_{el,j}\exp\left(-\frac{F\Delta G^{\neq}_{b,j}}{\mathcal{R}T}\right)$$

with

$$\Delta G^{\neq}_{b,j}=\frac{\lambda_t}{4}\left(1+\frac{\mathbf{E}-\mathbf{E}^\mathbf{0}}{\lambda_t}\right)^2=\frac{1}{4\lambda_t}\left[\lambda_t+(\mathbf{E}-\mathbf{E}^\mathbf{0})\right]^2$$

The overall rate constant, k_b, is obtained after multiplication by the Fermi–Dirac probability of finding a hole with the energy **E**

$$\frac{1}{1+\exp\left[-\left(\frac{F}{\mathcal{R}T}\right)(\mathbf{E}-\mathbf{E}_F)\right]}$$

by integration over the entire set of holes states in the metal:

$$\frac{k_b}{k_\infty}=\frac{\displaystyle\int_{-\infty}^{\infty}\kappa_{el}(\mathbf{E})\rho(\mathbf{E})\frac{\exp\left[-\frac{F}{4\mathcal{R}T\lambda_t}[\lambda_t+(\mathbf{E}-\mathbf{E}^\mathbf{0})]^2\right]}{1+\exp\left[-\frac{F}{\mathcal{R}T}(\mathbf{E}-\mathbf{E}_F)\right]}d\mathbf{E}}{\lim(\mathbf{E}_F-\mathbf{E}^\mathbf{0}\ll\lambda_t)\displaystyle\int_{-\infty}^{\infty}\kappa_{el}(\mathbf{E})\rho(\mathbf{E})\frac{\exp\left[-\frac{F}{4\mathcal{R}T\lambda_t}[\lambda_t+(\mathbf{E}-\mathbf{E}^\mathbf{0})]^2\right]}{1+\exp\left[-\frac{F}{\mathcal{R}T}(\mathbf{E}-\mathbf{E}_F)\right]}d\mathbf{E}}$$

Assuming, as discussed in Section 1.4.2, that ρ and κ_{el} are independent of $\mathbf{E}$, introducing $\zeta = F[(\mathbf{E} - \mathbf{E}_F)/\mathcal{R}T]$, and taking into account that $-\mathbf{E}_F = E$ and $-\mathbf{E}^0 = E^0$, we obtain

$$\frac{k_f}{k_\infty} = \frac{\displaystyle\int_{-\infty}^{\infty} \frac{\exp\left[-\dfrac{\mathcal{R}T}{4F\lambda_t}\left\{\dfrac{F}{\mathcal{R}T}[\lambda_t + (E - E^0)] - \zeta\right\}^2\right]}{1 + \exp(\zeta)} d\zeta}{\lim(E - E^0 \ll -\lambda_t)\displaystyle\int_{-\infty}^{\infty} \frac{\exp\left[-\dfrac{\mathcal{R}T}{4F\lambda_t}\left\{\dfrac{F}{\mathcal{R}T}[\lambda_t + (E - E^0)] - \zeta\right\}^2\right]}{1 + \exp(\zeta)} d\zeta}$$

Similarly, introducing $\zeta = -F[(\mathbf{E} - \mathbf{E}_F)/\mathcal{R}T]$ gives us

$$\frac{k_b}{k_\infty} = \frac{\displaystyle\int_{-\infty}^{\infty} \frac{\exp\left[-\dfrac{\mathcal{R}T}{4F\lambda_t}\left\{\dfrac{F}{\mathcal{R}T}[\lambda_t - (E - E^0)] - \zeta\right\}^2\right]}{1 + \exp(\zeta)} d\zeta}{\lim(E - E^0 \gg \lambda_t)\displaystyle\int_{-\infty}^{\infty} \frac{\exp\left[-\dfrac{\mathcal{R}T}{4F\lambda_t}\left\{\dfrac{F}{\mathcal{R}T}[\lambda_t - (E - E^0)] - \zeta\right\}^2\right]}{1 + \exp(\zeta)} d\zeta}$$

An alternative change of integration variable is as follows:

$$\upsilon = \frac{\zeta - \dfrac{F}{\mathcal{R}T}[\lambda_t + (E - E^0)]}{\sqrt{4\dfrac{F\lambda_t}{\mathcal{R}T}}}$$

leading to

$$\frac{k_f}{k_\infty} = \frac{\displaystyle\int_{-\infty}^{\infty} \frac{\exp(-\upsilon^2)d\upsilon}{1 + \exp\left\{\dfrac{F}{\mathcal{R}T}[\lambda_t + (E - E^0)]\right\}\exp\left(\sqrt{4\lambda_t\dfrac{F}{\mathcal{R}T}}\upsilon\right)}}{\lim(E - E^0 \ll -\lambda_t)\displaystyle\int_{-\infty}^{\infty} \frac{\exp(-\upsilon^2)d\upsilon}{1 + \exp\left\{\dfrac{F}{\mathcal{R}T}[\lambda_t + (E - E^0)]\right\}\exp\left(\sqrt{4\lambda_t\dfrac{F}{\mathcal{R}T}}\upsilon\right)}}$$

$$\lim(E - E^0 \ll -\lambda_t)\int_{-\infty}^{\infty} \frac{\exp(-\upsilon^2)d\upsilon}{1 + \exp\left\{\dfrac{F}{\mathcal{R}T}[\lambda_t + (E - E^0)]\right\}\exp\left(\sqrt{4\lambda_t\dfrac{F}{\mathcal{R}T}}\upsilon\right)}$$

$$= \int_{-\infty}^{\infty} \exp(-\upsilon^2)d\upsilon = \sqrt{\pi}$$

and thus

$$\frac{k_f}{k_\infty}=\frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}\frac{\exp(-v^2)\,dv}{1+\exp\left\{\frac{F}{\mathcal{R}T}\left[\lambda_t+\left(E-E^0\right)\right]\right\}\exp\left(\sqrt{4\lambda_t\frac{F}{\mathcal{R}T}}v\right)}$$

Similarly,

$$\frac{k_b}{k_\infty}=\frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}\frac{\exp(-v^2)\,dv}{1+\exp\left\{\frac{F}{\mathcal{R}T}\left[\lambda_t-\left(E-E^0\right)\right]\right\}\exp\left(\sqrt{4\lambda_t\frac{F}{\mathcal{R}T}}v\right)}$$

with $k_\infty = Z^{el}\kappa_{el}$. At zero driving force $(E = E^0)$, $k_f = k_b = k_S$, with

$$\frac{k_S}{k_\infty}=\frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}\frac{\exp(-v^2)dv}{1+\exp\left(\frac{F\lambda_t}{\mathcal{R}T}\right)\exp\left[\sqrt{4\lambda_t\frac{F}{\mathcal{R}T}}v\right]}$$

The expressions of the rate constants given in equations (1.37) to (1.39) follow.

6.1.9. Cyclic Voltammetry of Two-Electron Nernstian Systems. Disproportionation

In the absence of disproportionation reaction taking place in solution, the concentrations of A, B, and C obey the following system of partial derivative equations:

$$\frac{\partial C_{\mathrm{A}}}{\partial t}=D\frac{\partial^2 C_{\mathrm{A}}}{\partial x^2} \tag{6.6}$$

$$\frac{\partial C_{\mathrm{B}}}{\partial t}=D\frac{\partial^2 C_{\mathrm{B}}}{\partial x^2} \tag{6.7}$$

$$\frac{\partial C_{\mathrm{C}}}{\partial t}=D\frac{\partial^2 C_{\mathrm{C}}}{\partial x^2} \tag{6.8}$$

whereas if the disproportionation–coproportionation reaction is taken into account, the governing partial derivative equations become

$$\frac{\partial C_{\mathrm{A}}}{\partial t}=D\frac{\partial^2 C_{\mathrm{A}}}{\partial x^2}+k_D C_{\mathrm{B}}^2-k_{-D}C_{\mathrm{A}}C_{\mathrm{C}}$$

$$\frac{\partial C_{\mathrm{B}}}{\partial t}=D\frac{\partial^2 C_{\mathrm{B}}}{\partial x^2}-2(k_D C_{\mathrm{B}}^2-k_{-D}C_{\mathrm{A}}C_{\mathrm{C}})$$

$$\frac{\partial C_{\mathrm{C}}}{\partial t}=D\frac{\partial^2 C_{\mathrm{C}}}{\partial x^2}+k_D C_{\mathrm{B}}^2-k_{-D}C_{\mathrm{A}}C_{\mathrm{C}}$$

In both cases the accompanying initial and boundary conditions are:

$$t = 0, \quad x \geq 0 \quad \text{and} \quad x = \infty, t \geq 0: \quad C_{\mathrm{A}} = C^0, \quad C_{\mathrm{B}} = 0, \quad C_{\mathrm{C}} = 0$$

$$x = 0, \quad t \geq 0: \qquad \frac{\partial C_{\mathrm{A}}}{\partial x} + \frac{\partial C_{\mathrm{B}}}{\partial x} + \frac{\partial C_{\mathrm{C}}}{\partial x} = 0$$

$$\frac{C_{\mathrm{A}}}{C_{\mathrm{B}}} = \exp\left[\frac{F}{\mathcal{R}T}\left(E - E^0 - \frac{\Delta E^0}{2}\right)\right] \tag{6.9}$$

$$\frac{C_{\mathrm{B}}}{C_{\mathrm{C}}} = \exp\left[\frac{F}{\mathcal{R}T}\left(E - E^0 + \frac{\Delta E^0}{2}\right)\right] \tag{6.10}$$

There are two contributions to the current:

$$\frac{i}{FS} = D\left(\frac{\partial C_{\mathrm{A}}}{\partial x}\right)_{x=0} - D\left(\frac{\partial C_{\mathrm{C}}}{\partial x}\right)_{x=0}$$

We may therefore combined linearly the three partial derivative equations as follows in both cases:

$$\frac{\partial (C_{\mathrm{A}} + C_{\mathrm{B}} + C_{\mathrm{C}})}{\partial t} = D\frac{\partial^2 (C_{\mathrm{A}} + C_{\mathrm{B}} + C_{\mathrm{C}})}{\partial x^2}$$

$$\frac{\partial (C_{\mathrm{A}} - C_{\mathrm{C}})}{\partial t} = D\frac{\partial^2 (C_{\mathrm{A}} - C_{\mathrm{C}})}{\partial x^2}$$

taking into account the appropriate initial and boundary conditions:

$$\frac{(C_{\mathrm{A}})_{x=0}}{C^0} + \frac{(C_{\mathrm{B}})_{x=0}}{C^0} + \frac{(C_{\mathrm{B}})_{x=0}}{C^0} = 1 \tag{6.11}$$

and

$$\frac{(C_{\mathrm{A}})_{x=0}}{C^0} - \frac{(C_{\mathrm{C}})_{x=0}}{C^0} = 1 - \int_0^{\frac{Fvt}{\mathcal{R}T}} \frac{i}{FSC^0\sqrt{D}\sqrt{\dfrac{Fv}{\mathcal{R}T}}} \frac{d\eta}{\sqrt{\dfrac{Fvt}{\mathcal{R}T} - \eta}} \tag{6.12}$$

Combination of equations (6.9) to (6.12) leads to the final expression of the current [equation 1.58)], which is therefore exactly the same in the presence and absence of the disproportionation reaction, provided that the diffusion coefficients of the three species are the same. The individual fluxes and concentration profiles are different, however, as exemplified in Figure 6.3.

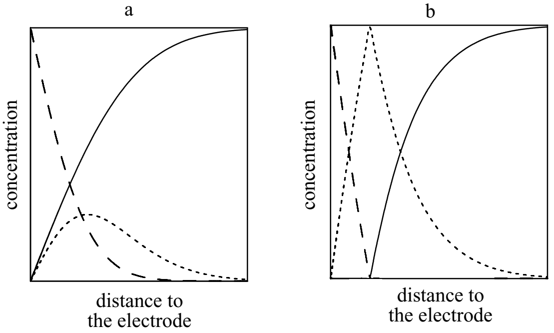


FIGURE 6.3. Concentration profiles for two separated waves (Figure 1.25) at a potential located beyond the second wave. a: with no disproportionation process. b: In the presence of a fast disproportionation. —, A; · · ·, B; – –, C.

6.2 COUPLING OF HOMOGENEOUS CHEMICAL REACTIONS WITH ELECTRON TRANSFER

6.2.1. The EC Mechanism

In the framework of Scheme 2.1, we start with the case where the electron transfer does not interfere kinetically. As compared to the simple Nernstian electron transfer case (Section 6.1.2), the main change occurs in the partial derivative equation pertaining to B, where a kinetic term is introduced in Fick's second law. A corresponding equation for C should also be taken into account, leading to the following system of partial derivative equations, accompanied by a series of initial and boundary conditions (assuming that the diffusion coefficients of A, B, and C are the same):

$$\frac{\partial C_A}{\partial t} = D\frac{\partial^2 C_A}{\partial x^2}$$

$$\frac{\partial C_B}{\partial t} = D\frac{\partial^2 C_B}{\partial x^2} - k_+ C_B + k_- C_C$$

$$\frac{\partial C_C}{\partial t} = D\frac{\partial^2 C_C}{\partial x^2} + k_+ C_B - k_- C_C$$

$$t = 0,\ x \geq 0 \text{ and } x = \infty,\ t \geq 0: \qquad C_A = C^0, \quad C_B = 0, \quad C_C = 0$$

$$x = 0,\ t \geq 0: \quad \frac{\partial C_A}{\partial x} + \frac{\partial C_B}{\partial x} = 0 \quad \text{(conservation of fluxes)}$$

$$C_A = C_B \exp\left[\frac{F}{\mathcal{R}T}(E - E^0)\right] \quad \text{(Nernst's law)}$$

$$\frac{\partial C_C}{\partial x} = 0 \quad \text{(C is not reduced at the electrode)}$$

where the electrode potential depends on time according to

$$\begin{aligned} 0 \le t \le t_R: &\qquad E = E_i - vt \\ t_R \le t \le 2t_R: &\qquad E = E_f + v(t - t_R) = 2E_f - E_i + vt \end{aligned}$$

The current is related to the fluxes of A and B according to

$$\frac{i}{FS} = D\left(\frac{\partial C_{\mathrm{A}}}{\partial x}\right)_{x=0} = -D\left(\frac{\partial C_{\mathrm{B}}}{\partial x}\right)_{x=0}$$

We introduce the same normalized variables and parameters as in Section 6.1.2 and, in addition,

$$\lambda_+ = \frac{\mathcal{R}T}{F}\frac{k_+}{v} \qquad \lambda_- = \frac{\mathcal{R}T}{F}\frac{k_-}{v} \qquad \lambda = \lambda_+ + \lambda_- \qquad \frac{\lambda_+}{\lambda_-} = \frac{k_+}{k_-} = K$$

which characterize the competition between the homogeneous reaction and diffusion.

The set of equations above thus becomes

$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} \tag{6.13}$$

$$\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - \lambda_+ b + \lambda_- c \tag{6.14}$$

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial y^2} + \lambda_+ b - \lambda_- c \tag{6.15}$$

$$\tau = 0,\ y \ge 0 \text{ and } y = \infty,\ \tau \ge 0: \qquad a = 1, \quad b = 0, \quad c = 0$$

$$y = 0,\ \tau \ge 0: \qquad a = b\exp(-\xi), \quad \frac{\partial a}{\partial y} + \frac{\partial b}{\partial y} = 0, \quad \frac{\partial c}{\partial y} = 0$$

where ξ and τ are related by

$$0 \le \tau \le \tau_R: \quad \xi = \xi_c = -u_i + \tau \tag{6.16}$$

$$\tau_R \le \tau \le 2\tau_R: \ \xi = \xi_a = -2u_f + u_i - \tau = -u_f - (\tau - \tau_R) \tag{6.17}$$

The dimensionless current is given by:

$$\psi = \left(\frac{\partial a}{\partial y}\right)_{y=0} = -\left(\frac{\partial b}{\partial y}\right)_{y=0}$$

Equations (6.14) and (6.15) may be combined linearly as

$$\frac{\partial(b+c)}{\partial\tau}=\frac{\partial^2(b+c)}{\partial y^2} \tag{6.18}$$

and

$$\frac{\partial(Kb-c)}{\partial\tau}=\frac{\partial^2(Kb-c)}{\partial y^2}-\lambda(Kb-c) \tag{6.19}$$

Integration of equation (6.13) leads as in Section 6.1.2 to

$$(a)_{y=0}=1-\frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta \tag{6.20}$$

Similarly, from equation (6.18),

$$(b)_{y=0}+(c)_{y=0}=\frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta \tag{6.21}$$

Integration of equation (6.19) in the Laplace space leads to

$$\begin{aligned}K\bar{b}-\bar{c}=&\left[(K\bar{b}-\bar{c})_{y=0}-\frac{1}{\sqrt{s+\lambda}}\left[\frac{\partial(K\bar{b}-\bar{c})}{\partial y}\right]_{y=0}\right]\frac{\exp(-\sqrt{s+\lambda}y)}{2}\\&+\left[(K\bar{b}-\bar{c})_{y=0}+\frac{1}{\sqrt{s+\lambda}}\left[\frac{\partial(K\bar{b}-\bar{c})}{\partial y}\right]_{y=0}\right]\frac{\exp(\sqrt{s+\lambda}y)}{2}\end{aligned}$$

and thus to

$$(K\bar{b}-\bar{c})_{y=0}=\frac{K}{\sqrt{s+\lambda}}\bar{\psi}$$

Returning to the original space (see Table 6.1), we have

$$(Kb-c)_{y=0}=\frac{K}{\sqrt{\pi}}\int_0^{\tau}\exp[-\lambda(\tau-\eta)]\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta \tag{6.22}$$

A combination of equations (6.21) and (6.22) leads to

$$(b)_{y=0}=\frac{1}{\sqrt{\pi}}\int_0^{\tau}\left\{\frac{K}{1+K}\exp[-\lambda(\tau-\eta)]+\frac{1}{1+K}\right\}\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta \tag{6.23}$$

TABLE 6.4. Equations of the Voltammograms for the EC Mechanism

Zone	Dimensionless Expression of the Voltammogram	
KG	$\frac{\exp(-\xi)}{\sqrt{\pi}}\frac{K}{1+K}\int_0^{\tau}\exp[-\lambda(\tau-\eta)]\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta+\left[1+\frac{\exp(-\xi)}{1+K}\right]\frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta=1$	
DO	K small and/or λ small	$\frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta=\frac{1}{1+\exp(-\xi)}$
KO	K large	$\frac{\exp(-\xi)}{\sqrt{\pi}}\int_0^{\tau}\exp[-\lambda(\tau-\eta)]\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta+\frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta=1$
KP	K large, λ large, $\sqrt{\lambda}/K$ small	$\frac{\psi\exp(-\xi)}{\sqrt{\lambda}}+\frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta=1$ $\left[\text{i.e., }\psi\exp(-\xi^{c})+\frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta,\ \text{with: }\xi^{c}=\xi+\ln\sqrt{\lambda}\right]$
KE	K large, λ large	$\psi\exp(-\xi^{\mathrm{eq}})\frac{K}{\sqrt{\lambda}}+[1+\exp(-\xi^{\mathrm{eq}})]\frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta=1$ with $\xi^{\mathrm{eq}}=\xi+\ln K$
DE	λ large, $\sqrt{\lambda}/K$ large	$\frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta=\frac{1}{1+\exp(-\xi^{\mathrm{eq}})}$ with $\xi^{\mathrm{eq}}=\xi+\ln(1+K)$

Application of Nernst's law to equations (6.20) and (6.23) finally leads to the dimensionless expression of the voltammogram in the general case (KG zone in Figure 2.1) reported in Table 6.4.

The response depends on two dimensionless parameters, K and λ. The number of independent parameters decreases for limiting values of the parameters where asymptotic behaviors are met, corresponding to the various zones in the kinetic zone diagram in Figure 2.1. The corresponding dimensionless expressions of the voltammograms are given in Table 6.4. As they stand in the table, the integral equations contain both the time (τ) and potential (ξ) dimensionless variables and are therefore suited for calculation of both the cathodic and anodic traces, using the relationships between ξ and τ pertaining to each part of the scan [equations (6.16) and (6.17), respectively]. Derivation of the characteristics of the forward trace is simplified when it is assumed, as is always the case in practice, that the initial potential is much more positive than the peak potential. Then integration over the 0–τ interval may be replaced by an integration over the $-\infty$–ξ interval.

It is worth noting that for large values of λ,

$$\frac{1}{\sqrt{\pi}}\int_0^{\tau}\exp[-\lambda(\tau-\eta)]\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta=\frac{\psi}{\sqrt{\lambda}}$$

as results immediately from examining the Laplace transform:

$$\frac{\bar{\psi}}{\sqrt{s+\lambda}}\xrightarrow{\lambda\to\infty}\frac{\bar{\psi}}{\sqrt{\lambda}}$$

The disappearance of the time variable s in front of λ corresponds to establishment of the steady state discussed in Section 2.2.1, leading to

$$b_{y=0}=\frac{\psi}{\sqrt{\lambda}} \tag{6.24}$$

It may also be obtained directly by equating to zero the term in the partial derivative equation (6.25) that governs the variations of the B concentration with time

$$\frac{\partial b}{\partial \tau}=\frac{\partial^2 b}{\partial y^2}-\lambda_+ b \tag{6.25}$$

leading to

$$\frac{\partial^2 b}{\partial y^2}=\lambda_+ b$$

After multiplication by $\partial b/\partial y$,

$$\frac{\partial^2 b}{\partial y^2}\frac{\partial b}{\partial y}=\lambda_+ b\frac{\partial b}{\partial y}$$

and integration, one obtains

$$\left(\frac{\partial b}{\partial y}\right)^2=\lambda_+ b^2+Cst$$

The constant is, in fact, zero, since there are points outside the thin reaction layer where both b and $\partial b/\partial y$ are equal to zero. It follows that

$$\left(\frac{\partial b}{\partial y}\right)^2=\lambda_+ b^2$$

leading, therefore, for $y = 0$, to equation (6.24). This possibility of an alternative demonstration of equation (6.24) will be precious when dealing with higher-order reactions, giving rise to nonlinear differential equations.

Still another approach to the notion of pure kinetic conditions and the related concept of reaction layer involves the following normalization of space and concentration:

$$y^* = y\sqrt{\lambda_+} = \frac{x}{\sqrt{\dfrac{D}{k_+}}}$$

(i.e., the distance to the electrode is normalized toward the thickness of the reaction layer) and

$$b^* = b\sqrt{\lambda_+} = C_{\mathrm{B}}\sqrt{\frac{\mathcal{R}T}{F}\frac{k_+}{v}}$$

which converts the very small b into a quantity, b^*, that is commensurable to 1 over the reaction layer. Equation (6.25) thus becomes

$$\frac{1}{\lambda_+}\frac{\partial b}{\partial \tau} = \frac{\partial^2 b^*}{\partial y^* 2} - b^* \xrightarrow{\lambda_+ \to \infty} 0 = \frac{\partial^2 b^*}{\partial y^* 2} - b^* \tag{6.26}$$

Integration of equation (6.26) again leads to equation (6.24).

The pure kinetic conditions still apply if electron transfer is not unconditionally fast and Nernst's law has to be replaced by the law that governs the electron transfer kinetics as boundary condition, that is, in dimensionless terms,

$$\psi = \Lambda_f(\xi)[a_{y=0} - b_{y=0}\exp(-\xi)]$$

with

$$\Lambda_f(\xi) = k_f(E)\sqrt{\frac{\mathcal{R}T}{FvD}}$$

thus leading to

$$\psi\left[\frac{1}{\Lambda_f(\xi)} + \frac{\psi\exp(-\xi)}{\sqrt{\lambda}}\right] = 1 - \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta$$

Since the wave is irreversible, interest is concentrated on the cathodic trace:

$$\psi\left[\frac{1}{\Lambda_f(\xi)} + \frac{\psi\exp(-\xi)}{\sqrt{\lambda}}\right] = 1 - \frac{1}{\sqrt{\pi}}\int_{-\infty}^\xi \frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta$$

thus leading to equation (2.22). When the Butler–Volmer law applies,

$$\Lambda_f(\xi) = \Lambda \exp(\alpha\xi),$$

and therefore

$$\psi\left[\frac{\exp(-\alpha\xi)}{\Lambda} + \frac{\psi \exp(-\xi)}{\sqrt{\lambda}}\right] = 1 - \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\xi} \frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta$$

thus leading to equation (2.11).

6.2.2. The CE Mechanism

In the framework of Scheme 2.2, we consider the case where the electron transfer is fast enough for not interfering kinetically. The governing system of partial derivative equations and of initial and boundary conditions writes in this case

$$\frac{\partial C_A}{\partial t} = D\frac{\partial^2 C_A}{\partial x^2} - k_- C_A + k_+ C_C$$

$$\frac{\partial C_B}{\partial t} = D\frac{\partial^2 C_B}{\partial x^2}$$

$$\frac{\partial C_C}{\partial t} = D\frac{\partial^2 C_C}{\partial x^2} + k_- C_A - k_+ C_C$$

$$t = 0,\ x \geq 0 \text{ and } x = \infty,\ t \geq 0:\ C_A = \frac{K}{1+K}C^0,\ C_B = 0,\ C_C = \frac{C^0}{1+K}$$

$$x = 0,\ t \geq 0:\ \frac{\partial C_A}{\partial x} + \frac{\partial C_B}{\partial x} = 0$$

$$C_A = C_B \exp\left[\frac{F}{\mathcal{R}T}(E - E^0)\right]$$

$$\frac{\partial C_C}{\partial x} = 0$$

The electrode potential depends on time according to the same relationships as in the preceding section.

The current is related to the fluxes of A and B according to

$$\frac{i}{FS} = D\left(\frac{\partial C_A}{\partial x}\right)_{x=0} = -D\left(\frac{\partial C_B}{\partial x}\right)_{x=0}$$

We introduce the same normalized variables and parameters as in Section 6.2.1, and in addition,

$$\lambda_+ = \frac{\mathcal{R}T}{F}\frac{k_+}{v} \qquad \lambda_- = \frac{\mathcal{R}T}{F}\frac{k_-}{v} \qquad \lambda = \lambda_+ + \lambda_- \qquad \frac{\lambda_+}{\lambda_-} = \frac{k_+}{k_-} = K$$

which characterize the competition between the homogeneous reaction and diffusion. The set of equations above thus becomes

$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} - \lambda_- a + \lambda_+ c \tag{6.27}$$

$$\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} \tag{6.28}$$

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial y^2} + \lambda_- a - \lambda_+ c \tag{6.29}$$

$$\tau = 0,\ y \geq 0 \text{ and } y = \infty,\ \tau \geq 0: \qquad a = 1, \quad b = 0, \quad c = 0$$

$$y = 0,\ \tau \geq 0: \qquad a = b\exp(-\xi), \quad \frac{\partial a}{\partial y} + \frac{\partial b}{\partial y} = 0, \quad \frac{\partial c}{\partial y} = 0$$

where ξ and τ are related by the same relationships as in the preceding section. The dimensionless current is given by

$$\psi = \left(\frac{\partial a}{\partial y}\right)_{y=0} = -\left(\frac{\partial b}{\partial y}\right)_{y=0}$$

Equations (6.27) and (6.29) may be linearly combined as

$$\frac{\partial(a+c)}{\partial \tau} = \frac{\partial^2 (a+c)}{\partial y^2} \tag{6.30}$$

and

$$\frac{\partial(Kc-a)}{\partial \tau} = \frac{\partial^2 (Kc-a)}{\partial y^2} - \lambda(Kc-a) \tag{6.31}$$

Integration of equation (6.28) leads to

$$(b)_{y=0} = \frac{1}{\sqrt{\pi}} \int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau-\eta}} d\eta \tag{6.32}$$

Similarly, from equation (6.30),

$$(a)_{y=0} + (c)_{y=0} = 1 - \frac{1}{\sqrt{\pi}} \int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau-\eta}} d\eta \tag{6.33}$$

Integration of equation (6.31) in the Laplace space leads to

$$K\bar{c}-\bar{a}=\left[(K\bar{c}-\bar{a})_{y=0}-\frac{1}{\sqrt{s+\lambda}}\left[\frac{\partial(K\bar{c}-\bar{a})}{\partial y}\right]_{y=0}\right]\frac{\exp(-\sqrt{s+\lambda}y)}{2}$$
$$+\left[(K\bar{c}-\bar{a})_{y=0}+\frac{1}{\sqrt{s+\lambda}}\left[\frac{\partial(K\bar{c}-\bar{a})}{\partial y}\right]_{y=0}\right]\frac{\exp(\sqrt{s+\lambda}y)}{2}$$

and thus to

$$(K\bar{c}-\bar{a})_{y=0}=\frac{\bar{\psi}}{\sqrt{s+\lambda}}$$

Coming back to the original space (see Table 6.1), we have

$$(Kc-a)_{y=0}=\frac{1}{\sqrt{\pi}}\int_0^{\tau}\exp[-\lambda(\tau-\eta)]\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta \tag{6.34}$$

Combination of equations (6.33) and (6.34) leads to

$$(a)_{y=0}=\frac{K}{1+K}\left[1-\frac{1}{\sqrt{\pi}}\int_0^{\tau}\left\{1+\frac{\exp[-\lambda(\tau-\eta)]}{K}\right\}\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta\right] \tag{6.35}$$

Application of Nernst's law to equations (6.32) and (6.35) finally leads to the dimensionless expression of the voltammogram in the general case (KG zone in Figure 2.8) reported in Table 6.5.

The response depends on two dimensionless parameters, K and λ. The number of independent parameters decreases for limiting values of the parameters where asymptotic behaviors are met, corresponding to the various zones in the kinetic zone diagram in Figure 2.8. The corresponding dimensionless expressions of the voltammograms are given in Table 6.5. As they stand in the table, the integral equations contain both the time (τ) and potential (ξ) dimensionless variables and are therefore suited for calculation of both the cathodic and anodic traces, using the relationships between ξ and τ pertaining to each part of the scan [equations (6.16) and (6.17), respectively]. Derivation of the characteristics of the forward trace is simplified, when it is considered, as always the case in practice, that the initial potential is much more positive than the peak potential. Then integration over the 0–τ interval may be replaced by an integration over the $-\infty$–ξ interval.

TABLE 6.5. Equations of the Voltammograms for the CE Mechanism

Zone	Dimensionless Expression of the Voltammogram	
KG	$\frac{1}{\sqrt{\pi}}\int_0^\tau \left\{1+\frac{\exp[-\lambda(\tau-\eta)]}{K}+\frac{1+K}{K}\exp(-\xi)\right\}\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta = 1$	
DO	λ small	$\frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta = \frac{K}{1+K}\frac{1}{1+\exp(-\xi)}$
KO	K small	$\frac{1}{\sqrt{\pi}}\int_0^\tau \{\exp[-\lambda(\tau-\eta)]+\exp(-\xi)\}\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta = K$
KP	K small, λ large, $K\sqrt{\lambda}$ small	$\psi+\frac{\sqrt{\lambda}\exp(-\xi)}{\sqrt{\pi}}\int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta = K\sqrt{\lambda}$ $\left[\text{i.e.,}\ \psi+\frac{\exp(-\xi^c)}{\sqrt{\pi}}\int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta = K\sqrt{\lambda}\ \text{with}\ \xi^c = \xi - \ln\sqrt{\lambda}\right]$ plateau-shaped wave with, as plateau height, $\psi(\xi\to\infty) = K\sqrt{\lambda}$ and as half-wave location, $\xi^c = 0.17$
KE	λ large	$\frac{\psi(\eta)}{K\sqrt{\lambda}}+[1+\exp(-\xi^{\text{eq}})]\frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta = 1$ with $\xi^{\text{eq}} = \xi - \ln\left(\frac{K}{1+K}\right)$
DE	λ large, $K\sqrt{\lambda}$ large	$\frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta = \frac{1}{1+\exp(-\xi^{\text{eq}})}$ with $\xi^{\text{eq}} = \xi + \ln\left(\frac{K}{1+K}\right)$

6.2.3. Double Potential Step Responses for Processes Involving First- or Second-Order Follow-up Reactions

The governing dimensionless partial derivative equations are similar to those derived for cyclic voltammetry in Section 6.2.2 for the various dimerization mechanisms and in Section 6.2.1 for the EC mechanism. They are summarized in Table 6.6. The definition of the dimensionless variables is different, however, the normalizing time now being the time t_R at which the potential is reversed. Definitions of the new time and space variables and of the kinetic parameter are thus changed (see Table 6.6). The equation systems are then solved numerically according to a finite difference method after discretization of the time and space variables (see Section 2.2.8). Computation of the

TABLE 6.6. Governing Equations for Mechanisms Involving First- or Second-Order Follow-up Reactions

Mechanism	$\lambda =$	Governing Equations	Dimensionless Variables and Parameters
EC	kt_R	$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2}$ $\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - \lambda b$	$\tau = \frac{t}{t_R}, \quad y = \frac{x}{\sqrt{Dt_R}}$ $a = \frac{C_A}{C_A^0}, \quad b = \frac{C_B}{C_A^0}$
RRD	$k_d C^0 t_R$	$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2}$ $\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - 2\lambda b^2$	Initial and Boundary Conditions $\tau = 0,\ y \geq 0$ and $y = \infty,\ \tau \geq 0$: $a = 1, b = 0$ $y = 0,\ \tau \geq 0$: $\quad \frac{\partial a}{\partial y} + \frac{\partial b}{\partial y} = 0$ first potential step: $y = 0,\ 0 < \tau < 1 : a = 0$ reverse potential step: $y = 0, 1 < \tau : b = 0$
RSD–ECE	$k_d C^0 t_R$	$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} - \lambda ab$ $\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} - \lambda ab$	
RSD–DISP1	$k_d C^0 t_R$	$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2}$ $\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - 2\lambda ab$	Anodic-to-Cathodic Current Ratio
RSD–DISP2	$K_d k_D C^{0^2} t_R$	$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2}$ $\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - 2\lambda ab^2$	$R_{DPS} = -\frac{1}{1 - (1/\sqrt{2})} \frac{(\partial a/\partial y)_{y=0,\tau=2}}{(\partial a/\partial y)_{y=0,\tau=1}}$

gradient of *a* then allows one to obtain the anodic-to-cathodic current ratio taken at the end of each step, according to the relationship given in Table 6.6.

6.2.4. The ECE and DISP Mechanisms

We consider the case where the follow-up reaction is irreversible, thus being characterized by the rate constant *k*, and the electron transfer is so fast as to obey Nernst's equilibrium law. The governing equations may thus be expressed as

$$\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial x^2}$$

$$\frac{\partial C_B}{\partial t} = D \frac{\partial^2 C_B}{\partial x^2} - kC_B$$

$$\frac{\partial C_C}{\partial t} = D \frac{\partial^2 C_C}{\partial x^2} + kC_B$$

$$\frac{\partial C_D}{\partial t} = D\frac{\partial^2 C_D}{\partial x^2}$$

$t = 0$, $x \geq 0$ and $x = \infty$, $t \geq 0$: $\quad C_A = C^0, \quad C_B = 0, \quad C_C = 0, \quad C_D = 0$

$x = 0$, $t \geq 0$: $\quad \dfrac{\partial C_A}{\partial x} + \dfrac{\partial C_B}{\partial x} = 0, \quad \dfrac{\partial C_C}{\partial x} + \dfrac{\partial C_D}{\partial x} = 0$

$$C_A = C_B \exp\left[\frac{F}{\mathcal{R}T}(E - E^0)\right] \quad \text{(Nernst's law)}$$

$$C_C = 0 \quad \text{(C is reduced at the electrode as soon as formed)}$$

where the electrode potential depends on time according to

$0 \leq t \leq t_R$: $\quad E = E_i - vt$

$t_R \leq t \leq 2t_R$: $\quad E = E_f + v(t - t_R) = 2E_f - E_i + vt$

The current is the sum of two contributions, i_1, which corresponds to the reduction of A, and i_2, which corresponds to the reduction of C:

$$i = i_1 + i_2$$

$$\frac{i_1}{FS} = D\left(\frac{\partial C_A}{\partial x}\right)_{x=0} = -D\left(\frac{\partial C_B}{\partial x}\right)_{x=0}$$

$$\frac{i_2}{FS} = D\left(\frac{\partial C_C}{\partial x}\right)_{x=0} = -D\left(\frac{\partial C_D}{\partial x}\right)_{x=0}$$

The main difference with the EC mechanism (Section 6.2.1) is that C is reduced as soon as it reaches the electrode: hence the replacement of the boundary condition $(\partial C_C/\partial x)_{x=0} = 0$ by the condition $(C_C)_{x=0} = 0$. A second difference is the contribution to the current provided by the reduction of C. Introduction of the same normalized variables and parameters as in Sections 6.1.2 and 6.2.1 leads to

$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} \tag{6.36}$$

$$\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - \lambda b \tag{6.37}$$

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial y^2} + \lambda b \tag{6.38}$$

$\tau = 0$, $y \geq 0$ and $y = \infty$, $\tau \geq 0$: $\quad a = 1, \quad b = 0, \quad c = 0$

$y = 0$, $\tau \geq 0$: $\quad a = b\exp(-\xi), \quad \dfrac{\partial a}{\partial y} + \dfrac{\partial b}{\partial y} = 0, \quad c = 0$

where ξ and τ are related by equations (6.16) and (6.17).

The dimensionless current is the sum of two contributions given by

$$\psi = \psi_1 + \psi_2$$
$$\psi_1 = \left(\frac{\partial a}{\partial y}\right)_{y=0} = -\left(\frac{\partial b}{\partial y}\right)_{y=0}$$
$$\psi_2 = \left(\frac{\partial c}{\partial y}\right)_{y=0} = -\left(\frac{\partial d}{\partial y}\right)_{y=0}$$

We see that to obtain the two contributions to the current, it is not necessary to take the partial derivative equation concerning d into consideration.

In the Laplace plane, equation (6.37) becomes, taking into account the initial condition on b,

$$s\bar{b} = \frac{\partial^2 \bar{b}}{\partial y^2} - \lambda \bar{b};$$

thus,

$$\bar{b} = \left[(\bar{b})_{y=0} - \frac{1}{\sqrt{s+\lambda}}\left(\frac{\partial \bar{b}}{\partial y}\right)_{y=0}\right]\frac{\exp(-\sqrt{s+\lambda}\,y)}{2} + \left[(\bar{b})_{y=0} + \frac{1}{\sqrt{s+\lambda}}\left(\frac{\partial \bar{b}}{\partial y}\right)_{y=0}\right]\frac{\exp(\sqrt{s+\lambda}\,y)}{2}$$

and from the $y = \infty$ boundary condition,

$$(\bar{b})_{y=0} = \frac{\bar{\psi}_1}{\sqrt{s+\lambda}}$$

Coming back to the original plane, we have

$$(b)_{y=0} = \frac{1}{\sqrt{\pi}}\int_0^{\tau} \exp[-\lambda(\tau-\eta)]\frac{\psi_1(\eta)}{\sqrt{\tau-\eta}}\,d\eta$$

Since, as in the absence of follow-up reactions,

$$(a)_{y=0} = 1 - \frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi_1(\eta)}{\sqrt{\tau-\eta}}\,d\eta$$

Application of Nernst's law as an $y = 0$ boundary condition thus leads to

$$\frac{\exp(-\xi)}{\sqrt{\pi}} \int_0^{\tau} \exp[-\lambda(\tau - \eta)] \frac{\psi_1(\eta)}{\sqrt{\tau - \eta}} d\eta + \frac{1}{\sqrt{\pi}} \int_0^{\tau} \frac{\psi_1(\eta)}{\sqrt{\tau - \eta}} d\eta = 1 \qquad (6.39)$$

The second contribution to the current may then be derived as follows. Addition of equations (6.37) and (6.38) leads to

$$\frac{\partial b + c}{\partial \tau} = \frac{\partial^2 b + c}{\partial y^2}$$

Using Laplace transformation in the same manner as in Section 6.2.1, we obtain

$$\bar{b}_0 + \bar{c}_0 + \frac{1}{\sqrt{s}} \left[\left(\frac{\partial \bar{b}}{\partial y} \right)_{y=0} + \left(\frac{\partial \bar{c}}{\partial y} \right)_{y=0} \right] = 0$$

and thus

$$\frac{\bar{\psi}_1 - \bar{\psi}_2}{\sqrt{s}} = \bar{b}_0 \qquad (6.40)$$

That is, in the original space,

$$\frac{1}{\sqrt{\pi}} \int_0^{\tau} \frac{\psi_2}{\sqrt{\tau - \eta}} d\eta = \frac{1}{\sqrt{\pi}} \int_0^{\tau} \frac{\psi_1}{\sqrt{\tau - \eta}} d\eta - b_0$$

and finally,

$$\frac{1}{\sqrt{\pi}} \int_0^{\tau} \frac{\psi_2}{\sqrt{\tau - \eta}} d\eta = \frac{1}{\sqrt{\pi}} \int_0^{\tau} \frac{\psi_1}{\sqrt{\tau - \eta}} d\eta - \frac{\exp(-\xi)}{\sqrt{\pi}} \int_0^{\tau} \exp[-\lambda(\tau - \eta)] \frac{\psi_1(\eta)}{\sqrt{\tau - \eta}} d\eta \qquad (6.41)$$

For each value of the kinetic parameter, λ, once ψ_1 has been computed from equation (6.39), ψ_2, and thus the total dimensionless current ψ, is obtained from equation (6.41).

The pure kinetic conditions, which are achieved for large values of λ, implies that $\bar{b}_0 = \bar{\psi}_1/\sqrt{\lambda} \rightarrow 0$ and thus, from equation (6.40), $\psi_2 = \psi_1$. It follows that the current is exactly the double of the irreversible EC current obtained under pure kinetic conditions along the entire current–potential curve.

In the DISP case the governing partial derivative equations and the set of initial and boundary conditions are written

$$\begin{aligned}
\frac{\partial C_{\mathrm{A}}}{\partial t} &= D\frac{\partial^2 C_{\mathrm{A}}}{\partial x^2} + k_D C_{\mathrm{B}} C_{\mathrm{C}} \\
\frac{\partial C_{\mathrm{B}}}{\partial t} &= D\frac{\partial^2 C_{\mathrm{B}}}{\partial x^2} - kC_{\mathrm{B}} - k_D C_{\mathrm{B}} C_{\mathrm{C}} \\
\frac{\partial C_{\mathrm{C}}}{\partial t} &= D\frac{\partial^2 C_{\mathrm{C}}}{\partial x^2} + kC_{\mathrm{B}} - k_D C_{\mathrm{B}} C_{\mathrm{C}} \\
\frac{\partial C_{\mathrm{D}}}{\partial t} &= D\frac{\partial^2 C_{\mathrm{D}}}{\partial x^2} + k_D C_{\mathrm{B}} C_{\mathrm{C}}
\end{aligned}$$

$t = 0$, $x \geq 0$ and $x = \infty$, $t \geq 0$: $\quad C_{\mathrm{A}} = C^0, \quad C_{\mathrm{B}} = 0, \quad C_{\mathrm{C}} = 0, \quad C_{\mathrm{D}} = 0$

$x = 0$, $t \geq 0$: $\quad \dfrac{\partial C_{\mathrm{A}}}{\partial x} + \dfrac{\partial C_{\mathrm{B}}}{\partial x} = 0, \quad \dfrac{\partial C_{\mathrm{C}}}{\partial x} + \dfrac{\partial C_{\mathrm{D}}}{\partial x} = 0$

$$C_{\mathrm{A}} = C_{\mathrm{B}} \exp\left[\frac{F}{\mathcal{R}T}(E - E^0)\right] \quad \text{(Nernst's law)}$$

where the electrode potential depends on time according to

$0 \leq t \leq t_R$: $\quad E = E_i - vt$

$t_R \leq t \leq 2t_R$: $\quad E = E_f + v(t - t_R) = 2E_f - E_i + vt$

Since reaction B → C is the rate-determining step, the concentration of C obeys the steady-state approximation leading to

$$C_{\mathrm{C}} = \frac{k}{k_D}$$

and therefore to

$$\begin{aligned}
\frac{\partial C_{\mathrm{A}}}{\partial t} &= D\frac{\partial^2 C_{\mathrm{A}}}{\partial x^2} + kC_{\mathrm{B}} \\
\frac{\partial C_{\mathrm{B}}}{\partial t} &= D\frac{\partial^2 C_{\mathrm{B}}}{\partial x^2} - 2kC_{\mathrm{B}} \\
\frac{\partial C_{\mathrm{D}}}{\partial t} &= D\frac{\partial^2 C_{\mathrm{D}}}{\partial x^2} + kC_{\mathrm{B}}
\end{aligned}$$

Only the reduction of A contributes to the current. Thus,

$$\frac{i}{FS} = D\left(\frac{\partial C_{\mathrm{A}}}{\partial x}\right)_{x=0} = -D\left(\frac{\partial C_{\mathrm{B}}}{\partial x}\right)_{x=0}$$

In dimensionless terms,

$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} + \lambda b \tag{6.42}$$

$$\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - 2\lambda b \tag{6.43}$$

$\tau = 0,\ y \geq 0$ and $y = \infty,\ \tau \geq 0$: $\quad a = 1, \quad b = 0$

$y = 0,\ \tau \geq 0$: $\quad a = b\exp(-\xi), \quad \dfrac{\partial a}{\partial y} + \dfrac{\partial b}{\partial y} = 0$

where ξ and τ are related by equations (6.16) and (6.17). The dimensionless current is given by

$$\psi = \left(\frac{\partial a}{\partial y}\right)_{y=0} = -\left(\frac{\partial b}{\partial y}\right)_{y=0}$$

Addition of equations (6.42) and (6.43) leads to

$$\frac{\partial(2a+b)}{\partial \tau} = \frac{\partial^2(2a+b)}{\partial y^2}$$

It follows that in the Laplace plane, taking into account the initial conditions

$$s(2\bar{a} + \bar{b}) - 2 = \frac{\partial^2(2\bar{a} + \bar{b})}{\partial y^2}$$

and therefore, taking account of the boundary conditions for $y = \infty$, we have

$$2(\bar{a})_{y=0} + (\bar{b})_{y=0} + \frac{\bar{\psi}}{\sqrt{s}} - \frac{2}{s} = 0$$

Coming back to the original space we find that

$$2(a)_{y=0} + (b)_{y=0} = 2 - \frac{1}{\sqrt{\pi}} \int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau - \eta}} d\eta$$

and thus, taking account of Nernst's law as $y = 0$ boundary condition,

$$(b)_{y=0}[1 + 2\exp(-\xi)] = 1 - \frac{1}{\sqrt{\pi}} \int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau - \eta}} d\eta$$

Integration of equation (6.42) with due attention to the initial and boundary conditions leads to

$$(b)_{y=0} = \frac{1}{\sqrt{\pi}} \int_0^\tau \exp[-2\lambda(\tau - \eta)] \frac{\psi(\eta)}{\sqrt{\tau - \eta}} d\eta$$

The dimensionless voltammogram is thus finally given by the equation

$$\frac{1 + 2\exp(-\xi)}{\sqrt{\pi}} \int_0^\tau \exp[-2\lambda(\tau - \eta)] \frac{\psi(\eta)}{\sqrt{\tau - \eta}} d\eta + \frac{1}{\sqrt{\pi}} \int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau - \eta}} d\eta = 1$$

When $\lambda \rightarrow \infty$, the pure kinetic conditions are achieved, and the wave is much displaced toward negative ξ values. It follows that

$$\exp(-\xi) \frac{\psi/2}{\sqrt{\lambda/2}} + \frac{1}{\sqrt{\pi}} \int_0^\tau \frac{\psi/2}{\sqrt{\tau - \eta}} d\eta = 1$$

that is,

$$\frac{\psi}{2} \exp(-\xi^D) + \frac{1}{\sqrt{\pi}} \int_0^\tau \frac{\psi/2}{\sqrt{\tau - \eta}} d\eta \qquad \text{with} \quad \xi^D = \xi + \ln(\sqrt{\lambda/2})$$

The current is then exactly twice that in the irreversible EC case under pure kinetic conditions after a shift of the potential scale by a factor of $(\mathcal{R}T/2F) \ln 2$.

Investigation of the competition between the ECE and DISP pathways requires considering the full partial derivative equation system involving all three species A, B, and C. In dimensionless terms,

$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} + \lambda_D bc \tag{6.44}$$

$$\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - \lambda b - \lambda_D bc \tag{6.45}$$

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial y^2} + \lambda b - \lambda_D bc \tag{6.46}$$

$\tau = 0$, $y \geq 0$ and $y = \infty$, $\tau \geq 0$: $\quad a = 1, \quad b = 0, \quad c = 0$

$y = 0$, $\tau \geq 0$: $\quad a = b\exp(-\xi), \quad \dfrac{\partial a}{\partial y} + \dfrac{\partial b}{\partial y} = 0, \quad c = 0$

where ξ and τ are related by equations (6.16) and (6.17).

The dimensionless current is the sum of two contributions given by

$$\psi = \psi_1 + \psi_2$$
$$\psi_1 = \left(\frac{\partial a}{\partial y}\right)_{y=0} = -\left(\frac{\partial b}{\partial y}\right)_{y=0}$$
$$\psi_2 = \left(\frac{\partial c}{\partial y}\right)_{y=0} = -\left(\frac{\partial d}{\partial y}\right)_{y=0}$$

The first of the partial derivative equation may be replaced by

$$\frac{\partial(2a+b+c)}{\partial\tau} = \frac{\partial^2(2a+b+c)}{\partial y^2}$$

leading to

$$2(\bar{a})_{y=0} + (\bar{b})_{y=0} + (\bar{c})_{y=0} + \frac{\bar{\psi}_1 + \bar{\psi}_2}{\sqrt{s}} - \frac{2}{s} = 0$$

and therefore, since $(c)_{y=0} = 0$, to

$$(\bar{a})_{y=0} + (\bar{b})_{y=0} + \frac{\bar{\psi}_1 + \bar{\psi}_2}{\sqrt{s}} - \frac{2}{s} = 0$$

That is, in the original plane and taking Nernst's law into account, we have

$$(b)_{y=0}[1 + 2\exp(-\xi)] = 2 - \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi_1 + \psi_2}{2}\frac{d\eta}{\sqrt{\tau - \eta}}$$

Insofar as the pure kinetic conditions are achieved ($\lambda \to \infty$), the wave is shifted toward positive potential (i.e., toward negative values of ξ). Thus,

$$(b)_{y=0}\exp(-\xi) = 1 - \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi_1 + \psi_2}{2}\frac{d\eta}{\sqrt{\tau - \eta}}$$

These conditions also imply that $\partial b/\partial\tau \simeq 0$ and $\partial c/\partial\tau \simeq 0$. Thus, after introduction of the renormalized variables, $y^* = y\sqrt{\lambda}$, $b^* = b\sqrt{\lambda}$, $c^* = c\sqrt{\lambda}$, which are suited to pure kinetic conditions as discussed in Section 6.2.1, equations (6.45) and (6.46) become

$$\frac{\partial^2 b^*}{\partial y^{*2}} - b^* - \frac{\lambda_D}{\lambda^{3/2}} b^* c^* = 0$$

$$\frac{\partial^2 c^*}{\partial y^{*2}} + b^* - \frac{\lambda_D}{\lambda^{3/2}} b^* c^* = 0$$

The problem is defined entirely by these partial derivative equations, associated with the following boundary conditions:

$$y^* = \infty: \qquad b^* = 0, \quad c^* = 0$$

$$y^* = 0: \qquad b^* \exp(-\xi^c) = 1 - \frac{1}{\sqrt{\pi}} \int_0^{\tau} \frac{\psi_1 + \psi_2}{2} \frac{d\eta}{\sqrt{\tau - \eta}}, \quad c^* = 0$$

It follows that the dimensionless current, defined by

$$\psi_1 + \psi_2 = -\left(\frac{\partial b^*}{\partial y^*}\right)_{y^*=0} + \left(\frac{\partial c^*}{\partial y^*}\right)_{y^*=0}$$

is a function of a single competition parameter:

$$p_{ECE}^{DISP} = \frac{\lambda}{\lambda_D^{3/2}}$$

6.2.5. Electrodimerization

In the radical–radical dimerization case, the governing partial derivative equations and the set of initial and boundary conditions are written

$$\frac{\partial C_{\mathrm{A}}}{\partial t} = D \frac{\partial^2 C_{\mathrm{A}}}{\partial x^2}$$

$$\frac{\partial C_{\mathrm{B}}}{\partial t} = D \frac{\partial^2 C_{\mathrm{B}}}{\partial x^2} - 2k_d C_{\mathrm{B}}^2$$

(note that with this formulation, k_d is the rate constant for the formation of the dimer)

$$t = 0,\ x \geq 0 \text{ and } x = \infty,\ t \geq 0: \qquad C_{\mathrm{A}} = C^0, \quad C_{\mathrm{B}} = 0$$

$$x = 0,\ t \geq 0: \qquad \frac{\partial C_{\mathrm{A}}}{\partial x} + \frac{\partial C_{\mathrm{B}}}{\partial x} = 0, \quad C_{\mathrm{A}} = C_{\mathrm{B}} \exp\left[\frac{F}{\mathcal{R}T}(E - E^0)\right]$$

where the electrode potential depends on time according to

$$0 \leq t \leq t_R: \qquad E = E_i - vt$$

$$t_R \leq t \leq 2t_R: \qquad E = E_f + v(t - t_R) = 2E_f - E_i + vt$$

the current being given by

$$\frac{i}{FS} = D\left(\frac{\partial C_{\mathrm{A}}}{\partial x}\right)_{x=0} = -D\left(\frac{\partial C_{\mathrm{B}}}{\partial x}\right)_{x=0}$$

Introducing the usual dimensionless variables plus the dimensionless parameter measuring the competition between diffusion and dimerization,

$$\lambda_d = \frac{\mathcal{R}T}{F}\frac{k_d C^0}{v} \tag{6.47}$$

leads to the following dimensionless formulation:

$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} \tag{6.48}$$

$$\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - 2\lambda_d b^2 \tag{6.49}$$

$$\tau = 0,\ y \geq 0 \text{ and } y = \infty,\ \tau \geq 0: \qquad a = 1, \quad b = 0$$

$$y = 0,\ \tau \geq 0: \qquad a = b\exp(-\xi), \quad \frac{\partial a}{\partial y} + \frac{\partial b}{\partial y} = 0$$

where ξ and τ are related by equations (6.16) and (6.17). The dimensionless current is given by

$$\psi = \left(\frac{\partial a}{\partial y}\right)_{y=0} = -\left(\frac{\partial b}{\partial y}\right)_{y=0}$$

As seen in several other cases, integration of the first partial derivative equation (6.48), taking into account the corresponding initial and boundary conditions leads to

$$(a)_{y=0} = (b)_{y=0}\exp(-\xi) = 1 - \frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi(\eta)}{\sqrt{\tau - \eta}}d\eta$$

In the general case, integration of equation (6.49) requires a finite difference computation (see Section 2.2.8). However, when pure kinetic conditions are achieved ($\lambda_d \to \infty$), $\partial b/\partial \tau \simeq 0$ in equation (6.49), which may then be integrated as follows:

$$\frac{\partial^2 b}{\partial y^2}\frac{\partial b}{\partial y} = \lambda_d b^2 \frac{\partial b}{\partial y}$$

the integration of which, after account has been taken of the fact that for $y = \infty$, not only $b = 0$ but also $\partial b / \partial y = 0$, leads to

$$\left(\frac{\partial b}{\partial y} \right)^2 = \frac{2\lambda_d}{3} b^3$$

Application for $y = 0$ provides a relationship between the current and the concentration of B at the electrode surface:

$$(b)_{y=0} = \frac{\psi^{2/3}}{(2\lambda_d/3)^{1/3}}$$

and therefore the dimensionless expression of the voltammogram:

$$\frac{\psi^{2/3} \exp(-\xi)}{(2\lambda_d/3)^{1/3}} = 1 - \frac{1}{\sqrt{\pi}} \int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau - \eta}} d\eta$$

that is,

$$\psi^{2/3} \exp(-\xi^{rrd}) = 1 - \frac{1}{\sqrt{\pi}} \int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau - \eta}} d\eta$$

with

$$\xi^{rrd} = \xi + \frac{1}{3} \ln \frac{2\lambda_d}{3} = -\left[\frac{F}{\mathcal{R}T} (E - E^0) \right] + \frac{1}{3} \ln \left(\frac{2\mathcal{R}T}{3F} \frac{k_d C^0}{v} \right)$$

In the RSD–ECE case, the problem may be formulated in dimensionless terms as

$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} - \lambda_d ab \tag{6.50}$$

$$\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - \lambda_d ab \tag{6.51}$$

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial y^2} + \lambda_d ab \tag{6.52}$$

with the same definition of λ_d as in equation (6.47):

$\tau = 0$, $y \geq 0$ and $y = \infty$, $\tau \geq 0$: $\quad a = 1, \quad b = 0, \quad c = 0$

$y = 0$, $\tau \geq 0$: $\quad a = b \exp(-\xi), \quad \frac{\partial a}{\partial y} + \frac{\partial b}{\partial y} = 0, \quad c = 0$

where ξ and τ are related by equations (6.16) and (6.17). The dimensionless current is given by the sum of two contributions, one, ψ_1, pertaining to the reduction of A, and the other, ψ_2, pertaining to the reduction of C:

$$\psi_1 = \left(\frac{\partial a}{\partial y}\right)_{y=0} = -\left(\frac{\partial b}{\partial y}\right)_{y=0} \qquad \psi_2 = \left(\frac{\partial c}{\partial y}\right)_{y=0}$$

Subtraction of equation (6.49) from equation (6.50) and addition of equations (6.51) and (6.52) leads to

$$\frac{\partial(a-b)}{\partial \tau} = \frac{\partial^2(a-b)}{\partial y^2}$$

and

$$\frac{\partial(b+c)}{\partial \tau} = \frac{\partial^2(b+c)}{\partial y^2}$$

respectively. Integration in the Laplace plane and application of the initial and boundary conditions yields

$$(\bar{a})_{y=0} - (\bar{b})_{y=0} + \frac{2\bar{\psi}_1}{\sqrt{s}} - \frac{1}{s} = 0$$

and

$$(\bar{b})_{y=0} + (\bar{c})_{y=0} - \frac{\bar{\psi}_1 - \bar{\psi}_2}{\sqrt{s}} = 0 \quad \text{and thus} \quad \frac{\bar{\psi}_1 - \bar{\psi}_2}{\sqrt{s}} = (\bar{b})_{y=0}$$

Besides of the irreversibility of the cyclic voltammetric trace, pure kinetic conditions ($\lambda_d \rightarrow \infty$) entail important simplifications. One is that the wave is shifted to infinitely positive potential from the standard potential. Another is that $(b)_{y=0}$ is very small. It follows that

$$\psi_1 = \psi_2 = \frac{\psi}{2},$$

and since $(b)_{y=0} \ll (a)_{y=0}$, that

$$(\bar{a})_{y=0} = \frac{1}{s} - \frac{2\bar{\psi}_1}{\sqrt{s}} = \frac{1}{s} - \frac{\bar{\psi}}{\sqrt{s}}$$

Therefore,

$$(a)_{y=0} = 1 - \frac{1}{\sqrt{\pi}} \int_0^{\tau} \frac{\psi(\eta)}{\sqrt{\tau - \eta}} d\eta$$

Focusing attention on equation (6.51), another implication of pure kinetic conditions is that $\partial b/\partial\tau \simeq 0$. Also, the fact that $(\partial a/\partial y)_{y=0}+(\partial b/\partial y)_{y=0}=0$ and $(b)_{y=0} \ll (a)_{y=0}$ implies that in the thin reaction layer containing the entire concentration profile of B,

$$a+b \simeq (a)_{y=0}+(b)_{y=0} \quad \text{and} \quad a \simeq (a)_{y=0}$$

Equation (6.51) may thus be reformulated as

$$\frac{\partial^2 b}{\partial y^2}=\lambda_d (a)_{y=0} b \quad \text{and thus} \quad \frac{\partial b}{\partial y}\frac{\partial^2 b}{\partial y^2}=\lambda_d (a)_{y=0}\, b\frac{\partial b}{\partial y}$$

and after integration, account being taken that for $y=\infty$, not only does $b=0$, but also $\partial b/\partial y=0$:

$$(b)_{y=0}=\frac{\psi_1}{\sqrt{\lambda_d (a)_{y=0}}}$$

and thus, after application of Nernst's law,

$$\frac{\psi^{2/3}\exp(-2\xi/3)}{(4\lambda_d)^{1/3}}=1-\frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta$$

The kinetic parameter may be incorporated in the dimensionless potential variable by introducing

$$\xi^{rsdECE}=\xi+\frac{1}{2}\ln(4\lambda_d)=-\left[\frac{F}{\mathcal{R}T}(E-E^0)\right]+\frac{1}{2}\ln\left(4\frac{\mathcal{R}T}{F}\frac{k_d C^0}{v}\right)$$

thus leading to the final dimensionless expression of the cyclic voltammetric response under pure kinetic conditions:

$$\psi^{2/3}\exp\left(-\frac{2\xi^{rsdECE}}{3}\right)=1-\frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta$$

With the RSD–DISP mechanism, the governing equations are written similarly:

$$\frac{\partial a}{\partial \tau}=\frac{\partial^2 a}{\partial y^2}-\lambda_d ab+\lambda_{-d}c+\lambda_D bc \qquad (6.53)$$

$$\frac{\partial b}{\partial \tau}=\frac{\partial^2 b}{\partial y^2}-\lambda_d ab+\lambda_{-d}c-\lambda_D bc \qquad (6.54)$$

with the same definition of λ_d as in equation (6.47) and with

$$\lambda_{-d} = \frac{\mathcal{R}T}{F}\frac{k_{-d}}{v} = \frac{\lambda_d}{K_d}$$

It is, moreover, assumed that C obeys the steady-state approximation:

$$\lambda_d ab - \lambda_{-d}c = \lambda_D bc \qquad c = \frac{\lambda_d ab}{\lambda_{-d} + \lambda_D b}$$

Thus equations (6.53) and (6.54) become

$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} \tag{6.55}$$

$$\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - 2\lambda_d a \frac{\lambda_D b^2}{\lambda_{-d} + \lambda_D b} \tag{6.56}$$

Equations (6.55) and (6.56) are accompanied by initial and boundary conditions:

$\tau = 0$, $y \geq 0$ and $y = \infty$, $\tau \geq 0$: $\quad a = 1, \quad b = 0$

$y = 0$, $\tau \geq 0$: $\quad a = b\exp(-\xi), \quad \dfrac{\partial a}{\partial y} + \dfrac{\partial b}{\partial y} = 0$

where ξ and τ are related by equations (6.16) and (6.17). The dimensionless current is given by

$$\psi = \left(\frac{\partial a}{\partial y}\right)_{y=0} = -\left(\frac{\partial b}{\partial y}\right)_{y=0}$$

Integration of equation (6.55) leads to the familiar relationship

$$(a)_{y=0} = (b)_{y=0}\exp(-\xi) = 1 - \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau - \eta}}d\eta$$

There are two subcases, according to whether the coupling step or the disproportionation step is rate-determining.

The first situation, termed the *rsd–DISP1 mechanism*, prevails when $\lambda_{-d} \ll \lambda_D b$. Then equation (6.56) becomes

$$\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - 2\lambda_d ab$$

For the same reasons as in the ECE case, the pure kinetic conditions allow this equation to be simplified as

$$\frac{\partial^2 b}{\partial y^2} = 2\lambda_d (a)_{y=0} b$$

integration of which, similarly to the ECE case, leads to

$$(b)_{y=0} = \frac{\psi}{\sqrt{2\lambda_d (a)_{y=0}}}$$

thus leading to

$$\frac{\psi^{2/3} \exp(-2\xi/3)}{(2\lambda_d)^{1/3}} = 1 - \frac{1}{\sqrt{\pi}} \int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau - \eta}} d\eta$$

and to the final dimensionless expression of the cyclic voltammetric response under pure kinetic conditions:

$$\psi^{2/3} \exp\left(-\frac{2\xi^{rsdDISP1}}{3}\right) = 1 - \frac{1}{\sqrt{\pi}} \int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau - \eta}} d\eta$$

after incorporation of the kinetic parameter in the dimensionless potential variable

$$\xi^{rsdDISP1} = \xi + \frac{1}{2}\ln(2\lambda_d) = -\left[\frac{F}{\mathcal{R}T}(E - E^0)\right] + \frac{1}{2}\ln\left(2\frac{\mathcal{R}T}{F}\frac{k_d C^0}{v}\right)$$

The situation where the radical–substrate coupling is a preequilibrium to the homogeneous electron transfer step, termed the *rsdDISP2 mechanism*, prevails when $\lambda_{-d} \gg \lambda_D b$. Then equation (6.56) becomes

$$\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - 2\kappa_d \lambda_D a b^2$$

with

$$\kappa_d = \frac{\lambda_d}{\lambda_{-d}} = K_d C^0$$

For the same reasons as in the ECE and DISP1cases, the pure kinetic conditions allow this equation to be simplified as

$$\frac{\partial^2 b}{\partial y^2} = 2\kappa_d \lambda_D (a)_{y=0} b^2$$

integration of which, similar to the rrc case, leads to

$$(b)_{y=0} = \frac{\psi^{2/3}}{\left(\frac{2}{3}\kappa_d\lambda_D(a)_{y=0}\right)^{1/3}}$$

thus leading to

$$\frac{\psi^{2/3}\exp(-\xi)}{\left(\frac{4}{3}\kappa_d\lambda_D(a)_{y=0}\right)^{1/3}} = 1 - \frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta$$

and to the final dimensionless expression of the cyclic voltammetric response under pure kinetic conditions:

$$\psi^{1/2}\exp\left(-\frac{3\xi^{rsdDISP2}}{4}\right) = 1 - \frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta$$

after incorporation of the kinetic parameter in the dimensionless potential variable:

$$\xi^{rsdDISP2} = \xi + \frac{1}{3}\ln\left(\frac{4}{3}\kappa_d\lambda_D\right) = -\left[\frac{F}{\mathcal{R}T}(E-E^0)\right] + \frac{1}{3}\ln\left(\frac{4\mathcal{R}T}{3F}\frac{K_d\lambda_D C^{0^2}}{v}\right)$$

A graphical representation of the dimensionless irreversible voltammograms obtained for the four dimerization mechanisms under pure kinetic conditions is given in Chapter 2 (Figure 2.14) together with their peak characteristics.

6.2.6. Competition Between Dimerization of and Electron Transfer to Intermediates

In a reaction scheme where dimerization of an intermediate and its reduction compete as in Scheme 6.1 (taking reductions as an example), the location and characteristics of the second wave in cyclic voltammetry at which the intermediate B is reduced are governed by the outcome of this competition.

$$\mathrm{A} + \mathrm{e}^- \rightleftharpoons \mathrm{B} \quad E_1^0, \alpha_1, k_{S,1}^{ap}$$

$$2\,\mathrm{B} \xrightarrow{k_d} \mathrm{C}$$

$$\mathrm{B} + \mathrm{e}^- \longrightarrow \mathrm{D} \quad E_2^0, \alpha_2, k_{S,2}^{ap}$$

$$\mathrm{D} \xrightarrow{\text{fast}} \text{products}$$

SCHEME 6.1

The two successive electron transfer reactions are assumed to obey the Butler–Volmer law with the values of standard potentials, transfer coefficient, and standard rate constants indicated in Scheme 6.1. It is also assumed, matching the examples dealt with in Sections 2.5.2 and 2.6.1, that the reduction product, D, of the intermediate C, is converted rapidly into other products at such a rate that the reduction of B is irreversible. With the same dimensionless variables and parameters as in Section 6.2.4, the following system of partial derivative equations, and initial and boundary conditions, is obtained:

$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} \tag{6.57}$$

$$\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - 2\lambda_d b^2 \tag{6.58}$$

$$\tau = 0,\ y \geq 0 \text{ and } y = \infty,\ \tau \geq 0: \qquad a = 1, \quad b = 0 \tag{6.59}$$

$y = 0,\ \tau \geq 0$:

$$\psi_1 = \Lambda_1 \exp\left[-\frac{\alpha_1 F}{\mathcal{R}T}(E - E_1^0)\right]\left\{a - b\exp\frac{\alpha_1 F}{\mathcal{R}T}(E - E_1^0)\right\} \tag{6.60}$$

$$\psi_2 = \Lambda_2 \exp\left[-\frac{\alpha_2 F}{\mathcal{R}T}(E - E_2^0)\right] b \tag{6.61}$$

There are two contributions, ψ_1 and ψ_2, to the total dimensionless current, ψ, with

$$\psi_1 = \left(\frac{\partial a}{\partial y}\right)_{y=0} \tag{6.62}$$

$$\psi_2 - \psi_1 = \left(\frac{\partial b}{\partial y}\right)_{y=0} \tag{6.63}$$

ξ and τ are related by equations (6.16) and (6.17):

$$\Lambda_1 = k_{S,1}^{ap}\sqrt{\frac{\mathcal{R}T}{FvD}} \qquad \Lambda_2 = k_{S,2}^{ap}\sqrt{\frac{\mathcal{R}T}{FvD}} \qquad \lambda_d = \frac{\mathcal{R}Tk_d C_{\mathrm{A}}^0}{Fv}$$

The potential distance between the first and second waves depends, in dimensionless terms, on the parameter

$$\Delta\xi = E_1^0 - E_2^0 + \frac{\mathcal{R}T}{\alpha_2 F}\ln \Lambda_2$$

Thus, the dimensionless current–potential curves depend on the dimensionless parameters λ_d, Λ_1, $\Delta\xi$, α_1, and α_2. Simulating the dimensionless cyclic voltammograms then consists of finite difference resolutions of equations (6.57) and (6.58), taking into account all initial and boundary conditions. Examples of such responses are given in Section 2.5.2 (Figure 2.35).

The preceding analysis is made simpler if, as often the case, the first as well as the electron transfer step may be regarded as totally irreversible, and dimerization is so fast that pure kinetic conditions are fulfilled. The last simplification implies that $\partial b/\partial\tau = 0$ in equation (6.58). Integration of this equation, taking into account initial and boundary conditions (6.59) and equations (6.63), leads to

$$b_{y=0} = \frac{3}{4\lambda_d}(\psi_1 - \psi_2)^{2/3} \tag{6.64}$$

Combining equations (6.64) and (6.61), then leads to

$$\psi_2 = \frac{3}{4\lambda_d}\exp\left[-\frac{\alpha_2 F}{\mathcal{R}T}(E - E_2^R)\right](\psi_1 - \psi_2)^{2/3} \tag{6.65}$$

with

$$E_2^R = E_2^0 + \frac{\mathcal{R}T}{\alpha_2 F}\ln\left(k_{S,2}^{ap}\sqrt{\frac{\mathcal{R}T}{FvD}}\right) \tag{6.66}$$

It just remains to compute ψ_1 from equations (6.57), (6.59), (6.62), and the simplified version of equation (6.60), which takes into account the assumed irreversibility of the first electron transfer step:

$$\psi_1 = \Lambda_1 \exp\left[-\frac{\alpha_1 F}{\mathcal{R}T}(E - E_1^0)\right]\left(1 - \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi_1(\eta)}{\sqrt{\tau - \eta}}d\eta\right) \tag{6.67}$$

The potential scale may then be redefined as

$$\xi_1 = -\left[\frac{F}{\mathcal{R}T}(E - E_1^R)\right]$$

after introduction of a potential, E_1^R, characterizing the irreversible reduction of A:

$$E_1^R = E_1^0 + \frac{\mathcal{R}T}{\alpha_1 F}\ln\left(k_{S,1}^{ap}\sqrt{\frac{\mathcal{R}T}{FvD}}\right)$$

leading to a simple integral equation for ψ_1:

$$\psi_1 = \exp(\alpha_1 \xi_1)\left[1 - \frac{1}{\sqrt{\pi}}\int_0^{\tau} \frac{\psi_1(\eta)}{\sqrt{\tau - \eta}} d\eta\right]$$

Since the waves are irreversible, the forward scan response,

$$\psi_1 = \exp(\alpha_1 \xi_1)\left[1 - \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\xi_1} \frac{\psi_1(\eta)}{\sqrt{\xi_1 - \eta}} d\eta\right] \tag{6.68}$$

is the only one needed. Equation (6.65) may be recast as

$$\psi_2 = \frac{3}{4\lambda_d}\exp[\alpha_2(\xi_1 - p_{ET}^{DIM})](\psi_1 - \psi_2)^{2/3} \tag{6.69}$$

with

$$p_{ET}^{DIM} = \frac{F}{\mathcal{R}T}(E_1^R - E_2^R) + \frac{1}{3\alpha_2}\ln\left(\frac{4\mathcal{R}Tk_d C_A^0}{3Fv}\right) \tag{6.70}$$

Combining equations (6.68) and (6.69) finally leads to the total forward scan response. Examples are given in Figure 6.4.

The same analysis may also be applied when B is a secondary radical formed upon fast and irreversible transformation of a primary radical, B'

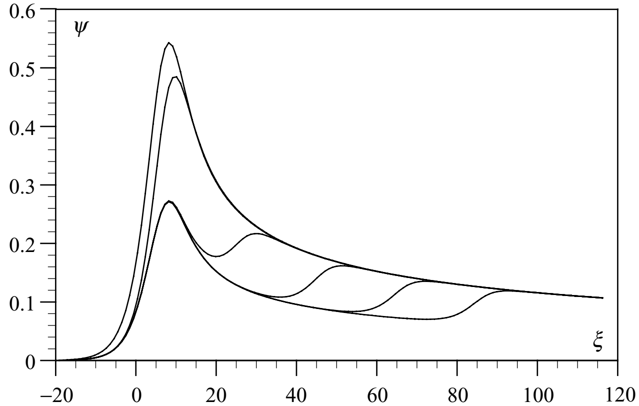
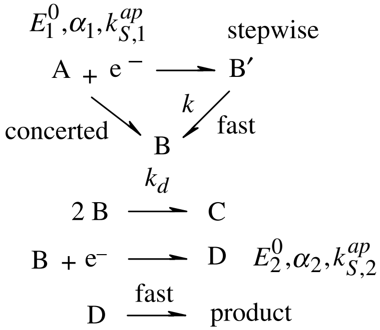


FIGURE 6.4. Dimensionless cyclic voltammograms for Schemes 6.1 and 6.2 for various values of the dimensionless competition parameter $p_{d/et}$ [equation (6.69)], from left to right: −20, 0, 20, 40, 60, 80.



SCHEME 6.2

(Scheme 6.2). In the previous mechanism, B was formed in concert with electron transfer, whereas the present mechanism follows the stepwise pathway. (The stepwise vs. concerted dichotomy is discussed in detail in Chapter 3 for the cased where the B′ → B step is a bond-breaking reaction.) Although equation (6.51) still applies, equation (6.58) is replaced by

$$\frac{\partial b'}{\partial \tau} = \frac{\partial^2 b'}{\partial y^2} - \lambda b' \tag{6.71}$$

$$\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} + \lambda b' - 2\lambda_d b^2 \tag{6.72}$$

where λ is the dimensionless rate factor corresponding to the rate constant $k(\lambda = \mathcal{R}Tk/Fv)$. Equation (6.59) still applies, while for $y = 0$, $\tau \geq 0$,

$$\psi_1 = \Lambda_1 \exp\left[-\frac{\alpha_1 F}{\mathcal{R}T}(E - E_1^0)\right] a \qquad \psi_2 = \Lambda_2 \exp\left[-\frac{\alpha_2 F}{\mathcal{R}T}(E - E_2^0)\right] b$$

with

$$\psi_1 = \left(\frac{\partial a}{\partial y}\right)_{y=0} = -\left(\frac{\partial b'}{\partial y}\right)_{y=0} \tag{6.73}$$

$$\psi_2 = \left(\frac{\partial b}{\partial y}\right)_{y=0} \tag{6.74}$$

Addition of equations (6.71) and (6.72) leads to

$$\frac{\partial (b' + b)}{\partial \tau} = \frac{\partial^2 (b' + b)}{\partial y^2} - 2\lambda_d b^2$$

which may be transformed into

$$\frac{\partial(b'+b)}{\partial\tau}=\frac{\partial^2(b'+b)}{\partial y^2}-2\lambda_d(b'+b)^2 \tag{6.75}$$

noting that b' is very small. Indeed, integration of equation (6.71), taking equation (6.74) into account, leads to

$$b'_{y=0}=\frac{\psi_1}{\sqrt{\lambda}},$$

in which λ is very large.

From equations (6.73) to (6.75), under pure kinetic conditions,

$$(b'+b)_{y=0}\simeq b_{y=0}=\frac{3}{4\lambda_d}(\psi_1-\psi_2)^{2/3}$$

We are thus back to equation (6.64), showing that the current–potential responses are the same as in the concerted case.

6.2.7. Homogeneous Catalysis

We first consider the case where the *rate-determining step is the forward homogeneous electron transfer step* (rate constant k_e). The governing equations are

$$\frac{\partial C_\mathrm{P}}{\partial t}=D_P\frac{\partial^2 C_\mathrm{P}}{\partial x^2}+k_eC_\mathrm{Q}C_\mathrm{A}$$

$$\frac{\partial C_\mathrm{Q}}{\partial t}=D_P\frac{\partial^2 C_\mathrm{Q}}{\partial x^2}-k_eC_\mathrm{Q}C_\mathrm{A}$$

$$\frac{\partial C_\mathrm{A}}{\partial t}=D_\mathrm{A}\frac{\partial^2 C_\mathrm{A}}{\partial x^2}-k_eC_\mathrm{Q}C_\mathrm{A}$$

with, as initial and boundary conditions:

$t=0$, $x\geq 0$ and $x=\infty$, $t\geq 0$: $\quad C_\mathrm{P}=C_\mathrm{P}^0,\quad C_\mathrm{Q}=0,\quad C_\mathrm{A}=C_\mathrm{A}^0$

$x=0$, $t\geq 0$: $\quad \dfrac{\partial C_\mathrm{P}}{\partial x}+\dfrac{\partial C_\mathrm{Q}}{\partial x}=0$ (conservation of fluxes)

$C_\mathrm{P}=C_\mathrm{Q}\exp\left[\dfrac{F}{\mathcal{R}T}(E-E^0_{\mathrm{P/Q}})\right]$ (Nernst's law)

$\dfrac{\partial C_\mathrm{A}}{\partial x}=0$ (A is not reduced at the electrode at the potential where the catalytic wave occurs).

Conversion into a dimensionless formulation follows the same principle and notations as in the preceding sections with, in addition, the following definitions:

$$\xi = -\frac{F}{\mathcal{R}T}(E - E^0_{\mathrm{P/Q}}) \qquad \psi = \frac{i}{FSC^0_{\mathrm{P}}\sqrt{D_P}\sqrt{\dfrac{Fv}{\mathcal{R}T}}}$$

$$p = \frac{C_{\mathrm{P}}}{C^0_{\mathrm{P}}} \qquad q = \frac{C_{\mathrm{Q}}}{C^0_{\mathrm{P}}} \qquad a = \frac{C_{\mathrm{A}}}{C^0_{\mathrm{P}}} \qquad \gamma = \frac{C^0_{\mathrm{A}}}{C^0_{\mathrm{P}}}$$

$$\lambda_e = \frac{\mathcal{R}T}{F}\frac{k_e C^0_{\mathrm{P}}}{v} \qquad \delta_D = \frac{D_P}{D_A}$$

Thus

$$\frac{\partial p}{\partial \tau} = \frac{\partial^2 p}{\partial y^2} + \lambda_e a q \tag{6.76}$$

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial y^2} - \lambda_e a q \tag{6.77}$$

$$\frac{\partial a}{\partial \tau} = \delta_D \frac{\partial^2 a}{\partial y^2} - \lambda_e a q \tag{6.78}$$

$\tau = 0$, $y \geq 0$ and $y = \infty$, $\tau \geq 0$: $\quad p = 1, \quad q = 0, \quad a = \gamma$

$y = 0$, $\tau \geq 0$: $\quad \dfrac{\partial p}{\partial y} + \dfrac{\partial q}{\partial y} = 0, \quad \dfrac{\partial a}{\partial y} = 0, \quad p = q\exp(-\xi)$

ξ and τ are related by equations (6.16) and (6.17) and

$$\psi = \left(\frac{\partial p}{\partial y}\right)_{y=0} = -\left(\frac{\partial q}{\partial y}\right)_{y=0}$$

Addition of equations (6.76) and (6.77) leads to

$$\frac{\partial p + q}{\partial \tau} = \frac{\partial^2 p + q}{\partial y^2}$$

integration of which, taking the initial and boundary conditions into account, provides an essential relationship in all catalytic problems:

$$(p)_{y=0} + (q)_{y=0} = 1 \tag{6.79}$$

and insofar as Nernst's law is obeyed,

$$(q)_{y=0} = \frac{1}{1 + \exp(-\xi)} \tag{6.80}$$

Resolution of the problem may therefore be pursued looking only at the fate of q and a.

A simple situation is reached if the excess is big enough for a to remain unconditionally equal to γ whatever τ and ξ. More precisely, this situation is reached when $\lambda_e/\gamma \to 0$, ensuring that the consumption of a is negligible. Equation (6.77) then becomes

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial y^2} - \lambda_e \gamma q$$

integration of which leads to

$$\frac{1}{\sqrt{\pi}} \int_0^{\tau} \frac{\exp[-\lambda_e(\tau - \eta)]}{\sqrt{\tau - \eta}} \psi(\eta)\, d\eta = \frac{1}{1 + \exp(-\xi)} \tag{6.81}$$

When $\lambda_e \to 0$, we are back to the reversible Nernstian wave. When, conversely, $\lambda_e \to \infty$ (pure kinetic conditions),

$$\psi = \frac{\sqrt{\lambda_e}}{1 + \exp(-\xi)}$$

leading to a plateau-shaped wave, the forward and reverse trace being superimposed [equations (2.18) and (2.19)]. The variation of the current–potential responses with λ_e between the reversible Nernstian wave and the plateau-shaped wave [equation (6.81)] is represented in Figure 2.18.

The total catalysis situation is reached when $\lambda_e \to \infty$ and $\lambda_e/\gamma \to \infty$. a is not longer independent of the space coordinate. Since λ_e is large, pure kinetic conditions are achieved and the q profile is squeezed into a thin reaction layer within which a is a constant equal to its value at the electrode surface, $a_{y=0}$. Equation (6.77) may thus be simplified into

$$\frac{\partial^2 q}{\partial y^2} - \lambda_e a_{y=0} q \simeq 0 \tag{6.82}$$

leading after integration to

$$\frac{\psi}{\sqrt{\lambda_e a_{y=0}}} = q_{y=0} = \frac{1}{1 + \exp(-\xi)}$$

$a_{y=0}$ may be obtained as follows. Subtraction of equation (6.82) from equation (6.78), taking the pure kinetic conditions into account, leads to

$$\frac{\partial(a - q)}{\partial \tau} \simeq \frac{a\left(\partial - \dfrac{q}{\delta_D}\right)}{\partial \tau} \simeq \delta_D \frac{\partial^2\left(a - \dfrac{q}{\delta_D}\right)}{\partial y^2}$$

and after integration,

$$a_{y=0} = \gamma + \frac{1}{\delta_D}\frac{1}{1+\exp(-\xi)} - \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi(\eta)}{\sqrt{\delta_D}}\frac{d\eta}{\sqrt{\tau-\eta}}$$

and thus

$$\frac{\psi[1+\exp(-\xi)]}{\sqrt{\lambda_e}} = \left[\gamma + \frac{1}{\delta_D}\frac{1}{1+\exp(-\xi)} - \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi(\eta)}{\sqrt{\delta_D}}\frac{d\eta}{\sqrt{\tau-\eta}}\right]^{1/2}$$

In the total catalysis zone (Figure 2.17), the current–potential response splits into two waves. One is the mediator reversible wave. The other is an irreversible wave arising in a much more positive potential region. The characteristics of the latter may be derived from the integral equation above, noting that since the wave is located at a very positive potential, $1/[1+\exp(-\xi)]$ is small compared to γ and $1+\exp(-\xi) \simeq \exp(-\xi)$. Thus,

$$\frac{\psi\exp(-\xi)}{\sqrt{\lambda_e}} = \left[\gamma - \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi(\eta)}{\sqrt{\delta_D}}\frac{d\eta}{\sqrt{\tau-\eta}}\right]^{1/2}$$

Introducing

$$\psi^{tc} = \frac{\psi}{\gamma\sqrt{\delta_D}} = \frac{i}{FSC_{\mathrm{A}}^0\sqrt{D_{\mathrm{A}}}\sqrt{\dfrac{Fv}{\mathcal{R}T}}}$$

and

$$\xi^{tc} = \xi + \frac{1}{2}\ln\left(\frac{\lambda_e}{\gamma\delta_D}\right) = -\frac{F}{\mathcal{R}T}(E - E_{\mathrm{P/Q}}^0) + \frac{1}{2}\ln\left(\frac{\mathcal{R}T}{Fv}\frac{k_e C_{\mathrm{P}}^{0^2}}{C_{\mathrm{A}}^0}\frac{D_{\mathrm{P}}}{D_{\mathrm{A}}}\right)$$

one finally obtains

$$\psi^{tc}\exp(-\xi tc) = \left[1 - \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi^{tc}(\eta)}{\sqrt{\tau-\eta}}d\eta\right]^{1/2}$$

that is, an irreversible peak-shaped curve (Figure 6.5), whose peak characteristics are

$$\psi_p^{tc} = 0.609 \qquad \xi_p^{tc} = 0.409 \qquad \xi_p^{tc} - \xi_{p/2}^{tc} = 1.41$$

leading to equations (2.20) to (2.22).

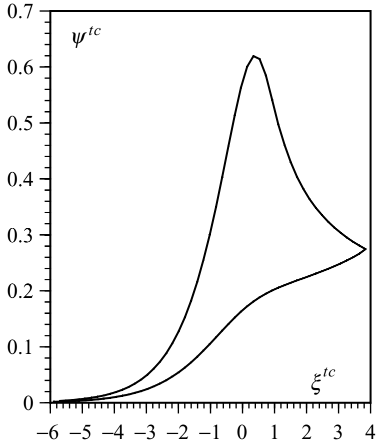


FIGURE 6.5. Homogeneous catalysis electrochemical reactions. Cyclic voltammetric response in a total catalysis situation.

Homogeneous Catalytic EC Mechanism The system is governed by the following dimensionless equations (we need not consider equations involving p, since as in all preceding cases, $p = 1 - q$), where two additional normalized rate parameters are introduced:

$$\lambda_{-e} = \frac{\mathcal{R}T}{F}\frac{k_{-e}}{v} \qquad \lambda = \frac{\mathcal{R}T}{F}\frac{k}{v}$$

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial y^2} - \lambda_e a q + \lambda_{-e} b(1-q)$$

$$\frac{\partial a}{\partial \tau} = \delta_D \frac{\partial^2 a}{\partial y^2} - \lambda_e a q + \lambda_{-e} b(1-q)$$

$$\frac{\partial b}{\partial \tau} = \delta_D \frac{\partial^2 b}{\partial y^2} + \lambda_e a q - \lambda_{-e} b(1-q) - \lambda b$$

$\tau = 0,\ y \geq 0$ and $y = \infty,\ \tau \geq 0$: $\qquad q = 0, \quad a = \gamma$

$y = 0,\ \tau \geq 0$: $\qquad q = \dfrac{1}{1+\exp(-\xi)}, \quad \dfrac{\partial a}{\partial y} = 0$

ξ and τ are related by equations (6.16) and (6.17) and the normalized current is given by $\psi = -(\partial q/\partial y)_{y=0}$. In most cases the reactions that destroy the transient intermediate B are faster than its production, meaning that it obeys the steady-state approximation

$$b = \frac{\lambda_e a q}{\lambda + \lambda_{-e}(1-q)}$$

Thus

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial y^2} - \frac{\lambda \lambda_e a q}{\lambda + \lambda_{-e}(1-q)} \tag{6.83}$$

$$\frac{\partial a}{\partial \tau} = \delta_D \frac{\partial^2 a}{\partial y^2} - \frac{\lambda \lambda_e a q}{\lambda + \lambda_{-e}(1-q)} \tag{6.84}$$

showing that the system depends on two parameters, λ_e and the competition parameter λ_{-e}/λ.

Two-Electron Catalytic Reactions The steady-state approximation may be applied to both transient intermediates B and C. It follows that not only does

$$b = \frac{\lambda_{e1} a q}{\lambda + \lambda_{-e1}(1-q)}$$

but also, $\lambda b = \lambda_{e2} c q$, where $\lambda_{e2} = (\mathcal{R}T/F)(k_{e2}/v)$ and thus

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial y^2} - \frac{\lambda \lambda_{e1} (2a) q}{\lambda + \lambda_{-e1}(1-q)} \tag{6.85}$$

and

$$\frac{\partial (2a)}{\partial \tau} = \delta_D \frac{\partial^2 (2a)}{\partial y^2} - \frac{\lambda \lambda_{e1} (2a) q}{\lambda + \lambda_{-e1}(1-q)} \tag{6.86}$$

with as boundary conditions

$\tau = 0,\ y \geq 0$ and $y = \infty, \tau \geq 0$: $\quad q = 0, \quad (2a) = 2\gamma$

$y = 0,\ \tau \geq 0$: $\quad q = \dfrac{1}{1 + \exp(-\xi)}, \quad \dfrac{\partial a}{\partial y} = 0$

ξ and τ are related by equations (6.16) and (6.17) and the normalized current is given by

$$\psi = -\left(\frac{\partial q}{\partial y}\right)_{y=0}$$

$$y = 0,\ \tau \geq 0: \qquad q = \frac{1}{1 + \exp(-\xi)}, \frac{\partial (2a)}{\partial y} = 0$$

Comparison of equations (6.85) and (6.86) with equations (6.83) and (6.84) shows that the previous analysis of the catalytic EC mechanism is applicable to the catalytic ECE mechanism after replacement of γ by 2γ.

Deactivation of the Mediator In the framework of Scheme 2.10 the system is governed by the following dimensionless equations and conditions:

$$\frac{\partial p}{\partial \tau} = \frac{\partial^2 p}{\partial y^2} + \lambda_{e1} aq + \lambda_{e2} cq$$

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial y^2} - \lambda_{e1} aq - \lambda_{e2} cq - \lambda_i cq$$

$$\frac{\partial a}{\partial \tau} = \delta_D \frac{\partial^2 a}{\partial y^2} - \lambda_{e1} aq$$

$\lambda_{e1} aq = \lambda_{e2} cq + \lambda_i cq = (\lambda_{e2} + \lambda_{in}) cq$ (steady-state approximation on C)

$\tau = 0$, $y \geq 0$ and $y = \infty$, $\tau \geq 0$: $q = 0$, $a = \gamma$

$y = 0$, $\tau \geq 0$: $p = q \exp(-\xi)$, $\dfrac{\partial a}{\partial y} = 0$

ξ and τ are related by equations (6.16) and (6.17) and the normalized current is given by $\psi = -(\partial q / \partial y)_{y=0}$. The relationship (6.79), characterizing unperturbed catalytic mechanisms leading to equation (6.80), is no longer applicable. The partial derivative equation system above may be recast as follows:

$$\frac{\partial p}{\partial \tau} = \frac{\partial^2 p}{\partial y^2} + \frac{\lambda_{e1}}{2}\left(1 + \frac{\lambda_{e2}}{\lambda_{e2} + \lambda_{in}}\right)(2a)q \tag{6.87}$$

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial y^2} - \lambda_{e1}(2a)q \tag{6.88}$$

$$\frac{\partial (2a)}{\partial \tau} = \delta_D \frac{\partial^2 (2a)}{\partial y^2} - \lambda_{e1}(2a)q \tag{6.89}$$

Combining equations (6.87) and (6.88), integrating, and applying Nernst's law leads to

$$\left[\frac{1}{2}\left(1 + \frac{\lambda_{e2}}{\lambda_{e2} + \lambda_{in}}\right) + \exp(-\xi)\right] q_{y=0} = 1 - \frac{1}{2}\left(1 - \frac{\lambda_{e2}}{\lambda_{e2} + \lambda_{in}}\right) \times \frac{1}{\sqrt{\pi}} \int_0^{\tau} \frac{\psi(\eta)}{\sqrt{\tau - \eta}} d\eta$$

which may serve as boundary conditions for the simultaneous computation of equations (6.88) and (6.89). It is useful to introduce the deactivation parameter, $\rho_c = \lambda_{e2}/(\lambda_{e2} + \lambda_{in})$, thus leading to

$$[(1 + \rho_c) + 2\exp(-\xi)] q_{y=0} = 2 - (1 - \rho_c) \frac{1}{\sqrt{\pi}} \int_0^{\tau} \frac{\psi(\eta)}{\sqrt{\tau - \eta}} d\eta$$

In summary, the system is governed by the following set of equations, thus depending on three independent parameters, λ_{e1}, γ, and ρ_c:

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial y^2} - \lambda_{e1}(2a)q$$

$$\frac{\partial (2a)}{\partial \tau} = \delta_D \frac{\partial^2 (2a)}{\partial y^2} - \lambda_{e1}(2a)q$$

$$\tau = 0,\ y \geq 0 \text{ and } y = \infty,\ \tau \geq 0: \qquad q = 0, \quad 2a = 2\gamma$$

$$y = 0,\ \tau \geq 0: \qquad q = \frac{1 - (1 - \rho_c)\dfrac{1}{\sqrt{\pi}}\displaystyle\int_0^\tau \frac{\psi(\eta)/2}{\sqrt{\tau - \eta}}\,d\eta}{\dfrac{1 + \rho_c}{2} + \exp(-\xi)}, \quad \frac{\partial a}{\partial y} = 0$$

ξ and τ are related by equations (6.16) and (6.17) and the normalized current is given by $\psi = -(\partial q/\partial y)_{y=0}$. When $\rho_c \rightarrow 1$, we are back to the two-electron ECE homogeneous catalytic mechanism analyzed in the preceding subsection. When $\rho_c \rightarrow 0$, there is no catalysis; the cyclic voltammograms are then obtained from the same two partial derivative equations and for the boundary condition at the electrode surface:

$$y = 0,\ \tau \geq 0: \qquad q = \frac{1 - \dfrac{1}{\sqrt{\pi}}\displaystyle\int_0^\tau \frac{\psi(\eta)/2}{\sqrt{\tau - \eta}}\,d\eta}{\dfrac{1}{2} + \exp(-\xi)}, \quad \frac{\partial a}{\partial y} = 0$$

Numerical resolution of the system above leads to the examples of current–potential responses and of i_p/i_p^0 vs. ρ_c plots in Figure 2.22.

Two-Step (Push-Pull, Ping-Pong) Mechanisms Dealing with Scheme 2.11a we impose two simplifying conditions, often fulfilled in practice. One is that there is no consumption of the substrate $[a(y, \tau) = \gamma]$. The other is that the intermediate C disappears faster than it is produced, thus obeying the steady-state approximation. Under these conditions, and introducing as rate parameters $\lambda_1 \gamma = (\mathcal{R}T/F)(k_1 C_{\mathrm{A}}^0/v)$ and $\lambda_2 = (\mathcal{R}T/F)(k_2 C_{\mathrm{Z}}^0/v)$ the catalytic response is governed by the following dimensionless equations and conditions:

$$\frac{\partial p}{\partial \tau} = \frac{\partial^2 p}{\partial y^2} + \lambda_1 \gamma q + \lambda_2 d \tag{6.90}$$

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial y^2} - 2\lambda_1 \gamma q \tag{6.91}$$

$$\frac{\partial d}{\partial \tau} = \frac{\partial^2 d}{\partial y^2} + \lambda_1 \gamma q - \lambda_2 d \tag{6.92}$$

$$\tau = 0,\ y \geq 0 \text{ and } y = \infty,\ \tau \geq 0: \qquad p = 1, \quad q = 0, \quad d = 0$$

$$y = 0,\ \tau \geq 0: \qquad p = q\exp(-\xi), \quad \frac{\partial d}{\partial y} = 0$$

ξ and τ are related by equations (6.16) and (6.17) and the normalized current is given by $\psi = -(\partial q/\partial y)_{y=0}$. Numerical resolution of the system allows the derivation of any cyclic voltammogram, such as, for example, those represented in Figure 2.23, which correspond to pure kinetic conditions (large values of $\lambda_1\gamma$). Under these conditions, and in the case where λ_2 is also large, variation of the plateau current with the rate parameters may be depicted by a closed-form expression that can be derived as follows.

Appropriate linear combination of equations (6.91) and (6.92) gives

$$\frac{\partial \left[q + \left(2 - \frac{\lambda_2}{\lambda_1\gamma}\right) d\right]}{\partial \tau} = \frac{\partial^2 \left[q + \left(2 - \frac{\lambda_2}{\lambda_1\gamma}\right) d\right]}{\partial y^2} - \lambda_2 \left[q + \left(2 - \frac{\lambda_2}{\lambda_1\gamma}\right) d\right]$$

which after integration leads in the Laplace plane to

$$\bar{q}_{y=0} + \left(2 - \frac{\lambda_2}{\lambda_1\gamma}\right)\bar{d}_{y=0} - \frac{\bar{\psi}}{\sqrt{s + \lambda_2}} = 0$$

Since λ_2 is large,

$$q_{y=0} + \left(2 - \frac{\lambda_2}{\lambda_1\gamma}\right) d_{y=0} - \frac{\psi}{\sqrt{\lambda_2}} = 0$$

Addition of equations (6.90) to (6.92) and integration leads to $p_{y=0} + q_{y=0} + d_{y=0} = 1$.

At the level of the plateau, $p_{y=0} = 0$ and thus, finally,

$$\frac{\psi}{\sqrt{\lambda_1\gamma}} = \frac{2 - \rho_c}{1 - \rho_c + \sqrt{\frac{2}{\rho_c}}}$$

($\rho_c = \lambda_2/\lambda_1\gamma = k_2 C_{\mathrm{Z}}^0 / k_1 C_{\mathrm{A}}^0$), from which Figure 2.23a has been constructed.

We now go to Scheme 2.11b with the same two simplifying conditions as before. We introduce the same rate parameters and, in addition, two dimensionless potential variables referred to the standard potentials of the

P/Q and C/D couples, respectively:

$$\xi_1 = -\frac{F}{\mathcal{R}T}\left(E - E^0_{\mathrm{P/Q}}\right) \quad \text{and} \quad \xi_2 = -\frac{F}{\mathcal{R}T}\left(E - E^0_{\mathrm{C/D}}\right)$$

The governing equation system is thus

$$\frac{\partial p}{\partial \tau} = \frac{\partial^2 p}{\partial y^2} + \lambda_2 d \tag{6.93}$$

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial y^2} - \lambda_1 \gamma q \tag{6.94}$$

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial y^2} + \lambda_1 \gamma q \tag{6.95}$$

$$\frac{\partial d}{\partial \tau} = \frac{\partial^2 d}{\partial y^2} - \lambda_2 d \tag{6.96}$$

$\tau = 0, y \geq 0$ and $y = \infty, \tau \geq 0$: $\quad p = 1, \quad q = 0, \quad c = 0, \quad d = 0$

$y = 0, \tau \geq 0$: $\quad p = q\exp(-\xi_1), \quad c = d\exp(-\xi_2), \quad \dfrac{\partial p + q}{\partial y} = 0, \quad \dfrac{\partial c + d}{\partial y} = 0$

ξ_1 and τ are related by equations similar to equations (6.16) and (6.17) and $\xi_2 = \xi_1 + \Delta\xi^0$, with

$$\Delta\xi^0 = \frac{F}{\mathcal{R}T}\left(E^0_{\mathrm{C/D}} - E^0_{\mathrm{P/Q}}\right)$$

There are two contributions, ψ_1 and ψ_2, to the total dimensionless current, ψ, involving the P/Q and the C/D couples, respectively. In normalized terms,

$$\psi_1 = \left(\frac{\partial p}{\partial y}\right)_{y=0} = -\left(\frac{\partial q}{\partial y}\right)_{y=0} \quad \text{and} \quad \psi_2 = \left(\frac{\partial c}{\partial y}\right)_{y=0} = -\left(\frac{\partial d}{\partial y}\right)_{y=0}$$

Addition of equations (6.93) to (6.96) followed by integration leads to

$$p_{y=0} + q_{y=0} + c_{y=0} + d_{y=0} = 1$$

and after introduction of the two Nernst's laws to

$$q_{y=0}[1 + \exp(-\xi_1)] + d_{y=0}[1 + \exp(-\xi_2)] = 1 \tag{6.97}$$

Addition of equations (6.93) and (6.96), followed by integration, leads in the Laplace plane to

$$\bar{p}_{y=0} + \bar{d}_{y=0} = \frac{1}{s} - \frac{\bar{\psi}_1 - \bar{\psi}_2}{\sqrt{s}} \tag{6.98}$$

that is, in the original plane,

$$p_{y=0} + d_{y=0} = 1 - \frac{1}{\sqrt{\pi}} \int_0^\tau \frac{\psi_1(\eta) - \psi_2(\eta)}{\sqrt{\tau - \eta}} d\eta \tag{6.99}$$

Since we assume that both λ_1 and λ_2 are large (pure kinetic conditions),

$$q_{y=0} = \frac{\psi_1}{\sqrt{\lambda_1 \gamma}} \quad \text{and} \quad d_{y=0} = \frac{\psi_2}{\sqrt{\lambda_2}}$$

as demonstrated repeatedly in previous sections.

At the first wave, $d_{y=0} = 0$, $\psi_2 = 0$, and thus, from equation (6.99),

$$\frac{\psi}{\sqrt{\lambda_1 \gamma}} \exp(-\xi_1) = 1 - \frac{1}{\sqrt{\pi}} \int_0^\tau \frac{\psi(\eta)}{\sqrt{\tau - \eta}} d\eta$$

(i.e., the equation of voltammogram corresponding to an irreversible EC mechanism). At the second wave, since $p_{y=0} = 0$, equation (6.98) becomes

$$\bar{d}_{y=0} = \frac{\psi_2}{\sqrt{\lambda_2}} = \frac{1}{s} - \frac{\bar{\psi}_1 - \bar{\psi}_2}{\sqrt{s}}$$

and since λ_2 is large,

$$\bar{\psi}_1 - \bar{\psi}_2 = \frac{1}{\sqrt{s}}, \quad \text{i.e.,} \quad \psi_1 - \psi_2 = \frac{1}{\sqrt{\pi \tau}}$$

At the level of the second wave, the right-hand side of the second equation is practically nil, thus leading to $\psi_1 = \psi_2 = \psi/2$. Equation (6.97) may be recast as

$$q_{y=0} + d_{y=0}[1 + \exp(-\xi_2)] = 1$$

that is,

$$\psi = \frac{2}{\dfrac{1}{\sqrt{\lambda_1 \gamma}} + \dfrac{1}{\sqrt{\lambda_2}} + \dfrac{\exp(-\xi_2)}{\sqrt{\lambda_2}}}$$

thus leading to equation (2.23) or, alternatively, to

$$\frac{\psi}{2}\left(\frac{1}{\sqrt{\lambda_1 \gamma}} + \frac{1}{\sqrt{\lambda_2}}\right) = \frac{1}{1 + \dfrac{\exp(-\xi_2)}{1 + \dfrac{\sqrt{\lambda_2}}{\sqrt{\lambda_1 \gamma}}}} = \frac{1}{1 + \exp(-\xi_{2,c})}$$

with

$$\xi_{2,c} = \xi_2 + \ln\left(1 + \frac{\sqrt{\lambda_2}}{\sqrt{\lambda_1 \gamma}}\right)$$

thus leading to equation (2.24).

6.2.8. Product Distribution in Preparative Electrolysis

As in preceding discussions, we take reductions as an example. Transposition to oxidations just requires a few changes of sign. *In the case of a simple* $A + e^- \rightarrow B$ *reaction*, equations (2.30) and (2.31) are obtained from the integration of equations (2.28) and (2.29), with $(C_A^b)_{t=0} = C^0$ and $(C_B^b)_{t=0} = 0$ as initial conditions, respectively. In the absence of coupled homogeneous reactions, the gradients of both A and B are constant over the entire diffusion layer (Figure 2.31). Thus, in the case where the potential the surface concentration of A is zero,

$$\frac{i}{FSD} = \left(\frac{dC_A}{dx}\right)_{x=\delta} = \left(\frac{dC_A}{dx}\right)_{x=0} = \frac{C_A^b - 0}{\delta} = -\frac{V}{SD}\frac{dC_A^b}{dt}$$

It follows that

$$\frac{dC_A^b}{C_A^b} = -d\left(\frac{t}{t_C}\right) \qquad [t_C \text{ is defined by equation (2.32)}]$$

Hence, knowing that $(C_A^b)_{t=0} = C^0$, equation (2.30) is obtained. Addition of equations (2.28) and (2.29), followed by time-integration, leads to

$$C_A^b + C_B^b = C^0$$

and thus, taking equation (2.30) into account, to equation (2.31).

In the case of constant reactant concentration–constant potential electrolysis, equation (2.28) does not apply since

$$\frac{dC_A^b}{dt} = 0 \qquad (C_A^b = C^0)$$

although

$$\frac{i}{FSD} = \left(\frac{dC_A}{dx}\right)_{x=\delta_-} = \left(\frac{dC_A}{dx}\right)_{x=0} = \frac{C_A^b}{\delta}$$

is still valid. It follows that equations (2.29) may be recast as

$$dC_B^b = C^0 \frac{dt}{t_C}$$

leading, after integration, to equation (2.33), since

$$(C_{\mathrm{B}}^{b})_{t=0} = 0.$$

In constant reactant concentration–constant current electrolysis, the bulk concentration of B also increase proportionally with time, but the proportionality factor is i/FV instead of C^0/t_C [equation (2.34)].

When *the reaction scheme involves first- or pseudo-first-order reactions*, fast enough for pure kinetic conditions to be achieved ($\sqrt{D/k} \ll \delta$), the concentration profile of B is squeezed within a thin reaction layer adjacent to the electrode surface as represented in Figure 2.31 (bottom diagram). Starting from the electrode surface, the following relationships apply.

At the electrode surface (i.e., for $x = 0$),

$$\frac{i}{FSD} = \left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=0} = -\left(\frac{dC_{\mathrm{B}}}{dx}\right)_{x=0} \tag{6.100}$$

$$\left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=0} = 0 \tag{6.101}$$

Within the reaction layer (i.e., for $0 \le x \le \mu$),

$$C_{\mathrm{A}} \simeq (C_{\mathrm{A}})_{x=0}$$

$$D\frac{d^2C_{\mathrm{B}}}{dx^2} - kC_{\mathrm{B}} = 0 \tag{6.102}$$

$$D\frac{d^2C_{\mathrm{C}}}{dx^2} + kC_{\mathrm{B}} = 0 \tag{6.103}$$

At the reaction layer/diffusion layer boundary (i.e., for $x = \mu$),

$$\begin{gathered}(C_{\mathrm{A}})_{x=0} \simeq (C_{\mathrm{A}})_{x=\mu}, \quad \left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=\mu} = \left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=0} = \frac{i}{FSD}\\ (C_{\mathrm{B}})_{x=\mu} = 0, \quad \left(\frac{dC_{\mathrm{B}}}{dx}\right)_{x=\mu} = 0\\ (C_{\mathrm{C}})_{x=\mu_-} = (C_{\mathrm{C}})_{x=\mu_+}\end{gathered} \tag{6.104}$$

Within the diffusion layer (i.e., for $\mu \le x \le \delta$),

$$\begin{gathered}\frac{dC_{\mathrm{A}}}{dx} = \left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=\mu} = \left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=\delta} = \left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=0} = \frac{i}{FSD}\\ \frac{dC_{\mathrm{C}}}{dx} = \left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=\mu} = \left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=\delta}\end{gathered} \tag{6.105}$$

At the diffusion layer–solution boundary, (i.e., for $x = \delta$),

$$\frac{i}{F} = -V\frac{dC_{\mathrm{A}}^{b}}{dt} = SD\left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=\delta}$$

$$V\frac{dC_{\mathrm{C}}^{b}}{dt} = -SD\left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=\delta} \tag{6.106}$$

Addition of equations (6.102) and (6.103), followed by integration, taking equations (6.100), (6.101), and (6.104) into account, leads to

$$\left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=\mu} = \left(\frac{dC_{\mathrm{B}}}{dx}\right)_{x=0} = -\frac{i}{FSD}$$

and therefore to

$$\left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=\delta_{-}} = \left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=\mu} = -\frac{i}{FSD}$$

which, taking equation (6.106) into account, means that the production of C follows exactly the same rules as the production of B in the preceding case.

Dealing now with Scheme 2.16, which involves two competing first-order reactions, the A concentration profile and gradients are not modified. The following differential equations govern the concentration profiles of the intermediate B and the two products C and D within the reaction layer:

$$D\frac{d^2C_{\mathrm{B}}}{dx^2} - (k_1 + k_2)C_{\mathrm{B}} = 0 \tag{6.107}$$

$$D\frac{d^2C_{\mathrm{C}}}{dx^2} + k_1C_{\mathrm{B}} = 0 \tag{6.108}$$

$$D\frac{d^2C_{\mathrm{D}}}{dx^2} + k_2C_{\mathrm{B}} = 0 \tag{6.109}$$

with as additional boundary conditions at the electrode surface,

$$\left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=0} = 0 \qquad \left(\frac{dC_{\mathrm{D}}}{dx}\right)_{x=0} = 0 \tag{6.110}$$

while, outside the reaction layer, equation (6.105) and a similar equation for D apply. At the diffusion layer–solution boundary,

$$V\frac{dC_{\mathrm{C}}^{b}}{dt} = -SD\left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=\delta} \qquad V\frac{dC_{\mathrm{D}}^{b}}{dt} = -SD\left(\frac{dC_{\mathrm{D}}}{dx}\right)_{x=\delta} \tag{6.111}$$

Summing equations (6.107) to (6.109) and integrating, taking equations (6.100), (6.104), (6.110), and (6.111) into account leads to

$$V\frac{d(C_{\mathrm{C}}^{b} + C_{\mathrm{D}}^{b})}{dt} = -SD\left[\frac{d(C_{\mathrm{C}} + C_{\mathrm{D}})}{dx}\right]_{x=\delta} = \frac{i}{F}$$

meaning that the build up of the sum of the two products follows exactly the same laws as B in the case of a simple electron transfer in any of the electrolysis regimes. Then, linear combination of equations (6.107) and (6.108),

$$D\frac{d^2\left(C_{\mathrm{B}} + \dfrac{k_1 + k_2}{k_1}C_{\mathrm{C}}\right)}{dx^2} = 0$$

followed by integration, with due account of the pertinent boundary conditions, leads to

$$V\frac{dC_{\mathrm{C}}^{b}}{dt} = \frac{k_1}{k_1 + k_2}\frac{i}{F}$$

thus yielding equations (2.35).

Passing to Scheme 2.17, where the competition involves two follow-up reactions of different orders, the governing differential equations for B, C, and D are now

$$D\frac{d^2C_{\mathrm{B}}}{dx^2} - k_1C_{\mathrm{B}} - 2k_2C_{\mathrm{B}}^2 = 0 \qquad (6.112)$$

$$D\frac{d^2C_{\mathrm{C}}}{dx^2} + k_1C_{\mathrm{B}} = 0 \qquad (6.113)$$

$$D\frac{d^2C_{\mathrm{D}}}{dx^2} + k_2C_{\mathrm{B}}^2 = 0 \qquad (6.114)$$

with the same boundary conditions as in the preceding case. From the linear combination of equations (6.112) to (6.114) and integration, taking the appropriate boundary conditions into account, one obtains

$$V\frac{d(C_{\mathrm{C}}^{b} + 2C_{\mathrm{D}}^{b})}{dt} = -SD\left[\frac{d(C_{\mathrm{C}} + 2C_{\mathrm{D}})}{dx}\right]_{x=\delta} = \frac{i}{F}$$

This means that the build up of the sum of the first-order reaction product and twice the second-order reaction product follows exactly the same laws as B in the case of a simple electron transfer in any of the electrolysis regimes. The yields are obtained from

$$Y^{\mathrm{D}} = 1 - Y^{\mathrm{C}} = \frac{2\dfrac{dC_{\mathrm{D}}^{b}}{dt}}{\dfrac{dC_{\mathrm{C}}^{b}}{dt} + 2\dfrac{dC_{\mathrm{D}}^{b}}{dt}} = \frac{2\left(\dfrac{dC_{D}}{dx}\right)_{x=\delta}}{\left(\dfrac{dC_{\mathrm{C}}}{dx}\right)_{x=\delta} + 2\left(\dfrac{dC_{\mathrm{D}}}{dx}\right)_{x=\delta}}$$

Addition of equation (6.112) and twice equation (6.114) leads to

$$D\frac{d^2(2C_{\mathrm{D}} + C_{\mathrm{B}})}{dx^2} = k_1 C_{\mathrm{B}}$$

(i.e., after integration), taking into account equations (6.104) and (6.110),

$$D\left(\frac{d2C_{\mathrm{D}}}{dx}\right)_{x=\delta} = D\left(\frac{dC_{\mathrm{B}}}{dx}\right)_{x=0} + k_1 \int_{x=0}^{x=\delta} C_{\mathrm{B}}\, dx$$

and therefore

$$Y^{\mathrm{D}} = 1 - Y^{\mathrm{C}} = \frac{-D\left(\dfrac{dC_{\mathrm{B}}}{dx}\right)_{x=0} - k_1 \displaystyle\int_{x=0}^{x=\delta} C_{\mathrm{B}} dx}{\dfrac{i}{FS}}$$

that is, taking account of equation (6.100),

$$Y^{\mathrm{D}} = 1 - Y^{\mathrm{C}} = 1 - \frac{k_1 \displaystyle\int_{x=0}^{x=\delta} C_{\mathrm{B}} dx}{i/FS} \tag{6.115}$$

The concentration profile of B is squeezed within the reaction layer. It may be analyzed in dimensionless term so as to obtain the expression of the yields with introduction of a minimal number of parameters. This is arrived at by normalizing the space variable versus the reaction layer thickness as $y^* = x\sqrt{k_1/D}(y^* = 1$ corresponds to $x = \mu)$ and the concentrations as

$$b^* = C_{\mathrm{B}}\sqrt{k_1 D}\frac{FS}{i} \qquad c^* = C_{\mathrm{C}}\sqrt{k_1 D}\frac{FS}{i} \qquad d^* = C_{\mathrm{D}}\sqrt{k_1 D}\frac{FS}{i}$$

in the two constant-concentration regimes considered so far. In the constant-current regime, the normalizing factor is indeed a constant, independent of time. This is also true for the constant-potential regime when the potential is negative enough for the condition $(C_{\mathrm{A}})_{x=0} = 0$, implying that

$i/FS = C^0 D/\delta$ is also time-independent. The competition between the two follow-up reactions is consequently a function of a single parameter:

$$p_{1st}^{2nd} = \frac{k_2}{k_1^{3/2}} \frac{i}{FSD^{1/2}} \tag{6.116}$$

which applies as such in the constant-current regime and becomes

$$p_{1st}^{2nd} = \frac{k_2}{k_1^{3/2}} \frac{C^0 D^{1/2}}{\delta}$$

in the constant-potential regime just defined.

With these changes of variables, the expression of the yields in equation (6.115) becomes

$$Y^{\mathrm{D}} = 1 - Y^{\mathrm{C}} = 1 - \int_{y^*=0}^{y^*=\infty} b^* dy^* \tag{6.117}$$

while equation (6.102) is transformed into

$$\frac{d^2 b^*}{dy^{*2}} = b^* + 2p_{1st}^{2nd} b^{*^2} \tag{6.118}$$

the integration of which, taking equation (6.104) into account, leads to

$$-\frac{db^*}{dy^*} = b^* \left(1 + \frac{4}{3} p_{1st}^{2nd} b^*\right)^{1/2} \tag{6.119}$$

The integral in equation (6.117) may be recast as

$$\begin{aligned}\int_{y^*=0}^{y^*=\infty} b^*\, dy^* &= -\int_{b^*=0}^{b^*=(b^*)_{y^*=0}} \frac{b^* db^*}{db^*/dy^*} \\ &= \int_{b^*=0}^{b^*=(b^*)_{y^*=0}} \frac{db^*}{\sqrt{1 + \frac{4p_{1st}^{2nd}}{3} b^*}} = \frac{3}{2p}\left[\sqrt{1 + \frac{4p_{1st}^{2nd}}{3}(b^*)_{y^*=0}} - 1\right]\end{aligned}$$

where $(b^*)_{y^*=0}$ is provided by the application of equation (6.119) for $y^* = 0$:

$$(b^*)_{y^*=0}\left[1 + \frac{4}{3} p_{1st}^{2nd} (b^*)_{y^*=0}\right]^{1/2} = 1$$

leading to an alternative expression of the yields:

$$Y^{\mathrm{D}} = 1 - Y^{\mathrm{C}} = 1 - \frac{3}{2p_{1st}^{2nd}}\left[\frac{1}{(b^*)_{y^*=0}} - 1\right]$$

Computation of Y^{C} and Y^{D} as a function of the competition parameter from the two equations above leads to the curves in Figure 2.32. Since $C_{\mathrm{C}}^b + 2C_{\mathrm{D}}^b$ increases proportionally with time and since the competition parameter is independent of time, the concentration of each product also increases proportionally with time.

In the exhaustive electrolysis constant potential regime,

$$C_{\mathrm{A}}^b = C^0 \exp\left(-\frac{t}{t_C}\right)$$

and

$$C_{\mathrm{C}}^b + 2C_{\mathrm{D}}^b = C^0\left[1 - \exp\left(-\frac{t}{t_C}\right)\right]$$

We therefore introduced newly normalized concentrations, taking the exponential time variation into account:

$$b^{\blacktriangle} = b^* \exp\left(\frac{t}{t_C}\right) \qquad c^{\blacktriangle} = c^* \exp\left(\frac{t}{t_C}\right) \qquad d^{\blacktriangle} = d^* \exp\left(\frac{t}{t_C}\right)$$

as well as a modified form of the competition parameter,

$$p_{1st}^{2nd\blacktriangle} = p_{1st}^{2nd} \exp\left(-\frac{t}{t_C}\right) \tag{6.120}$$

Equation (6.118) still applies to these modified variables and parameter, leading to the following expressions:

$$\frac{d^2 b^{\blacktriangle}}{dy^{*2}} = b^{\blacktriangle} + 2p_{1st}^{2nd\blacktriangle} b^{\blacktriangle^2}$$

$$\frac{d^2 c^{\blacktriangle}}{dy^{*2}} = -b^{\blacktriangle}$$

$$\frac{d^2 d^{\blacktriangle}}{dy^{*2}} = -p_{1st}^{2nd\blacktriangle} b^{\blacktriangle^2}$$

The yields ensue (ECP for exhaustive constant potential electrolysis):

$$(Y^{\mathrm{D}})_{ECP} = 1 - (Y^{\mathrm{C}})_{ECP} = \frac{\displaystyle\int_0^{t/t_C} \left[1 - \int_0^{\infty} b^{\blacktriangle}\, dy^*\right] \exp(-\eta)\, d\eta}{1 - \exp\left(-\dfrac{t}{t_C}\right)}$$

that is,

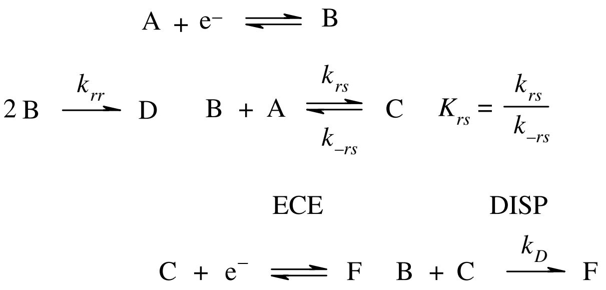
$$(Y^{\mathrm{D}})_{ECP} = 1 - (Y^{\mathrm{D}})_{ECP} = \frac{\displaystyle\int_{p_{1st}^{2nd\blacktriangle}}^{p_{1st}^{2nd}} (Y^{\mathrm{D}})_{CC}\, d\eta}{p_{1st}^{2nd} - p_{1st}^{2nd\blacktriangle}} \tag{6.121}$$

where $(Y^{\mathrm{D}})_{CC}$ is the yield under constant concentration conditions. At the end of the electrolysis $(t/t_C \to \infty)$,

$$Y^{\mathrm{D}} = 1 - Y^{\mathrm{C}} = \frac{1}{p_{1st}^{2nd}} \int_0^{p_{1st}^{2nd}} (Y^{\mathrm{D}})_{CC}\, d\eta \tag{6.122}$$

The curves in Figure 2.32b are thus obtained from integration of the curves in Figure 2.32a.

The *reduction of carbon dioxide* (Section 2.5.4) raises the question of possible *competition between a radical–radical coupling and a radical–substrate coupling* according to Scheme 6.3, in which the competition shown in the upper part of Scheme 2.34 is represented symbolically.



$$\mathrm{A} + e^- \rightleftharpoons \mathrm{B}$$

$$2\mathrm{B} \xrightarrow{k_{rr}} \mathrm{D} \qquad \mathrm{B} + \mathrm{A} \underset{k_{-rs}}{\overset{k_{rs}}{\rightleftharpoons}} \mathrm{C} \qquad K_{rs} = \frac{k_{rs}}{k_{-rs}}$$

$$\mathrm{C} + e^- \rightleftharpoons \mathrm{F} \qquad \mathrm{B} + \mathrm{C} \xrightarrow{k_D} \mathrm{F}$$

SCHEME 6.3

The mechanism, albeit somewhat more complicated than in the preceding case, also involves competition between a first- and second-order follow-up reaction. For this reason, a similar analysis applies and the yields vs. competition parameter curves can be derived from those pertaining to the preceding case.

The data shown in Figure 2.36 were gathered at constant current with a value of the current density that brought the electrode potential at the foot of the current–potential characteristic of the system. The concentration of substrate may thus be considered as constant. As discussed in Section 2.5, we consider only the case where the second electron transfer in the radical–substrate coupling pathway occurs at the electrode (ECE). The following equations and conditions apply.

At the electrode surface (i.e., for $x = 0$),

$$(C_\mathrm{C})_{x=0} = 0 \tag{6.123}$$

$$\left(\frac{dC_\mathrm{D}}{dx}\right)_{x=0} = 0 \tag{6.124}$$

$$\left(\frac{dC_\mathrm{F}}{dx}\right)_{x=0} = -\left(\frac{dC_\mathrm{C}}{dx}\right)_{x=0} \tag{6.125}$$

$$\frac{i}{FS} = -D\left[\frac{d(C_\mathrm{B} + C_\mathrm{F})}{dx}\right]_{x=0} \tag{6.126}$$

Within the reaction layer (i.e., for $0 \le x \le \mu$),

$$D\frac{d^2C_\mathrm{B}}{dx^2} = 2k_{rr}C_\mathrm{B}^2 + k_{rs}C^0C_\mathrm{B} \tag{6.127}$$

$$D\frac{d^2C_\mathrm{C}}{dx^2} = -k_{rs}C^0C_\mathrm{B} \tag{6.128}$$

$$D\frac{d^2C_\mathrm{D}}{dx^2} + k_{rr}C_\mathrm{B}^2 = 0 \tag{6.129}$$

$$D\frac{d^2C_\mathrm{F}}{dx^2} = 0 \tag{6.130}$$

In the rest of the diffusion layer (i.e., for $\mu \le x \le \delta$),

$$C_\mathrm{B} = 0 \qquad \frac{dC_\mathrm{B}}{dx} = 0 \tag{6.131}$$

$$\frac{dC_\mathrm{C}}{dx} = 0 \tag{6.132}$$

$$D\frac{d^2C_\mathrm{D}}{dx^2} = 0 \tag{6.133}$$

$$D\frac{d^2C_\mathrm{F}}{dx^2} = 0 \tag{6.134}$$

At the diffusion layer–solution boundary (i.e., for $x = \delta$),

$$V\frac{dC_{\mathrm{D}}^{b}}{dt} = -SD\left(\frac{dC_{\mathrm{D}}}{dx}\right)_{x=\delta} \qquad V\frac{dC_{\mathrm{F}}^{b}}{dt} = -SD\left(\frac{dC_{\mathrm{F}}}{dx}\right)_{x=\delta}$$

The yields in the two products are obtained from

$$Y^{\mathrm{D}} = 1 - Y^{\mathrm{F}} = \frac{dC_{\mathrm{D}}^{b}/dt}{\dfrac{dC_{\mathrm{D}}^{b}}{dt} + \dfrac{dC_{\mathrm{F}}^{b}}{dt}} = \frac{dC_{\mathrm{D}}/dx_{x=\delta}}{\left(\dfrac{dC_{\mathrm{D}}}{dx}\right)_{x=\delta} + \left(\dfrac{dC_{F}}{dx}\right)_{x=\delta}}$$

A first linear combination of equations (6.127) to (6.130) aiming at the elimination of the kinetic terms gives

$$D\frac{d^2C_{\mathrm{B}} + C_{\mathrm{C}} + 2C_{\mathrm{D}} + 2C_{\mathrm{F}}}{dx^2} = 0$$

which is valid within and outside the reaction layer. Integration, taking into account equations (6.124), (6.125), (6.131), and (6.132), leads to

$$D\left[\frac{d(2C_{\mathrm{D}} + 2C_{\mathrm{F}})}{dx}\right]_{x=\delta} = D\left[\frac{d(C_{\mathrm{B}} + C_{\mathrm{F}})}{dx}\right]_{x=0} = -\frac{i}{FS}$$

The yields are thus expressed as

$$Y^{\mathrm{D}} = 1 - Y^{\mathrm{F}} = \frac{-2D\left(\dfrac{dC_{\mathrm{D}}}{dx}\right)_{x=\delta}}{\dfrac{i}{FS}}$$

Another linear combination involving equations (6.127) to (6.129) gives

$$D\frac{d^2C_{\mathrm{B}} - C_{\mathrm{C}} + 2C_{\mathrm{D}}}{dx^2} = 2k_{rs}C^0C_{\mathrm{B}}$$

and after integration and introduction of (6.124), (6.125), (6.131), and (6.132),

$$-D\left[\frac{d(2C_{\mathrm{D}})}{dx}\right]_{x=\delta} = \frac{i}{FS} - 2k_{rs}C^0\int_{x=0}^{x=\delta} C_{\mathrm{B}}\,dx$$

and therefore

$$Y^{\mathrm{D}} = 1 - Y^{\mathrm{F}} = 1 - \frac{2k_{rs}C^0 \displaystyle\int_{x=0}^{x=\delta} C_{\mathrm{B}}\,dx}{\dfrac{i}{FS}} \tag{6.135}$$

The search of the minimal number of competition parameters calls for normalizing the space and concentration as follows:

$$y^* = x\sqrt{\frac{2k_{rs}C^0}{D}}$$

$$b^* = C_{\mathrm{B}}\sqrt{2k_{rs}C^0 D}\,\frac{FS}{i}$$

Then equations (6.127) and (6.133) become, after introduction of a single dimensionless competition parameter,

$$p_{rs1}^{rr} = \frac{k_{rr}}{(2k_{rs})^{3/2}}\frac{i}{FSD^{1/2}C^{0^{3/2}}} \tag{6.136}$$

$$Y^{\mathrm{D}} = 1 - Y^{\mathrm{F}} = 1 - \int_{y^*=0}^{y^*=\infty} b^* dy^* \tag{6.137}$$

$$\frac{d^2b^*}{dy^{*^2}} = b^* + 2p_{rs1}^{rr}b^{*^2} \tag{6.138}$$

Comparison of equations (6.136), (6.137), and (6.138) with equations (6.116), (6.117) and (6.118), respectively, shows that the variations of the yields with the competition parameter are exactly the same as already computed for the case of competition between a first- and second-order follow-up reaction (Scheme 2.17), although definition of the competition parameter is different.

For the *ECE–DISP competition*, the following equations and conditions apply. At the electrode surface (i.e., for $x = 0$),

$$\left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=0} = -\left(\frac{dC_{\mathrm{B}}}{dx}\right)_{x=0} \tag{6.139}$$

$$\left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=0} = -\left(\frac{dC_{\mathrm{D^E}}}{dx}\right)_{x=0} \tag{6.140}$$

$$\left(\frac{dC_{\mathrm{D^D}}}{dx}\right)_{x=0} = 0 \tag{6.141}$$

$$(C_{\mathrm{C}})_{x=0} = 0 \tag{6.142}$$

For a constant-potential regime, if the electrode potential is set negative enough (for a reduction, positive enough for an oxidation), $(C_\mathrm{A})_{x=0} = 0$. For a constant-current regime,

$$\frac{i}{FSD} = \left(\frac{dC_\mathrm{A}}{dx}\right)_{x=0} + \left(\frac{dC_\mathrm{C}}{dx}\right)_{x=0} \tag{6.143}$$

is maintained constant.

Within the reaction layer (i.e., for $0 \le x \le \mu$),

$$D\frac{d^2C_\mathrm{A}}{dx^2} + k_D C_\mathrm{B} C_\mathrm{C} = 0 \tag{6.144}$$

$$D\frac{d^2C_\mathrm{B}}{dx^2} - kC_\mathrm{B} - k_D C_\mathrm{B} C_\mathrm{C} = 0 \tag{6.145}$$

$$D\frac{d^2C_\mathrm{C}}{dx^2} + kC_\mathrm{B} - k_D C_\mathrm{B} C_\mathrm{C} = 0 \tag{6.146}$$

$$D\frac{d^2C_{\mathrm{D^E}}}{dx^2} = 0 \tag{6.147}$$

$$D\frac{d^2C_{\mathrm{D^D}}}{dx^2} + k_D C_\mathrm{B} C_\mathrm{C} = 0 \tag{6.148}$$

At the reaction layer–diffusion layer boundary (i.e., for $x = \mu$),

$$(C_\mathrm{B})_{x=\mu} = 0 \qquad \left(\frac{dC_\mathrm{B}}{dx}\right)_{x=\mu} = 0 \tag{6.149}$$

and the conditions expressing the continuity of concentrations and gradients for A, C, $\mathrm{D^E}$, and $\mathrm{D^D}$.

Within the diffusion layer (i.e., for $\mu \le x \le \delta$),

$$D\frac{d^2C_\mathrm{A}}{dx^2} = 0 \tag{6.150}$$

$$D\frac{d^2C_\mathrm{C}}{dx^2} = 0 \tag{6.151}$$

$$D\frac{d^2C_{\mathrm{D^E}}}{dx^2} = 0 \tag{6.152}$$

$$D\frac{d^2C_{\mathrm{D^D}}}{dx^2} = 0 \tag{6.153}$$

$$C_\mathrm{B} = 0 \qquad \frac{dC_\mathrm{B}}{dx} = 0 \tag{6.154}$$

At the diffusion layer–solution boundary (i.e., for $x = \delta$),

$$-V\frac{dC_{\mathrm{A}}^{b}}{dt} = SD\left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=\delta}$$

in exhaustive electrolysis, and $C_{\mathrm{A}} = C^{0}$ in constant-concentration regimes. In addition,

$$-V\frac{dC_{\mathrm{C}}^{b}}{dt} = SD\left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=\delta} \tag{6.155}$$

$$-V\frac{dC_{\mathrm{D^E}}^{b}}{dt} = SD\left(\frac{dC_{\mathrm{D^E}}}{dx}\right)_{x=\delta} \tag{6.156}$$

$$-V\frac{dC_{\mathrm{D^D}}^{b}}{dt} = SD\left(\frac{dC_{\mathrm{D^D}}}{dx}\right)_{x=\delta} \tag{6.157}$$

Linear combination of equations (6.144) to (6.146) leads to

$$D\frac{d^{2}2C_{\mathrm{A}} + C_{\mathrm{B}} + C_{\mathrm{C}}}{dx^{2}} = 0 \tag{6.158}$$

which applies not only within the reaction layer but also over the entire diffusion layer [from equations (6.150) to (6.154)]. It follows that

$$\begin{aligned} 2C_{\mathrm{A}} + C_{\mathrm{B}} + C_{\mathrm{C}} = {} & 2(C_{\mathrm{A}})_{x=0} + (C_{\mathrm{B}})_{x=0} + (C_{\mathrm{C}})_{x=0} \\ & + \left[2\left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=0} + \left(\frac{dC_{\mathrm{B}}}{dx}\right)_{x=0} + \left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=0}\right]x \end{aligned} \tag{6.159}$$

which becomes

$$2C_{\mathrm{A}} + C_{\mathrm{B}} + C_{\mathrm{C}} = 2(C_{\mathrm{A}})_{x=0} + \left[\left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=0} + \left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=0}\right]x \tag{6.160}$$

in view of equations (6.140) and (6.143), and of the fact that $(C_{\mathrm{B}})_{x=0} \simeq 0$ (achievement of pure kinetic conditions). Application of equation (6.160) for $x = \delta$, taking equation (6.154) into account, gives

$$2(C_{\mathrm{A}})_{x=\delta} + (C_{\mathrm{C}})_{x=\delta} = 2(C_{\mathrm{A}})_{x=0} + \left[\left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=0} + \left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=0}\right]\delta$$

It also results from equation (6.145) that

$$2\left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=\delta}+\left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=\delta}=\left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=0}+\left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=0}$$

Therefore,

$$2(C_{\mathrm{A}})_{x=\delta}+(C_{\mathrm{C}})_{x=\delta}=2(C_{\mathrm{A}})_{x=0}+\left[2\left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=\delta}+\left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=\delta}\right]\delta$$

From equations (6.150) and from the fact that $\mu \ll \delta$, we infer that

$$\begin{aligned}\left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=\delta}&=\frac{(C_{\mathrm{A}})_{x=\delta}-(C_{\mathrm{A}})_{x=\mu}}{\delta-\mu}\\&\simeq\frac{(C_{\mathrm{A}})_{x=\delta}-(C_{\mathrm{A}})_{x=\mu}}{\delta}\simeq\frac{(C_{\mathrm{A}})_{x=\delta}-(C_{\mathrm{A}})_{x=0}}{\delta}\end{aligned}$$

and similarly, from equation (6.151),

$$\begin{aligned}\left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=\delta}&=\frac{(C_{\mathrm{C}})_{x=\delta}-(C_{\mathrm{C}})_{x=\mu}}{\delta-\mu}\\&\simeq\frac{(C_{\mathrm{C}})_{x=\delta}-(C_{\mathrm{C}})_{x=\mu}}{\delta}\end{aligned}$$

Therefore,

$$\begin{aligned}2(C_{\mathrm{A}})_{x=\delta}+(C_{\mathrm{C}})_{x=\delta}&=2(C_{\mathrm{A}})_{x=0}\\&\quad+2[(C_{\mathrm{A}})_{x=\delta}-(C_{\mathrm{A}})_{x=\mu}]+[(C_{\mathrm{C}})_{x=\delta}-(C_{\mathrm{C}})_{x=\mu}]\end{aligned}$$

Since $(C_{\mathrm{A}})_{x=\mu}\simeq(C_{\mathrm{A}})_{x=\mu}$ and $(C_{\mathrm{C}})_{x=\mu}\simeq 0$, then

$$\left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=\delta}=\frac{(C_{\mathrm{C}})_{x=\delta}}{\delta}$$

implying that

$$\frac{dC_{\mathrm{C}}^{b}}{dt}=-C_{\mathrm{C}}^{b}\frac{SD}{V\delta}$$

Since there is no C at the start of electrolysis, the concentration of C and its gradient are negligible [on the order of $(C_{\mathrm{B}})_{x=0}$] within the diffusion layer. Thus, $(dC_{\mathrm{C}}/dx)_{x=\mu}=0$ may serve as a boundary condition.

Addition of equations (6.144) to (6.148) gives

$$D\frac{d^2 C_{\mathrm{A}} + C_{\mathrm{B}} + C_{\mathrm{C}} + C_{\mathrm{D^E}} + C_{\mathrm{D^D}}}{dx^2} = 0$$

which applies within the reaction layer but also outside it [equations (6.150) to (6.154)]. It follow that the sum of all gradients is conserved from $x = \mu$ to $x = \delta$. Thus, taking into account equations (6.140) to (6.142) and (6.149) and the fact that

$$\left(\frac{dC_{\mathrm{B}}}{dx}\right)_{x=\delta} = \left(\frac{dC_{\mathrm{B}}}{dx}\right)_{x=\mu} = 0$$

and

$$\left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=\delta} = 0$$

It follows that:

$$\left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=\delta} + \left(\frac{dC_{\mathrm{D^E}}}{dx}\right)_{x=\delta} + \left(\frac{dC_{\mathrm{D^D}}}{dx}\right)_{x=\delta} = 0$$

meaning that the production of the sum of $\mathrm{D^E}$ and $\mathrm{D^D}$ equals the consumption of A.

From equations (6.147) and (6.152),

$$\left(\frac{dC_{\mathrm{D^E}}}{dx}\right)_{x=\delta} = \left(\frac{dC_{\mathrm{D^E}}}{dx}\right)_{x=0}$$

and therefore from equation (6.140),

$$\left(\frac{dC_{\mathrm{D^E}}}{dx}\right)_{x=\delta} = \left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=0}$$

In constant-concentration regimes,

$$C^b_{\mathrm{D^E}} + C^b_{\mathrm{D^D}} = C^0 \frac{t}{t_C}$$

and

$$C^b_{\mathrm{D^E}} = \frac{t\delta}{t_C}\left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=0}$$

The yields are thus expressed as

$$Y^{\mathrm{D^E}} = 1 - Y^{\mathrm{D^D}} = \frac{\delta}{C^0}\left(\frac{dC_\mathrm{C}}{dx}\right)_{x=0}$$

The gradient of C at the electrode surface may be obtained from the simultaneous resolution of equations (6.145) and (6.146). As in the preceding case, convenient dimensionless expressions are obtained after normalization of the space variable as $y^* = x\sqrt{k_1/D}$ and of the concentration as

$$b^* = \frac{C_\mathrm{B}}{C^0}\sqrt{\frac{k_1}{D}}\delta \qquad c^* = \frac{C_\mathrm{C}}{C^0}\sqrt{\frac{k_1}{D}}\delta \qquad d^* = \frac{C_\mathrm{D}}{C^0}\sqrt{\frac{k_1}{D}}\delta$$

in the constant-potential regime and

$$b^* = C_\mathrm{B}\sqrt{k_1 D}\frac{FS}{i} \qquad c^* = C_\mathrm{C}\sqrt{k_1 D}\frac{FS}{i}$$

in the constant-current regime with introduction of the competition parameters

$$p_{ECE}^{DISP} = \frac{k_2}{k_1^{3/2}}\frac{C^0 D^{1/2}}{\delta} \quad \text{and} \quad \frac{k_2}{k_1^{3/2}}\frac{iD^{1/2}}{FS}$$

in the two regimes, respectively, convert equations (6.145) and (6.146) into the following dimensionless system, which depends on the single competition parameter p_{ECE}^{DISP}.

$$\frac{d^2 b^*}{dy^{*2}} = b^* + p_{ECE}^{DISP} b^* c^*$$

$$\frac{d^2 c^*}{dy^{*2}} = -b^* + p_{ECE}^{DISP} b^* c^*$$

with as boundary conditions

$$\left(\frac{dc^*}{dy^*}\right)_{y^*=0} - \left(\frac{db^*}{dy^*}\right)_{y^*=0} = 2$$

[from equations (6.142) and (6.160)]

$$\begin{aligned}(c^*)_{y^*=0} &= 0\\ (b^*)_{y^*=\infty} &= 0\\ \left(\frac{dc^*}{dy^*}\right)_{y^*=\infty} &= 0\end{aligned}$$

Finite difference resolution of this system of partial derivative equations with their boundary conditions allows calculation of $(dc^*/dy^*)_{y^*=0}$ and thereby of

$$Y^{\mathrm{D^E}} = 1 - Y^{\mathrm{D^D}} = \left(\frac{dc^*}{dy^*}\right)_{y^*=0}$$

finally leading to the curves in Figure 2.33a.

As in the preceding case, yields at the end of a constant-potential exhaustive electrolysis are obtained by integration of the constant-concentration yields [see the establishment of equations (6.121) and (6.122)]:

$$Y^{D^E} = 1 - Y^{D^D} = \frac{1}{p_{ECE}^{DISP}} \int_0^{p_{ECE}^{DISP}} \left(Y^{D^E}\right)_{CC} d\eta$$

finally leading to the curves in Figure 2.33b.

The *competition between H-atom transfer and electron + proton transfer*, exemplified by the reduction of aryl halides in Section 2.5.5, corresponds to the symbolic Scheme 6.4.

$$\begin{aligned}\mathrm{A} + \mathrm{e}^- &\rightleftharpoons \mathrm{B}\\ \mathrm{B} &\xrightarrow{k_1} \mathrm{C}\\ \mathrm{C} &\xrightarrow{k_2} \mathrm{F} + \mathrm{G}\end{aligned}$$

$$\begin{array}{lcl} \text{ECE} & \qquad & \text{DISP}\\ \mathrm{C} + \mathrm{e}^- \rightleftharpoons \mathrm{D^E} & & \mathrm{B} + \mathrm{C} \xrightarrow{k_D} \mathrm{A} + \mathrm{D^D}\\ \mathrm{G} + \mathrm{e}^- \rightleftharpoons \mathrm{H} & & \mathrm{B} + \mathrm{G} \xrightarrow{k_D} \mathrm{A} + \mathrm{H} \end{array}$$

SCHEME 6.4

This three-cornered competition may be analyzed on the basis of three two-cornered competitions, ECE–HAT, DISP–HAT, and ECE–DISP, where "HAT" stands for the formation of products F and H even if this type of reaction scheme may involve reactions other than H-atom transfer and substrates other than aryl halides. The ECE–DISP competition was just analyzed in Section 6.2.7. Before examining the ECE–HAT and DISP–HAT pathways separately, we establish several relationships that hold when both pathways are involved simultaneously and are therefore valid in each of the two cases.

At the electrode surface,

$$\left(\frac{dC_\mathrm{A}}{dx}\right)_{x=0} = -\left(\frac{dC_\mathrm{B}}{dx}\right)_{x=0} \tag{6.161}$$

$$\left(\frac{dC_\mathrm{C}}{dx}\right)_{x=0} = -\left(\frac{dC_\mathrm{D}}{dx}\right)_{x=0} \tag{6.162}$$

$$\left(\frac{dC_\mathrm{F}}{dx}\right)_{x=0} = 0 \tag{6.163}$$

$$\left(\frac{dC_\mathrm{G}}{dx}\right)_{x=0} = -\left(\frac{dC_\mathrm{H}}{dx}\right)_{x=0} \tag{6.164}$$

$$(C_\mathrm{C})_{x=0} = 0 \qquad (C_\mathrm{G})_{x=0} = 0$$

For a constant-potential regime, if the electrode potential is set negative enough (for a reduction, positive enough for an oxidation), $(C_\mathrm{A})_{x=0} = 0$.

For a constant-current regime,

$$\frac{i}{FSD} = \left(\frac{dC_\mathrm{A}}{dx}\right)_{x=0} + \left(\frac{dC_\mathrm{C}}{dx}\right)_{x=0} + \left(\frac{dC_\mathrm{G}}{dx}\right)_{x=0} \tag{6.165}$$

is maintained constant.

Within the reaction layer (i.e., for $0 \leq x \leq \mu$),

$$D\frac{d^2C_\mathrm{A}}{dx^2} + k_D C_\mathrm{B} C_\mathrm{C} + k_D C_\mathrm{B} C_\mathrm{G} = 0 \tag{6.166}$$

$$D\frac{d^2C_\mathrm{B}}{dx^2} - k_1 C_\mathrm{B} - k_D C_\mathrm{B} C_\mathrm{C} - k_D C_\mathrm{B} C_\mathrm{G} = 0 \tag{6.167}$$

$$D\frac{d^2C_\mathrm{C}}{dx^2} + k_1 C_\mathrm{B} - k_2 C_\mathrm{C} - k_D C_\mathrm{B} C_\mathrm{C} = 0 \tag{6.168}$$

$$D\frac{d^2C_\mathrm{D}}{dx^2} + k_D C_\mathrm{B} C_\mathrm{C} = 0 \tag{6.169}$$

$$D\frac{d^2C_\mathrm{F}}{dx^2} + k_2 C_\mathrm{C} = 0 \tag{6.170}$$

$$D\frac{d^2C_\mathrm{G}}{dx^2} + k_2 C_\mathrm{C} - k_D C_\mathrm{B} C_\mathrm{G} = 0 \tag{6.171}$$

$$D\frac{d^2C_\mathrm{H}}{dx^2} + k_D C_\mathrm{B} C_\mathrm{G} = 0 \tag{6.172}$$

At the reaction layer–diffusion layer boundary (i.e., for $x = \mu$),

$$(C_{\mathrm{B}})_{x=\mu} = 0 \qquad \left(\frac{dC_{\mathrm{B}}}{dx}\right)_{x=\mu} = 0 \tag{6.173}$$

$$\left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=\mu} = 0 \tag{6.174}$$

$$\left(\frac{dC_{\mathrm{G}}}{dx}\right)_{x=\mu} = 0 \tag{6.175}$$

Within the diffusion layer (i.e., for $\mu \leq x \leq \delta$),

$$D\frac{d^2C_{\mathrm{A}}}{dx^2} = 0 \tag{6.176}$$

$$C_{\mathrm{B}} = 0 \qquad \frac{dC_{\mathrm{B}}}{dx} = 0 \tag{6.177}$$

$$C_{\mathrm{C}} = 0 \qquad \frac{dC_{\mathrm{C}}}{dx} = 0 \tag{6.178}$$

$$C_{\mathrm{G}} = 0 \qquad \frac{dC_{\mathrm{G}}}{dx} = 0 \tag{6.179}$$

$$D\frac{d^2C_{\mathrm{D}}}{dx^2} = 0 \tag{6.180}$$

$$D\frac{d^2C_{\mathrm{F}}}{dx^2} = 0 \tag{6.181}$$

$$D\frac{d^2C_{\mathrm{H}}}{dx^2} = 0 \tag{6.182}$$

At the diffusion layer–solution boundary (i.e., for $x = \delta$) there is no production of B, C, and G because there is no gradient of these species. We are thus left with the following boundary conditions, which express the consumption of the substrate and the generation of the products $\mathrm{D^E}$, F, and G:

$$-V\frac{dC_{\mathrm{A}}^{b}}{dt} = SD\left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=\delta}$$

in exhaustive electrolysis, and $C_A^b = C^0$ in constant-concentration regimes. In addition,

$$-V\frac{dC_D^b}{dt} = SD\left(\frac{dC_D}{dx}\right)_{x=\delta} \tag{6.183}$$

$$-V\frac{dC_F^b}{dt} = SD\left(\frac{dC_F}{dx}\right)_{x=\delta} \tag{6.184}$$

$$-V\frac{dC_H^b}{dt} = SD\left(\frac{dC_H}{dx}\right)_{x=\delta} \tag{6.185}$$

Addition of equations (6.171), (6.172), and subtraction of equation (6.170) yields

$$D\frac{d^2(C_G + C_H - C_F)}{dx^2} = 0$$

which is valid within and outside [equations (6.179), (6.181), (6.182)] the reaction layer. After integration, while taking account of equation (6.179),

$$\left(\frac{dC_F}{dx}\right)_{x=\delta} = \left(\frac{dC_G}{dx}\right)_{x=\delta}$$

meaning that, as expected, the rates of production of F and G are the same.

Summing equations (6.166) to (6.169), (6.171), and (6.172) leads to

$$D\frac{d^2(C_A + C_B + C_C + C_D + C_G + C_H)}{dx^2} = 0$$

which is valid within and outside [equations (6.176) to (6.180) and (6.182)] the reaction layer. Therefore,

$$D\left[\frac{d(C_A + C_B + C_C + C_D + C_G + C_H)}{dx}\right]_{x=0} = D\left[\frac{d(C_A + C_B + C_C + C_D + C_G + C_H)}{dx}\right]_{x=\delta}$$

and thus, in view of equations (6.162) to (6.164) and (6.177) to (6.179), the first member of the equation above is equal to zero. Therefore,

$$\left[\frac{d(C_D + C_{F\,\mathrm{or}\,H})}{dx}\right]_{x=\delta} = -\left(\frac{dC_A}{dx}\right)_{x=\delta}$$

meaning, after application of equations (6.183) to (6.185) that the production of D and H (or F) amounts to the consumption of A.

Still another linear combination of the reactant, intermediate, and product concentrations leads to

$$D\frac{d^2(2C_{\mathrm{A}} + C_{\mathrm{B}} + C_{\mathrm{C}} + C_{\mathrm{G}})}{dx^2} = 0$$

which is valid within [equations (6.166) to (6.168) and (6.172)] and outside [equations (6.176) to (6.179)] the reaction layer. After integration,

$$\frac{i}{FSD} = -\left(\frac{dC_{\mathrm{B}}}{dx}\right)_{x=0} + \left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=0} + \left(\frac{dC_{\mathrm{G}}}{dx}\right)_{x=0} = 2\left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=\delta}$$

Because the ratio of the reaction layer over the diffusion layer thickness tends toward zero, $(C_{\mathrm{A}})_{x=\mu} \simeq (C_{\mathrm{A}})_{x=0}$, and thus

$$-\left(\frac{dC_{\mathrm{B}}}{dx}\right)_{x=0} + \left(\frac{dC_{\mathrm{C}}}{dx}\right)_{x=0} + \left(\frac{dC_{\mathrm{G}}}{dx}\right)_{x=0} \simeq 2\frac{C_{\mathrm{A}}^{b} - (C_{\mathrm{A}})_{x=0}}{\delta}$$

It also follows that

$$\frac{i}{2FSD} = \left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=\delta} = -\left[\frac{d(C_{\mathrm{D}} + C_{\mathrm{F\,or\,H}})}{dx}\right]_{x=\delta} \tag{6.186}$$

From equations (6.163), (6.170), and (6.181),

$$D\left(\frac{dC_{\mathrm{F}}}{dx}\right)_{x=\delta} = -k_2\int_{x=0}^{x=\delta} C_{\mathrm{C}}dx$$

As in the preceding cases, the following transformations are suggested by search for the minimal number of governing parameters, thanks to the fact that pure kinetic conditions are assumed to hold: $y^* = x\sqrt{k_1/D}$ and of the concentration as

$$b^* = C_{\mathrm{B}}\sqrt{k_1 D}\frac{2FS}{i} \quad c^* = C_{\mathrm{C}}\sqrt{k_1 D}\frac{2FS}{i} \quad g^* = C_{\mathrm{G}}\sqrt{k_1 D}\frac{2FS}{i}$$

with introduction of two competition parameters:

$$p_{HAT}^{ECE} = \frac{k_1}{k_2} \tag{6.187}$$

and

$$p_{HAT}^{DISP} = \frac{k_D}{k_2 k_1^{1/2}} \frac{iD^{1/2}}{2FS} \tag{6.188}$$

We may note in passing (compare equations (6.187) and (6.188) with equation (2.37)) that

$$\frac{p_{HAT}^{DISP}}{p_{HAT}^{ECE}} = p_{ECE}^{DISP}$$

These transformations apply for both the constant-current and constant-potential regimes, noting that in the latter case, $i/2FS = DC^0/\delta$ in the conditions assumed to hold so far where the electrode potential is negative enough for $(C_\mathrm{A})_{x=0} = 0$. Then, equations (6.167), (6.168), and (6.171) become

$$\frac{d^2b^*}{dy^{*2}} - b^* - \frac{p_{HAT}^{DISP}}{p_{HAT}^{ECE}} b^*(c^* + g^*) = 0 \tag{6.189}$$

$$\frac{d^2c^*}{dy^{*2}} + b^* - \frac{p_{HAT}^{DISP}}{p_{HAT}^{ECE}} b^* c^* - \frac{1}{p_{HAT}^{ECE}} c^* = 0 \tag{6.190}$$

$$\frac{d^2g^*}{dy^{*2}} + \frac{1}{p_{HAT}^{ECE}} c^* - \frac{p_{HAT}^{DISP}}{p_{HAT}^{ECE}} b^* g^* = 0 \tag{6.191}$$

with, as boundary conditions,

$$\begin{gathered} (c^*)_{y^*=0} = (g^*)_{y^*=0} = 0 \\ -\left(\frac{db^*}{dy^*}\right)_{y^*=0} + \left(\frac{dc^*}{dy^*}\right)_{y^*=0} + \left(\frac{dg^*}{dy^*}\right)_{y^*=0} = 2 \end{gathered} \tag{6.192}$$

It follows that:

$$\frac{dC_\mathrm{F}^b}{dt} = -\frac{SD}{V}\left(\frac{dC_\mathrm{F}}{dx}\right)_{x=\delta} = \frac{i}{2FS}\frac{S}{V}\frac{1}{p_{HAT}^{ECE}}\int_{y^*=0}^{y^*=\infty} c^* dy^*$$

Combination with equation (6.186), taking equations (6.183) to (6.185) into account leads to

$$\frac{\dfrac{dC_{\mathrm{F\,or\,H}}^b}{dt}}{\dfrac{dC_\mathrm{D}^b}{dt} + \dfrac{dC_{\mathrm{F\,or\,H}}^b}{dt}} = \frac{1}{p_{HAT}^{ECE}} \int_{y^*=0}^{y^*=\infty} c^* dy^* \tag{6.193}$$

In the two constant-concentration regimes, all terms of equation (6.193) are independent of time. Therefore,

$$Y^{\mathrm{F\,or\,H}} = 1 - Y^{\mathrm{D}} = \frac{1}{p_{HAT}^{ECE}} \int_{y^*=0}^{y^*=\infty} c^* dy^* \tag{6.194}$$

In the exhaustive electrolysis regime, following the analysis as developed previously to derive equations (6.121) and (6.122), the yields are obtained by integration of the constant-concentration yields:

$$(Y^{\mathrm{F\,or\,H}})_{ECP} = 1 - (Y^{\mathrm{D}})_{ECP} = \frac{\int_{p_{HAT}^{DISP\blacktriangle}}^{p_{HAT}^{DISP}} (Y^{\mathrm{F\,or\,H}})_{CC}\, d\eta}{p_{HAT}^{DISP} - p_{HAT}^{DISP\blacktriangle}} \tag{6.195}$$

where

$$p_{HAT}^{DISP\blacktriangle} = p_{HAT}^{DISP} \exp\left(-\frac{t}{t_C}\right) \tag{6.196}$$

At the end of the electrolysis $(t/t_C \to \infty)$,

$$Y^{\mathrm{F\,or\,H}} = 1 - Y^{\mathrm{D}} = \frac{1}{p_{HAT}^{DISP}} \int_{0}^{p_{HAT}^{DISP}} (Y^{\mathrm{F\,or\,H}})_{CC}\, d\eta \tag{6.197}$$

Based on these general relationships, we may now examine separately the ECE–HAT and DISP–HAT pathways.

In the *ECE–HAT competition*, $p_{HAT}^{DISP}/p_{HAT}^{ECE} = p_{ECE}^{DISP} \to 0$. Equations (6.189) to (6.191) simplify to

$$\frac{d^2 b^*}{dy^{*2}} - b^* = 0 \tag{6.198}$$

$$\frac{d^2 c^*}{dy^{*2}} + b^* - \frac{1}{p_{HAT}^{ECE}} c^* = 0 \tag{6.199}$$

$$\frac{d^2 g^*}{dy^{*2}} + \frac{1}{p_{HAT}^{ECE}} c^* = 0 \tag{6.200}$$

Addition of equations (6.198) to (6.200), followed by integration, taking into account equations (6.173) to (6.175) leads to

$$\left(\frac{db^*}{dy^*}\right)_{y^*=0} + \left(\frac{dc^*}{dy^*}\right)_{y^*=0} + \left(\frac{dg^*}{dy^*}\right)_{y^*=0} = 0$$

implying after connection with equation (6.192) that

$$\left(\frac{db^*}{dy^*}\right)_{y^*=0} = -1$$

Applying this condition after integration of equation (6.198) leads to $b^* = \exp(-y^*)$, and therefore from integration of equation (6.199),

$$c^* = \frac{p_{HAT}^{ECE}}{1 - p_{HAT}^{ECE}}\left[\exp(-y^*) - \exp\left(-\frac{y^*}{\sqrt{p_{HAT}^{ECE}}}\right)\right]$$

It then follows from equation (6.194) that in the constant-concentration regimes,

$$Y^{\mathrm{F\,or\,H}} = 1 - Y^{\mathrm{D}} = \frac{1}{1 + \sqrt{p_{HAT}^{ECE}}} \qquad (6.201)$$

In the exhaustive electrolysis regime, the same relationship applies as results from the combination of equations (6.195) and (6.201). The resulting variations are represented in Figure 2.38*a*.

In the *DISP–HAT competition*, $p_{HAT}^{DISP}/p_{HAT}^{ECE} = p_{ECE}^{DISP} \to \infty$. An homogeneous steady-state is established for C, resulting in

$$c^* = \frac{p_{HAT}^{ECE} b^*}{1 + p_{HAT}^{DISP} b^*}$$

and

$$\frac{d^2b^*}{dy^{*2}} - 2b^* = 0$$

with

$$\left(\frac{db^*}{dy^*}\right)_{y^*=0} = -2$$

It follows that

$$b^* = \sqrt{2}\exp(-\sqrt{2}y^*)$$

and thus that

$$c^* = \frac{\sqrt{2}p_{HAT}^{ECE}\exp(-\sqrt{2}y^*)}{1 + \sqrt{2}p_{HAT}^{DISP}\exp(-\sqrt{2}y^*)}$$

The yields in the two constant concentration regimes are thus obtained by application of equation (6.194):

$$Y^{\mathrm{F\,or\,H}} = 1 - Y^{\mathrm{D}} = \frac{\ln\left(1 + \sqrt{2}\,p_{HAT}^{DISP}\right)}{\sqrt{2}\,p_{HAT}^{DISP}} \tag{6.202}$$

In the exhaustive electrolysis regime, combination of equations (6.202) and (6.195) leads to

$$\left(Y^{\mathrm{F\,or\,H}}\right)_{ECP} = 1 - \left(Y^{\mathrm{D}}\right)_{ECP} = \frac{\displaystyle\int_{\sqrt{2}p_{HAT}^{DISP\blacktriangle}}^{\sqrt{2}p_{HAT}^{DISP}} \frac{\ln(1+\eta)}{\eta}\,d\eta}{\sqrt{2}\left(p_{HAT}^{DISP} - p_{HAT}^{DISP\blacktriangle}\right)}$$

At the end of the electrolysis $(t/t_C \rightarrow \infty)$,

$$Y^{\mathrm{F\,or\,H}} = 1 - Y^{\mathrm{D}} = \frac{1}{\sqrt{2}p_{HAT}^{DISP}} \int_0^{p\sqrt{2}_{HAT}^{DISP}} \frac{\ln(1+\eta)}{\eta}\,d\eta$$

The resulting variations are represented in Figure 2.38*b*.

6.3. ELECTRON TRANSFER, BOND BREAKING, AND BOND FORMATION

6.3.1. Contribution of the Cleaving Bond Stretching to Internal Reorganization of the First Step of the Stepwise Mechanism

Assuming that the most important contribution to the internal reorganization is the stretching of the cleaving bond, the free energy surfaces for the reactant (G_{RX}) and product $(G_{\mathrm{RX}^{\bullet -}})$ may be written as

$$G_{\mathrm{RX+e^-}} = \lambda_{0,\mathrm{RX+e^-}\leftrightarrow\mathrm{RX}^{\bullet -}} X^2 + D_{\mathrm{RX}}\{1 - \exp[-\beta(y - y_{\mathrm{RX}})]\}^2 \tag{6.203}$$

$$\begin{aligned} G_{\mathrm{RX}^{\bullet -}} = {} & \lambda_{0,\mathrm{RX}\leftrightarrow\mathrm{RX}^{\bullet -}}(1 - X)^2 + D_{\mathrm{RX}^{\bullet -}}\{1 - \exp[-\beta(y - y_{\mathrm{RX}^{\bullet -}})]\}^2 \\ & + \Delta G^0_{\mathrm{RX+e^-}\rightarrow\mathrm{RX}^{\bullet -}} \end{aligned} \tag{6.204}$$

It is also assumed that the repulsive terms in the two Morse curves are approximately the same, leading to an equation that relates the difference in the equilibrium distances to the ratio of the dissociation energies:

$$y_{\mathrm{RX}^{\bullet -}} = y_{\mathrm{RX}} + \frac{1}{2\beta}\ln\frac{D_{\mathrm{RX}}}{D_{\mathrm{RX}^{\bullet -}}} \tag{6.205}$$

Equations (6.203) and (6.204) may then be recast as follows:

$$G_{\mathrm{RX+e^-}} = D_R Y^2 + \lambda_{0,\mathrm{RX+e^-}\leftrightarrow\mathrm{RX^{\bullet-}}} X^2 \tag{6.206}$$

$$G_{\mathrm{RX^{\bullet-}}} = D_{\mathrm{RX}}\left[\left(1-\sqrt{\frac{D_{\mathrm{RX^{\bullet-}}}}{D_{\mathrm{RX}}}}\right)-Y\right]^2 + \lambda_{0,\mathrm{RX+e^-}\to\mathrm{RX^{\bullet-}}}(1-X)^2 + \Delta G^0_{\mathrm{RX+e^-}\to\mathrm{RX^{\bullet-}}} \tag{6.207}$$

with

$$Y = 1 - \exp[-\beta(y - y_{\mathrm{RX}})] \tag{6.208}$$

The activation free energy is then obtained by the usual minimization procedure, thus leading to equation (3.22).

6.3.2. Morse Curve Model of Intramolecular Dissociative Electron Transfer

The classical Morse curve model of intramolecular dissociative electron transfer, leading to equations (3.23) to (3.27), involves the following free energy surfaces for the reactant ($G_{\mathrm{RX^{\bullet-}}}$) and product ($G_{\mathrm{R^{\bullet}+X^-}}$) systems, respectively:

$$G_{\mathrm{RX^{\bullet-}}} = \lambda_{0,\mathrm{RX^{\bullet-}}\leftrightarrow\mathrm{R^{\bullet}+X^-}} X^2 + D_{\mathrm{RX^{\bullet-}}} Y^2 \tag{6.209}$$

$$G_{\mathrm{R^{\bullet}+X^-}} = \lambda_{0,\mathrm{RX^{\bullet-}}\leftrightarrow\mathrm{R^{\bullet}+X^-}}(1-X)^2 + D_{\mathrm{RX^{\bullet-}}}(1-Y)^2 + \Delta G^0_{\mathrm{RX^{\bullet-}}\to\mathrm{R^{\bullet}+X^-}} \tag{6.210}$$

As previously, X is a fictitious charge borne by the X portion of the molecule serving as index for solvent reorganization upon shifting the charge from the R to the X portion of the molecule:

$$Y = 1 - \exp[-\beta(y - y_{\mathrm{RX^{\bullet-}}})]$$

with $\beta = \nu_c(2\pi^2/D_{\mathrm{RX^{\bullet-}}})^{1/2}$ (y: bond length, $y_{\mathrm{RX^{\bullet-}}}$: equilibrium value of y in the anion radical, ν_c: frequency of the cleaving bond, m: reduced mass) is a variable representing the stretching of the cleaving bond. The saddle point on the intersection of the two surfaces leads, exactly as for the Marcus model of outer-sphere electron transfer or for the Morse curve model of extramolecular dissociative electron transfer, to equations (3.23) to (3.27).

Extension of the model to take into account the bond bending effect and the interactions within the product cluster leads to the following modification of equations (6.209) and (6.210), in which the diabatic character of the surfaces is emphasized in the subscript notations:

$$G_{\mathrm{RX}^{\bullet-},dia} = \lambda_{0,\mathrm{RX}^{\bullet-}\leftrightarrow\mathrm{R}+\mathrm{X}^-} X^2 + D_{\mathrm{RX}^{\bullet-}} Y^2 + \frac{f_b}{2}\theta_b^{\,2}$$

$$G_{\mathrm{R}^\bullet+\mathrm{X}^-,dia} = \lambda_{0,\mathrm{RX}^{\bullet-}\leftrightarrow\mathrm{R}^\bullet+\mathrm{X}^-}(1-X)^2 + D_{\mathrm{RX}^{\bullet-}}\left(1-\sqrt{\frac{D_{\mathrm{R}^\bullet,\mathrm{X}^-}}{D_{\mathrm{RX}^{\bullet-}}}}-Y\right)^2 + \frac{f_b}{2}\theta_b^{\,2} + \Delta G^0_{\mathrm{RX}^{\bullet-}\to\mathrm{R}^\bullet+\mathrm{X}^-}$$

where θ_b is the bending angle and f the corresponding force constant. $D_{\mathrm{R}^\bullet,\mathrm{X}^-}$ is a measure of the energy of interaction in the product cluster. Mixing the two diabatic surfaces through the following secular determinant produces the two adiabatic surfaces

$$G_{adia,\pm}\begin{vmatrix} G_{\mathrm{RX}^{\bullet-},dia} - G_{adia,\pm} & H \\ H & G_{\mathrm{R}^\bullet+\mathrm{X}^-,dia} - G_{adia,\pm} \end{vmatrix} = 0$$

with $H = h_0\theta_b$, thus leading to

$$G_{adia,\pm}(X,Y,\theta) = \frac{G_{\mathrm{RX}^{\bullet-},dia} + G_{\mathrm{R}^\bullet+\mathrm{X}^-,dia}}{2} \pm \frac{1}{2}\sqrt{\left(G_{\mathrm{RX}^{\bullet-},dia} - G_{\mathrm{R}^\bullet+\mathrm{X}^-,dia}\right)^2 + 4(h_0\theta_b)^2}$$

The transition state corresponds to

$$\frac{\partial G_{adia,-}}{\partial\theta_b} = 0 \qquad \frac{\partial G_{adia,-}}{\partial X} = 0 \qquad \frac{\partial G_{adia,-}}{\partial Y} = 0$$

It follows that

$$X^{\neq} = \frac{Y^{\neq}}{1-\sqrt{\dfrac{D_{\mathrm{R},\mathrm{X}^-}}{D_{\mathrm{RX}^{\bullet-}}}}} = \frac{1}{2}\left(1 + \frac{\Delta G^0_{\mathrm{RX}^{\bullet-}\to\mathrm{R}^\bullet+\mathrm{X}^-}}{\lambda_{0,\mathrm{RX}^{\bullet-}\leftrightarrow\mathrm{R}^\bullet+\mathrm{X}^-} + D_{\mathrm{R}^\bullet,\mathrm{X}^-}\left(1-\sqrt{\dfrac{D_{\mathrm{R}^\bullet,\mathrm{X}^-}}{D_{\mathrm{RX}^{\bullet-}}}}\right)^2 - \dfrac{2h_0^{\,2}}{f_b}}\right)$$

and

$$\theta^{\neq} = \frac{h_0}{f}\sqrt{1-\left(\frac{\Delta G^0_{\mathrm{RX}^{\bullet-}\rightarrow\mathrm{R}^\bullet+\mathrm{X}^-}}{\lambda_{0,\mathrm{RX}^{\bullet-}\leftrightarrow\mathrm{R}^\bullet+\mathrm{X}^-}+D_{\mathrm{R}^\bullet,\mathrm{X}^-}\left(1-\sqrt{\dfrac{D_{\mathrm{R}^\bullet,\mathrm{X}^-}}{D_{\mathrm{RX}^{\bullet-}}}}\right)^2-\dfrac{2h_0^{\,2}}{f_b}}\right)^2}$$

Finally,

$$G^{\neq}_{adia,\pm} = \Delta G^{\neq}_0\left(1+\frac{\Delta G^0_{\mathrm{Ar}^{\bullet-}\rightarrow\mathrm{Ar}^\bullet+\mathrm{X}^-}}{4\Delta G^{\neq}_0}\right)^2$$

with

$$\Delta G^{\neq}_0 = \frac{\lambda_0+D_{\mathrm{ArX}^{\bullet-}}\left(1-\sqrt{\dfrac{D_{\mathrm{Ar}^\bullet,\mathrm{X}^-}}{D_{\mathrm{ArX}^{\bullet-}}}}\right)^2}{4}-\frac{h_0^{\,2}}{2f_b}$$

thus showing the validity of equation (3.31) as an expression of the intrinsic barrier.

6.4. ANALYSIS OF SUPPORTED MOLECULAR CATALYSIS BY ROTATING DISK ELECTRODE VOLTAMMETRY AND CYCLIC VOLTAMMETRY

6.4.1. Catalysis at Monolayer Electrode Coatings

The sum of the surface concentrations of the two forms of the catalyst Γ_P and Γ_Q is equal to the total catalyst surface concentration, Γ^0. In the case of a Nernstian system,

$$\frac{\Gamma_\mathrm{P}}{\Gamma_\mathrm{Q}} = \exp\left[\frac{F}{\mathcal{R}T}(E-E^0_{\mathrm{P/Q}})\right]$$

and therefore

$$\frac{\Gamma_\mathrm{Q}}{\Gamma^0} = \frac{1}{1+\exp\left[\dfrac{F}{\mathcal{R}T}(E-E^0_{\mathrm{P/Q}})\right]} \tag{6.211}$$

Material balance in the monolayer electrode coating leads to

$$\frac{d\Gamma_\mathrm{Q}}{dt} = \frac{i}{FS} - k\,\Gamma_\mathrm{Q}(C_\mathrm{A})_{x=0} \tag{6.212}$$

Since RDEV experiments entail steady-state conditions, $d\Gamma_{\mathrm{Q}}/dt = 0$, and thus

$$\frac{i}{FS} = k\Gamma_{\mathrm{Q}}(C_{\mathrm{A}})_{x=0} \tag{6.213}$$

Diffusion of A between the bulk of the solution and the electrode coating is expressed as

$$D_{\mathrm{A}}\left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=0} = k\Gamma_{\mathrm{Q}}(C_{\mathrm{A}})_{x=0} \tag{6.214}$$

It follows that

$$D_{\mathrm{A}}\left(\frac{dC_{\mathrm{A}}}{dx}\right)_{x=0} = \frac{D_{\mathrm{A}}C_{\mathrm{A}}^0}{\delta}\left[1 - \frac{(C_{\mathrm{A}})_{x=0}}{C_{\mathrm{A}}^0}\right] = k\Gamma_{\mathrm{Q}}(C_{\mathrm{A}})_{x=0} \tag{6.215}$$

and thus that

$$\frac{(C_{\mathrm{A}})_{x=0}}{C_{\mathrm{A}}^0} = \frac{1}{1 + \dfrac{k\Gamma^0\delta}{D_{\mathrm{A}}}\dfrac{\Gamma_{\mathrm{Q}}}{\Gamma^0}} \tag{6.216}$$

Combination of equations (6.211), (6.213) to (6.215) finally leads to equations (4.1) to (4.3).

We consider now the case where the kinetics of the electrode electron transfer may interfere. Equations (6.213) and (6.214) are still valid and Nernst's law is replaced by equation (4.9). Combination of these three equations leads to equation (4.10), and from it, to equation (4.11).

In cyclic voltammetry, equation (6.212) applies and, in general, $d\,\Gamma_{\mathrm{Q}}/dt \neq 0$. For a Nernstian electrode electron transfer, from equation (6.211),

$$\frac{d\Gamma_{\mathrm{Q}}}{dt} = 0.25\frac{\exp\left[\dfrac{F}{\mathcal{R}T}(E - E_{\mathrm{P/Q}}^0)\right]}{\left\{1 + \exp\left[\dfrac{F}{\mathcal{R}T}(E - E_{\mathrm{P/Q}}^0)\right]\right\}} \tag{6.217}$$

which is the current response of the immobilized catalyst in the absence of substrate. Diffusion of the substrate from the bulk of the solution to the electrode surface is described by the following integral equation:

$$\frac{(C_{\mathrm{A}})_{x=0}}{C_{\mathrm{A}}^0} = 1 - \frac{1}{\sqrt{\pi}}\int_0^{\frac{Fv}{\mathcal{R}T}t} \frac{\dfrac{D_{\mathrm{A}}\left(\dfrac{dC_{\mathrm{A}}}{dx}\right)_{x=0}(\eta)}{C_{\mathrm{A}}^0\sqrt{\dfrac{Fv}{\mathcal{R}T}D_{\mathrm{A}}}}}{\sqrt{\dfrac{Fv}{\mathcal{R}T}t - \eta}}\,d\eta \tag{6.218}$$

The total current, i, may be corrected by subtraction of $d\Gamma_{\mathrm{Q}}/dt$ as given by equation (6.217):

$$\frac{i_{corr}}{FS} = \frac{i}{FS} - \frac{d\Gamma_{\mathrm{Q}}}{dt} = \frac{i}{FS} - 0.25\frac{\exp\left[\frac{F}{\mathcal{R}T}(E - E^{0}_{\mathrm{P/Q}})\right]}{\left\{1 + \exp\left[\frac{F}{\mathcal{R}T}(E - E^{0}_{\mathrm{P/Q}})\right]\right\}}$$

Then

$$\frac{i_{corr}}{FS} = D_{\mathrm{A}}\left(\frac{\partial C_{\mathrm{A}}}{\partial x}\right)_{x=0}$$

and

$$\frac{i_{corr}}{FSC^{0}_{\mathrm{A}}\sqrt{\frac{Fv}{\mathcal{R}T}D_{\mathrm{A}}}} = \frac{k\Gamma^{0}}{\sqrt{\frac{Fv}{\mathcal{R}T}D_{\mathrm{A}}}}\frac{(C_{\mathrm{A}})_{x=0}}{C^{0}_{\mathrm{A}}}\frac{\Gamma_{\mathrm{Q}}}{\Gamma^{0}} \tag{6.219}$$

It follows that

$$\frac{i_{corr}}{FSC^{0}_{\mathrm{A}}\sqrt{\frac{Fv}{\mathcal{R}T}D_{\mathrm{A}}}} = \frac{k\Gamma^{0}}{\sqrt{\frac{Fv}{\mathcal{R}T}D_{\mathrm{A}}}}\frac{1}{1 + \exp\left[\frac{F}{RT}(E - E^{0}_{\mathrm{P/Q}})\right]}\left[1 - \frac{1}{\sqrt{\pi}}\int_{0}^{\frac{Fv}{\mathcal{R}T}t}\frac{\frac{i_{corr}(\eta)}{FSC^{0}_{\mathrm{A}}\sqrt{\frac{Fv}{\mathcal{R}T}D_{\mathrm{A}}}}}{\sqrt{\frac{Fv}{\mathcal{R}T}t - \eta}}d\eta\right]$$

thus leading to equation (4.12).

In the case where the electrode electron transfer kinetics interferes, equation (4.9) replaces Nernst's law, and therefore

$$\frac{i}{FSC^{0}_{\mathrm{A}}\sqrt{\frac{Fv}{\mathcal{R}T}D_{\mathrm{A}}}} = \frac{\Gamma^{0}k_{f}^{het}(E)}{\sqrt{\frac{Fv}{\mathcal{R}T}D_{\mathrm{A}}}}\left\{1 - \frac{\Gamma_{\mathrm{Q}}}{\Gamma^{0}}\left\{1 + \exp\left[\frac{F}{\mathcal{R}T}(E - E^{0}_{\mathrm{P/Q}})\right]\right\}\right\} \tag{6.220}$$

Equation (6.219) is still valid. Its combination with (6.220) thus yields equation (4.15).

6.4.2. Inhibition of Electron Transfer at Partially Blocked Electrodes

As pictured in the top right-hand corner of Figure 4.16, diffusion takes places in two dimensions, denoted x and R, within the constrained diffusion layer, which can be expressed by means of the following set of partial derivative equation and initial and boundary conditions:

$$\frac{\partial^2 C_{\mathrm{A}}}{\partial x^2} + \frac{1}{R}\frac{\partial C_{\mathrm{A}}}{\partial R} + \frac{\partial^2 C_{\mathrm{A}}}{\partial R^2} = 0$$

$x = 2R_0,\ 0 \leq R \leq R_0$: $\quad D_{\mathrm{A}}\dfrac{\partial C_{\mathrm{A}}}{\partial x} = \dfrac{i}{FS}$

$R = 0,\ 0 \leq x \leq 2R_0$: $\quad \dfrac{\partial C_{\mathrm{A}}}{\partial r} = 0$

$R = R_0,\ 0 \leq x \leq 2R_0$: $\quad \dfrac{\partial C_{\mathrm{A}}}{\partial r} = 0$

$x = 0,\ R_a \leq R \leq R_0$: $\quad \dfrac{\partial C_{\mathrm{A}}}{\partial x} = 0$

and for $0 \leq R \leq R_a (= R_0\sqrt{1-\theta})$,

$$D_{\mathrm{A}}\left(\frac{\partial C_{\mathrm{A}}}{\partial x}\right)_{x=0} = k_f(E)\left[(C_{\mathrm{A}})_{x=0}\left\{1 + \exp\left[\frac{F}{\mathcal{R}T}(E - E^0_{\mathrm{P/Q}})\right]\right\} - \exp\left[\frac{F}{\mathcal{R}T}(E - E^0_{\mathrm{P/Q}})\right]\right]$$

and thus

$$\frac{i}{FS} = (1-\theta)k_f(E)\left[(C_{\mathrm{A}})_{x=0}\left\{1+\exp\left[\frac{F}{\mathcal{R}T}(E-E^0_{\mathrm{P/Q}})\right]\right\} - \exp\left[\frac{F}{\mathcal{R}T}\left(E-E^0_{\mathrm{P/Q}}\right)\right]\right] \tag{6.221}$$

An approximate resolution of the system above leads to an equation relating the substrate concentration at the active sites, $(C_{\mathrm{A}})_{x=0}$, to its value at the boundary between the constrained diffusion layer and the linear diffusion layer, $(C_{\mathrm{A}})_{x=2R_0}$:

$$\frac{(C_{\mathrm{A}})_{x=0}}{C^0_{\mathrm{A}}} = \frac{(C_{\mathrm{A}})_{x=2R_0}}{C^0_{\mathrm{A}}} - \frac{0.6R_0}{D_{\mathrm{A}}C^0_{\mathrm{A}}\sqrt{1-\theta}}\frac{i}{FS} \tag{6.222}$$

At the external boundary of the constrained diffusion layer, application of the linear diffusion characteristic equations leads to

$$\frac{(C_{\mathrm{A}})_{x=2R_0}}{C_{\mathrm{A}}^0} = 1 - \frac{1}{\sqrt{\pi}} \int_0^{\frac{Fv}{\mathcal{R}T}t} \frac{D_{\mathrm{A}}\left(\dfrac{\partial C_{\mathrm{A}}}{\partial x}\right)_{x=2R_0}}{C_{\mathrm{A}}^0 \sqrt{\dfrac{Fv}{\mathcal{R}T} D_{\mathrm{A}}} \sqrt{\dfrac{Fv}{\mathcal{R}T}t - \eta}} d\eta$$

$$= 1 - \frac{1}{\sqrt{\pi}} \int_0^{\frac{Fv}{\mathcal{R}T}t} \frac{\dfrac{i}{FS}}{C_{\mathrm{A}}^0 \sqrt{\dfrac{Fv}{\mathcal{R}T} D_{\mathrm{A}}} \sqrt{\dfrac{Fv}{\mathcal{R}T}t - \eta}} d\eta \qquad (6.223)$$

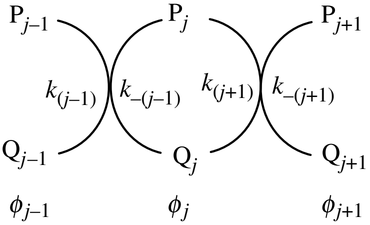
Combining equations (6.221) to (6.223) finally produces equation (4.16).

6.4.3. Equivalent Diffusion and Migration Laws for Electron Hopping Between Fixed Sites

In the monolayer j the two members of the redox couple undergo the electron transfer reactions depicted in Scheme 6.5 with the molecules located in the $j+1$ and $j-1$ layers. The rates of the two electron transfer reactions between two adjacent sites may be written as

$$\frac{dC_{\mathrm{P}_j}}{dt} = -\frac{dC_{\mathrm{Q}_j}}{dt} = -k_{j-1} C_{\mathrm{P}_j} C_{\mathrm{Q}_{j-1}} + k_{-(j-1)} C_{\mathrm{P}_{j-1}} C_{\mathrm{Q}_j}$$

$$+ k_{j+1} C_{\mathrm{P}_{j1+1}} C_{\mathrm{Q}_j} - k_{j+1} C_{\mathrm{P}_j} C_{\mathrm{Q}_{j+1}} \qquad (6.224)$$



The k and the ϕ are the rate constants and electrical potential, respectively.

SCHEME 6.5

The rate constants may be expressed as functions of the self-exchange rate constant, k_0, and the potential difference, linearizing the activation–driving force law and taking a value of 0.5 for the symmetry factor. Thus,

$$k_{j-1} = k_0 \exp\left[\frac{F}{2\mathcal{R}T}(\phi_j - \phi_{j-1})\right] \qquad k_{-(j-1)} = k_0 \exp\left[-\frac{F}{2\mathcal{R}T}(\phi_j - \phi_{j-1})\right]$$

$$k_{(j+1)} = k_0 \exp\left[\frac{F}{2\mathcal{R}T}(\phi_{j+1} - \phi_j)\right] \qquad k_{-(j+1)} = k_0 \exp\left[-\frac{F}{2\mathcal{R}T}(\phi_{j+1} - \phi_j)\right]$$

Since the variation of the electrical potential between two adjacent sites are small, the exponentials can be linearized, leading to

$$k_{j-1} = k_0\left[1 + \frac{F}{2\mathcal{R}T}(\phi_j - \phi_{j-1})\right] \qquad k_{-(j-1)} = k_0\left[1 - \frac{F}{2\mathcal{R}T}(\phi_j - \phi_{j-1})\right]$$

$$k_{j+1} = k_0\left[1 + \frac{F}{2\mathcal{R}T}(\phi_{j+1} - \phi_j)\right] \qquad k_{-(j+1)} = k_0\left[1 - \frac{F}{2\mathcal{R}T}(\phi_{j+1} - \phi_j)\right]$$

Substitution in equation (6.224) thus leads to

$$\begin{aligned}\frac{dC_{\mathrm{P}_j}}{dt} = -\frac{dC_{\mathrm{Q}_j}}{dt} = {} & k_0 C_e\{C_{\mathrm{P}_{j-1}} - 2C_{\mathrm{P}_j} + C_{\mathrm{P}_{j1+1}}\} + k_0\frac{F}{2\mathcal{R}T} \\ & \times [-\{[C_{\mathrm{P}_j}C_{\mathrm{Q}_j} - C_{\mathrm{P}_j}(C_{\mathrm{Q}_j} - C_{\mathrm{Q}_{j-1}})] + [C_{\mathrm{P}_j}C_{\mathrm{Q}_j} - C_{\mathrm{Q}_j}(C_{\mathrm{P}_j} - C_{\mathrm{P}_{j-1}})]\} \\ & \times (\phi_j - \phi_{j-1}) + \{[C_{\mathrm{P}_j}C_{\mathrm{Q}_j} + (C_{\mathrm{P}_{j+1}} - C_{\mathrm{P}_j})C_{\mathrm{Q}_j}] \\ & + [C_{\mathrm{P}_j}C_{\mathrm{Q}_j} + C_{\mathrm{P}_j}(C_{\mathrm{Q}_{j+1}} - C_{\mathrm{Q}_j})]\}(\phi_{j+1} - \phi_j)]\end{aligned}$$

that is,

$$\begin{aligned}\frac{dC_{\mathrm{P}_j}}{dt} = -\frac{dC_{\mathrm{Q}_j}}{dt} = {} & k_0 C_e\{C_{\mathrm{P}_{j-1}} - 2C_{\mathrm{P}_j} + C_{\mathrm{P}_{j1+1}}\} + k_0\frac{F}{\mathcal{R}T}\{C_{\mathrm{P}_j}C_{\mathrm{Q}_j}(\phi_{j+1} \\ & - 2\phi_j + \phi_{j-1}) + [C_{\mathrm{P}_j}(C_{\mathrm{Q}_j} - C_{\mathrm{Q}_{j-1}}) + C_{\mathrm{Q}_j}(C_{\mathrm{P}_j} - C_{\mathrm{P}_{j-1}})](\phi_j - \phi_{j-1}) \\ & + [C_{\mathrm{P}_j}(C_{\mathrm{Q}_{j+1}} - C_{\mathrm{Q}_j}) + C_{\mathrm{Q}_j}(C_{\mathrm{P}_{j+1}} - C_{\mathrm{P}_j})](\phi_{j+1} - \phi_j)\}\end{aligned}$$

Replacement of the finite difference expression by the corresponding differential expression finally leads to equations (4.22) to (4.24).

6.4.4. Catalysis at Multilayered Electrode Coatings

For the simple irreversible reaction, Q + A → P + B, the concentrations of the various species at steady state are solutions of the following set of differential equations and boundary conditions:

$$D_e\frac{d^2C_{\mathrm{P}}}{dx^2} + kC_{\mathrm{A}}C_{\mathrm{Q}} = 0 \qquad (6.225)$$

$$D_e\frac{d^2C_{\mathrm{Q}}}{dx^2} - kC_{\mathrm{A}}C_{\mathrm{Q}} = 0 \qquad (6.226)$$

$$D_{\mathrm{S}}\frac{d^2C_{\mathrm{A}}}{dx^2} - kC_{\mathrm{A}}C_{\mathrm{Q}} = 0 \qquad (6.227)$$

From the combination of equations (6.225) and (6.226), it follows that $C_\mathrm{P} + C_\mathrm{Q} = C_e$ throughout the film.

At the plateau of the first wave,

$$(C_\mathrm{P})_{x=0} = 0 \qquad (C_\mathrm{Q})_{x=0} = C_e \qquad \left(\frac{dC_\mathrm{A}}{dx}\right)_{x=0} = 0$$

and the current is given by

$$\frac{i_{l_1}}{FS} = D_e\left(\frac{dC_\mathrm{P}}{dx}\right)_{x=0} = -D_e\left(\frac{dC_\mathrm{Q}}{dx}\right)_{x=0}$$

At a still more negative potential (for reductions, positive for oxidations), the plateau of the second wave is reached, where the substrate is reduced (or oxidized) directly at the electrode. Then

$$(C_\mathrm{P})_{x=0} = 0 \qquad (C_\mathrm{Q})_{x=0} = C_e \qquad (C_\mathrm{A})_{x=0} = 0$$

and the current is given by

$$\frac{i_{l_1} + i_{l_2}}{FS} = -D_e\left(\frac{dC_\mathrm{Q}}{dx}\right)_{x=0} + D_\mathrm{S}\left(\frac{dC_\mathrm{A}}{dx}\right)_{x=0}$$

At the film–solution interface,

$$\left(\frac{dC_\mathrm{Q}}{dx}\right)_{x=d_f} = 0$$

$$D_\mathrm{S}\left(\frac{dC_\mathrm{A}}{dx}\right)_{x=d_{f-}} = D_\mathrm{A}\left(\frac{dC_\mathrm{A}}{dx}\right)_{x=d_{f+}} = D_\mathrm{A}\frac{C_A^0 - (C_\mathrm{A})_{x=d_{f+}}}{\delta}$$

$$(C_\mathrm{A})_{x=d_{f-}} = \kappa(C_\mathrm{A})_{x=d_{f+}}$$

It is convenient to introduce the following dimensionless variables: $y = x/d_f$, $q = C_\mathrm{Q}/C_e$, and $a = C_\mathrm{A}/\kappa C_\mathrm{A}^0$. Introduction of these changes in variables into equations (6.226) and (6.227) leads to

$$i_e\frac{d^2q}{dy^2} - i_k aq = 0 \tag{6.228}$$

$$i_\mathrm{S}\frac{d^2a}{dy^2} - i_k aq = 0 \tag{6.229}$$

i_e, i_S, and i_k being defined by equations (4.29) to (4.31). The fourth characteristic current, i_A, relative to substrate diffusion in solution (Levich current), is defined as

$$\frac{i_\mathrm{A}}{FS} = \frac{D_\mathrm{A} C_\mathrm{A}^0}{\delta}$$

At the plateau of the first wave,

$$q_{y=0} = 1 \qquad \left(\frac{da}{dy}\right)_{y=0} = 0$$

and the current is given by

$$i_{l_1} = -i_e \left(\frac{dq}{dy}\right)_{y=0}$$

At the plateau of the second wave, $q_{y=0} = 1$, $a_{y=0} = 0$ and the current is given by

$$i_{l_1} + i_{l_2} = -i_e \left(\frac{dq}{dy}\right)_{y=0} + i_\mathrm{S} \left(\frac{da}{dy}\right)_{y=0}$$

At the other boundary,

$$\left(\frac{dq}{dy}\right)_{y=1} = 0 \qquad \left(\frac{da}{dy}\right)_{y=1} = \frac{i_\mathrm{A}}{i_\mathrm{S}} (1 - a_{y=1})$$

Subtraction of equation (6.228) from equation (6.229) after integration and taking the appropriate boundary conditions into account, provides an equation relating a to q:

$$a = 1 - \frac{i_e}{i_\mathrm{S}} \left[q_{y=1} - q - \left(\frac{dq}{dy}\right)_{y=0} \left(1 + \frac{i_\mathrm{S}}{i_\mathrm{A}} - y\right) \right]$$

at the first wave and

$$a = \frac{i_\mathrm{A}}{i_\mathrm{S} + i_\mathrm{A}} \left[1 + \frac{i_e}{i_\mathrm{S}} (1 - q_{y=1}) \right] y - \frac{i_e}{i_\mathrm{S}} (1 - q)$$

at the second wave. After substitution in equation (6.228), one obtains the set of differential equation and boundary conditions given in Table 4.1 under the heading “General Case.”

An alternative formulation is based on a rather than on q. It starts with the expression of q as a function of a and introduction in equation (6.229). After integration, taking into account the appropriate boundary conditions, one obtains, at the first wave, $i_{l1} = i_{\mathrm{A}}(1 - a_{y=1})$, with

$$\frac{d^2a}{dy^2} - \frac{i_k}{i_{\mathrm{S}}}a\left\{1 - \frac{i_{\mathrm{S}}}{i_e}\left[a_{y=0} - a + \frac{i_{\mathrm{A}}}{i_{\mathrm{S}}}(1 - a_{y=1})y\right]\right\} = 0$$

$$\left(\frac{da}{dy}\right)_{y=0} = 0 \qquad 1 - a_{y=1} = \frac{i_{\mathrm{S}}}{i_{\mathrm{A}}}\left(\frac{da}{dy}\right)_{y=1}$$

and at the second wave, $i_{l1} + i_{l2} = i_{\mathrm{A}}(1 - a_{y=1})$, with

$$\frac{d^2q}{dy^2} - \frac{i_k}{i_{\mathrm{S}}}a\left\{\frac{i_{\mathrm{S}}}{i_e}a + 1 - \frac{i_{\mathrm{A}}}{i_e}(1 - a_{y=1})y\right\} = 0$$

$$a_{y=0} = 0 \qquad 1 - a_{y=1} = \frac{i_{\mathrm{S}}}{i_{\mathrm{A}}}\left(\frac{da}{dy}\right)_{y=1}$$

Manipulation of these equations or of those pertaining to the q formulation for various limiting values of the two dimensionless parameters defining the zone diagram allows derivation of the expressions of the plateau currents given in Table 4.1. With the two-step reaction scheme discussed in Section 4.3.6, a similar procedure may be used to obtain the various expressions of the plateau currents given in Table 4.2.

We assumed that the adduct formed between the substrate and the active form of the catalyst obeys the steady-state assumption. Equations (6.225) to (6.227) are thus replaced by

$$D_e\frac{d^2C_{\mathrm{P}}}{dx^2} + \frac{k_1k_2C_{\mathrm{A}}C_{\mathrm{Q}}}{k_{-1} + k_2C_{\mathrm{Q}}} = 0 \qquad (6.230)$$

$$D_e\frac{d^2C_{\mathrm{Q}}}{dx^2} - \frac{k_1k_2C_{\mathrm{A}}C_{\mathrm{Q}}}{k_{-1} + k_2C_{\mathrm{Q}}} = 0 \qquad (6.231)$$

$$D_{\mathrm{S}}\frac{d^2C_{\mathrm{A}}}{dx^2} - \frac{k_1k_2C_{\mathrm{A}}C_{\mathrm{Q}}}{k_{-1} + k_2C_{\mathrm{Q}}} = 0 \qquad (6.232)$$

while boundary conditions and expressions of the plateau currents remain the same. After introduction of the two currents characterizing catalysis

TABLE 6.7. Expressions of the REDV Plateau Currents for the Reaction Scheme in Figure 4.21 in the General Case

In terms of q:

At the first wave, $i_{l1}=-i_e\left(\frac{dq}{dy}\right)_{y=0}$ with

$$\frac{d^2q}{dy^2}-\frac{i_k}{i_e}q\frac{1-\frac{i_e}{i_S}\left[q_{y=1}-q-\left(\frac{dq}{dy}\right)_{y=0}\left(1+\frac{i_S}{i_A}-y\right)\right]}{1+\frac{i_k}{i_{k_1}}q}=0$$

$$q_{y=0}=1,\quad \left(\frac{dq}{dy}\right)_{y=1}=0$$

At the second wave, $i_{l1}+i_{l2}=\frac{i_A}{i_S+i_A}[i_S+i_e(1-q_{y=1})]$ with

$$\frac{d^2q}{dy^2}-\frac{i_k}{i_e}q\frac{\frac{i_A}{i_S+i_A}\left[1+\frac{i_e}{i_S}(1-q_{y=1})\right]y-\frac{i_e}{i_S}(1-q)}{1+\frac{i_k}{i_{k_1}}q}=0$$

$$q_{y=0}=1,\quad \left(\frac{dq}{dy}\right)_{y=1}=0$$

In terms of a:

At the first wave, $i_{l1}=i_A(1-a_{y=1})$ with

$$\frac{d^2a}{dy^2}-\frac{i_k}{i_S}a\frac{1-\frac{i_S}{i_e}\left[a_{y=0}-a+\frac{i_A}{i_S}(1-a_{y=1})y\right]}{1+\frac{i_k}{i_{k_1}}\left\{1-\frac{i_S}{i_e}\left[a_{y=0}-a+\frac{i_A}{i_S}(1-a_{y=1})y\right]\right\}}=0,$$

$$\left(\frac{da}{dy}\right)_{y=0}=0, 1-a_{y=1}=\frac{i_S}{i_A}\left(\frac{da}{dy}\right)_{y=1}$$

At the second wave, $i_{l1}+i_{l2}=i_A(1-a_{y=1})$ with

$$\frac{d^2q}{dy^2}-\frac{i_k}{i_S}a\frac{1+\frac{i_S}{i_e}a-\frac{i_A}{i_e}(1-a_{y=1})y}{1+\frac{i_k}{i_{k_1}}\left\{1+\frac{i_S}{i_e}a-\frac{i_A}{i_e}(1-a_{y=1})y\right\}}=0,$$

$$a_{y=0}=0, 1-a_{y=1}=\frac{i_S}{i_A}\left(\frac{da}{dy}\right)_{y=1}$$

[equations (4.32) and (4.33)], the same procedure as applied earlier allows derivation of the various expressions of the limiting currents gathered in Tables 6.7 and 6.8. The expressions given in Table 4.2 apply for the particular case where $i_k/i_{k_1}\rightarrow 0$.

TABLE 6.8. Expressions of the REDV Plateau Currents for the Reaction Scheme in Figure 4.21: Limiting Cases[a]

<table>
<tr><td></td><td>R
$\frac{1}{i_{l1}} = \frac{1}{i_\mathrm{A}} + \frac{1+\frac{i_k}{i_{k_1}}}{i_k}$ linKL
$\frac{1}{i_{l2}} = \frac{1}{i_\mathrm{A}} + \frac{1}{i_\mathrm{S}}$ linKL</td><td></td></tr>
<tr><td>E+R
$i_{l1} = -i_e\left(\frac{dq}{dy}\right)_{y=0}$ with
$\frac{d^2q}{dy^2} - \frac{i_k}{i_e}q\frac{\left[1+\frac{i_e}{i_\mathrm{A}}\left(\frac{dq}{dy}\right)_{y=0}\right]}{1+\frac{i_k}{i_{k_1}}q} = 0$
$q_{y=0} = 1, \quad \left(\frac{dq}{dy}\right)_{y=1} = 0$
$\frac{1}{i_{l1}+i_{l2}} = \frac{1}{i_\mathrm{A}} + \frac{1}{i_\mathrm{S}}$ linKL</td><td colspan="2">S+R
$\frac{1}{i_{l1}} = \frac{1}{i_\mathrm{A}} + \frac{\sqrt{1+\frac{i_k}{i_{k_1}}}}{\sqrt{i_k i_\mathrm{S}}\tanh\left(\sqrt{\frac{i_k}{i_\mathrm{S}}}\right)}$ linKL
$\frac{1}{i_{l1}+i_{l2}} = \frac{1}{i_\mathrm{A}} + \frac{\sqrt{1+\frac{i_k}{i_{k_1}}}}{\sqrt{i_k i_\mathrm{S}}}\tanh\left(\sqrt{\frac{i_k}{i_\mathrm{S}\left(1+\frac{i_k}{i_{k_1}}\right)}}\right)$ linKL</td></tr>
<tr><td>ER
$\frac{1}{i_{l1}} = \frac{1}{i_\mathrm{A}} + \frac{i_{l1}}{i_k i_e}\frac{\left(\frac{i_k}{i_{k_1}}\right)^2}{2\left[\frac{i_k}{i_{k_1}} - \ln\left(\frac{i_k}{i_{k_1}}\right)\right]}$
$\frac{1}{i_{l1}+i_{l2}} = \frac{1}{i_\mathrm{A}} + \frac{1}{i_\mathrm{S}}$ linKL</td><td rowspan="2"></td><td>SR
$\frac{1}{i_{l1}} = \frac{1}{i_\mathrm{A}} + \frac{\sqrt{1+\frac{i_k}{i_{k_1}}}}{\sqrt{i_k i_\mathrm{S}}}$ linKL
$i_{l2} = 0$</td></tr>
<tr><td>ER+S
$\frac{1}{i_{l1}} = \frac{1}{i_\mathrm{A}} + \frac{i_{l1}}{i_k i_e} + \frac{1}{i_\mathrm{S}}\frac{\left(\frac{i_k}{i_{k_1}}\right)^2}{2\left[\frac{i_k}{i_{k_1}} - \ln\left(\frac{i_k}{i_{k_1}}\right)\right]}$
$\frac{1}{i_{l1}+i_{l2}} = \frac{1}{i_\mathrm{A}} + \frac{1}{i_\mathrm{S}}$ linKL</td><td>SR+E
$\frac{1}{i_{l1}} = \frac{1}{i_\mathrm{A}} + \sqrt{\frac{1+\frac{i_k}{i_{k_1}}\left(1-\frac{i_{l1}}{i_e}\right)}{i_k i_\mathrm{S}\left(1-\frac{i_{l1}}{i_e}\right)}}$
$i_{l2} = 0$</td></tr>
<tr><td>S
$\frac{1}{i_{l1}} = \frac{1}{i_\mathrm{A}} + \frac{1}{i_\mathrm{S}}$ linKL
$i_{l2} = 0$</td><td>S+E
$\frac{1}{i_{l1}} = \frac{i_\mathrm{S}}{i_\mathrm{S}+i_e}\frac{1}{i_\mathrm{A}} + \frac{1}{i_\mathrm{S}+i_e}$ linKL
$i_{l2} = 0$</td><td>E
$i_{l1} = i_e$ linKL
$i_{l2} = 0$</td></tr>
</table>

[a] linKL, linear Koutecky–Levich plots.

6.5. ENZYMATIC CATALYSIS RESPONSES

6.5.1. The Ping-Pong Mechanism in Homogeneous Enzymatic Catalysis

Under the assumption that the reactions in the catalytic cycle are so fast as to make the various forms of the enzyme be at steady state, their concentrations (noted [species]) obey the following equations, obtained by expressing the steady-state conditions for each form of the enzyme:

$$\mathrm{E_1S}: \quad k_{1,1}[\mathrm{S}][\mathrm{E_1}] = (k_{1,-1}+k_{1,2})[\mathrm{E_1S}] \quad \left(\text{i.e, } [\mathrm{E_1}] = \frac{k_{1,-1}+k_{1,2}}{k_{1,1}[\mathrm{S}]}[\mathrm{E_1S}]\right)$$

$$\mathrm{E_2}: \quad k_{1,2}[\mathrm{E_1S}] + k_{2,-1}[\mathrm{E_2Q}] = k_{2,1}[\mathrm{Q}][\mathrm{E_2}] \quad (\text{i.e, } k_{1,2}[\mathrm{E_1S}] = k_{2,2}[\mathrm{E_2Q}])$$

$$\mathrm{E_2Q}: \quad k_{2,1}[\mathrm{Q}][\mathrm{E_2}] = (k_{2,-1}+k_{2,2})[\mathrm{E_2Q}] \quad \left(\text{i.e, } [\mathrm{E_2}] = \frac{k_{2,-1}+k_{2,2}}{k_{2,1}[\mathrm{Q}]}[\mathrm{E_2Q}]\right)$$

leading to:

$$k_{1,2}[\mathrm{E_1S}] = k_{2,2}[\mathrm{E_2Q}] = \frac{C_\mathrm{E}^0}{\dfrac{1}{k_{2,2}} + \dfrac{k_{2,-1}+k_{2,2}}{k_{2,1}k_{2,2}[\mathrm{Q}]} + \dfrac{1}{k_{1,2}}\left\{1 + \dfrac{k_{1,-1}+k_{1,2}}{k_{1,1}[\mathrm{S}]}\right\}}$$

or in terms of the rate constants and Michaelis constants defined in equations (5.1) and (5.2):

$$k_{1,2}[\mathrm{E_1S}] = k_{2,2}[\mathrm{E_2Q}] = \frac{C_\mathrm{E}^0}{\dfrac{1}{k_2[\mathrm{Q}]} + \dfrac{1}{k_{2,2}} + \dfrac{1}{k_{1,2}} + \dfrac{1}{k_1[\mathrm{S}]}}$$

The diffusion-reaction problem is set by the following partial derivative equations accompanied by a set of initial and boundary conditions.
For Q:

$$\frac{\partial[\mathrm{Q}]}{\partial t} = D_\mathrm{P}\frac{\partial^2[\mathrm{Q}]}{\partial x^2} - k_{2,1}[\mathrm{Q}][\mathrm{E_2}] + k_{2,-1}[\mathrm{E_2Q}] = D_\mathrm{P}\frac{\partial^2[\mathrm{Q}]}{\partial x^2} - k_{2,2}[\mathrm{E_2Q}]$$

that is,

$$\frac{\partial[\mathrm{Q}]}{\partial t} = D_\mathrm{P}\frac{\partial^2[\mathrm{Q}]}{\partial x^2} - \frac{C_\mathrm{E}^0}{\dfrac{1}{k_2[\mathrm{Q}]} + \dfrac{1}{k_{2,2}} + \dfrac{1}{k_{1,2}} + \dfrac{1}{k_1[\mathrm{S}]}} \tag{6.233}$$

For S:

$$\frac{\partial[\mathrm{S}]}{\partial t} = D_{\mathrm{S}}\frac{\partial^2[\mathrm{S}]}{\partial x^2} - k_{1,1}[\mathrm{S}][\mathrm{E}_2] + k_{1,-1}[\mathrm{E}_1\mathrm{S}] = D_{\mathrm{S}}\frac{\partial^2[\mathrm{Q}]}{\partial x^2} - k_{1,2}[\mathrm{E}_1\mathrm{S}]$$

that is,

$$\frac{\partial[\mathrm{S}]}{\partial t} = D_{\mathrm{S}}\frac{\partial^2[\mathrm{S}]}{\partial x^2} - \frac{C_{\mathrm{E}}^0}{\dfrac{1}{k_2[\mathrm{Q}]} + \dfrac{1}{k_{2,2}} + \dfrac{1}{k_{1,2}} + \dfrac{1}{k_1[\mathrm{S}]}} \tag{6.234}$$

where D_{S} and D_{P} are the diffusion coefficient of the substrate and cosubstrate, respectively; and

$t = 0,\ x \geq 0$ and $x = \infty,\ t \geq 0$: $\quad [\mathrm{Q}] = 0, \quad [\mathrm{S}] = C_{\mathrm{S}}^0$

$x = 0,\ t \geq 0$: $\quad [\mathrm{Q}] = \dfrac{C_{\mathrm{P}}^0}{1 + \exp\left[\dfrac{F}{\mathcal{R}T}(E - E_{\mathrm{P/Q}}^0)\right]}, \quad \dfrac{\partial[\mathrm{S}]}{\partial x} = 0$

where C_{S}^0 and C_{P}^0 are the bulk concentration of substrate and cosubstrate, respectively; E is the electrode potential; and E_{PQ}^0 is the standard potential of the P/Q couple. Q is assumed here to be produced by a reduction process. Transposition to oxidation is straightforward. The current flowing through the electrode is obtained from

$$i = FSD_{\mathrm{P}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{x=0}$$

The potential is scanned according to equations (1.2).

Assuming that pure kinetic conditions are fulfilled, the Q profile is confined within a thin layer adjacent to the electrode surface. It therefore follows from the condition $(\partial[\mathrm{S}]/\partial x)_{x=0} = 0$ that [S] may be regarded as constant throughout the reaction layer and equal to its value, $[\mathrm{S}]_{x=0}$, at the electrode surface. Within this framework, we consider the case where the catalytic response is controlled by the enzymatic reaction. Equations (6.233) may be simplified upon consideration that $[\mathrm{S}] = C_{\mathrm{S}}^0$ and also from the fact that pure kinetic conditions implies that $\partial[\mathrm{Q}]/\partial t = 0$. It follows that

$$D_{\mathrm{P}}\frac{d^2[\mathrm{Q}]}{dx^2} - \frac{C_{\mathrm{E}}^0}{\dfrac{1}{k_{1,2}} + \dfrac{1}{k_1 C_S^0} + \dfrac{1}{k_{2,2}} + \dfrac{1}{k_2[\mathrm{Q}]}} = 0 \tag{6.235}$$

In addition, at $x = \infty$, not only $[\mathrm{Q}] = 0$, but also, because of the thinness of the reaction layer, $d[\mathrm{Q}]/dx = 0$.

A dimensionless formulation is obtained by means of the following changes of variables and parameters.

$$z = x\sqrt{\frac{k_2 C_E^0}{D_P}} \qquad q = \frac{[Q]}{C_P^0} \qquad \xi = -\frac{F}{\mathcal{R}T}(E - E_{P/Q}^0)$$

$$\sigma = k_2 C_P^0 \left(\frac{1}{k_{2,2}} + \frac{1}{k_{1,2}} + \frac{1}{k_1 C_S^0}\right)$$

Thus,

$$\frac{\partial^2 q}{\partial z^2} - \frac{q}{1+\sigma q} = 0 \tag{6.236}$$

with

$$z = 0: \qquad q = \frac{1}{1+\exp(-\xi)} \tag{6.237}$$

and an additional boundary condition indicating that there exists a point outside the reaction layer where both

$$q = 0 \quad \text{and} \quad \frac{dq}{dz} = 0 \tag{6.238}$$

The dimensionless current and thus the current are obtained from

$$\varphi = \frac{i}{FSC_P^0\sqrt{D_P}\sqrt{k_2 C_E^0}} = -\left(\frac{\partial q}{\partial z}\right)_{z=0}$$

We may now integrate equation (6.236), taking conditions (6.237) and (6.238) into account. It follows that

$$\frac{i}{FSC_P^0\sqrt{D_P}\sqrt{k_2 C_E^0}} = \sqrt{\frac{2}{\sigma}\left[\frac{1}{1+\exp(-\xi)} - \frac{\ln\left(1+\dfrac{\sigma}{1+\exp(-\xi)}\right)}{\sigma}\right]}$$

thus establishing equation (5.3).

Passing now to control by substrate diffusion, a simplification of equation (6.235) and of the expression of the competition parameter σ arises from the fact that the substrate concentration is small:

$$\frac{\partial[\mathrm{Q}]}{\partial t} = D_{\mathrm{P}}\frac{\partial^2[\mathrm{Q}]}{\partial x^2} - \frac{C_{\mathrm{E}}^0}{\dfrac{1}{k_2[\mathrm{Q}]} + \dfrac{1}{k_1[\mathrm{S}]}}$$

$$\sigma = \frac{k_2 C_{\mathrm{P}}^0}{k_1 C_{\mathrm{S}}^0}$$

and thus, equation (6.236) becomes

$$\frac{\partial^2 q}{\partial z^2} - \frac{q}{1 + \sigma\dfrac{q}{s_{z=0}}} = 0$$

with $s = [\mathrm{S}]/C_{\mathrm{P}}^0$. After integration,

$$\varphi^2 = \frac{2(s_{z=0})^2}{\sigma}\left[\frac{q_{z=0}}{s_{z=0}} - \frac{\ln\left(1 + \sigma\dfrac{q_{z=0}}{s_{z=0}}\right)}{\sigma}\right]$$

which, owing to the fact that σ is large, may be further simplified to

$$\frac{\sigma}{2q_{z=0}}\varphi^2 = s_{z=0} \tag{6.239}$$

An expression of $s_{y=0}$ may be derived from the combination of equations (6.233) and (6.234):

$$\frac{\partial([\mathrm{S}] - [\mathrm{Q}])}{\partial t} = \frac{\partial^2(D_{\mathrm{S}}[\mathrm{S}] - D_{\mathrm{P}}[\mathrm{Q}])}{\partial x^2}$$

which can be approximated by

$$\frac{\partial\left([\mathrm{S}] - \dfrac{D_{\mathrm{P}}}{D_{\mathrm{S}}}[\mathrm{Q}]\right)}{\partial t} \approx D_{\mathrm{S}}\frac{\partial^2\left([\mathrm{S}] - \dfrac{D_{\mathrm{P}}}{D_{\mathrm{S}}}[\mathrm{Q}]\right)}{\partial x^2} \tag{6.240}$$

because, since pure kinetic conditions are fulfilled, $\partial[\mathrm{Q}]/\partial t = 0$. In dimensionless terms, introducing $y = x\sqrt{Fv/\mathcal{R}TD_{\mathrm{S}}}$,

$$\frac{\partial\left(s - \dfrac{D_{\mathrm{P}}}{D_{\mathrm{S}}}q\right)}{\partial\tau} = \frac{\partial^2\left(s - \dfrac{D_{\mathrm{P}}}{D_{\mathrm{S}}}q\right)}{\partial y^2}$$

and thus, after integration,

$$s_{y=0} = \gamma\left(1 + \frac{D_\mathrm{P} C_\mathrm{P}^0}{D_\mathrm{S} C_\mathrm{S}^0} q_{y=0} - I\psi\right)$$

with

$$\gamma = \frac{C_\mathrm{S}^0}{C_\mathrm{P}^0} \quad \text{and} \quad \psi = \frac{i}{FS\sqrt{D_\mathrm{S}}C_\mathrm{S}^0\sqrt{\dfrac{Fv}{\mathcal{R}T}}}$$

$$I\psi = \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{\psi d\eta}{\sqrt{\tau - \eta}} = \frac{1}{\sqrt{\pi}}\int_{-\infty}^\xi \frac{\psi d\eta}{\sqrt{\xi - \eta}}$$

$q_{y=0}$ is small compared to 1 because the wave occurs at a more positive potential than the standard potential of the P/Q couple. It follows that $s_{y=0} = \gamma(1 - I\psi)$. Introducing this expression in equation (6.239) or in the following equivalent equation,

$$\frac{\sigma}{2q_{y=0}}\varphi^2 = s_{y=0}$$

leads to

$$\frac{\psi^2}{2\dfrac{D_\mathrm{P}}{D_\mathrm{S}}\dfrac{\mathcal{R}T}{F}\dfrac{k_1 C_\mathrm{E}^0}{v}q_{z=0}} = 1 - I\psi$$

that is,

$$\frac{[1 + \exp(-\xi)]}{2\dfrac{D_\mathrm{P}}{D_\mathrm{S}}\dfrac{\mathcal{R}T}{F}\dfrac{k_1 C_\mathrm{E}^0}{v}q_{z=0}}\psi^2 = 1 - I\psi$$

Introducing a new potential variable,

$$\xi' = \xi + \ln\left(2\frac{D_\mathrm{P}}{D_\mathrm{S}}\frac{\mathcal{R}T}{F}\frac{k_1 C_\mathrm{E}^0}{v}\right) = -\frac{F}{\mathcal{R}T}(E - E') \tag{6.241}$$

with

$$E' = E_{\mathrm{P/Q}}^0 + \frac{\mathcal{R}T}{F}\ln\left(\frac{D_\mathrm{P}}{D_\mathrm{S}}\frac{\mathcal{R}T}{2F}\frac{k_1 C_\mathrm{E}^0}{v}\right) \tag{6.242}$$

Since the kinetic term is large, it follows that the equation of the wave becomes

$$\psi^2 \exp(-\xi') = 1 - I\psi$$

The peak characteristics are thus $\psi_p = 0.609$, $\xi'_p = 0.409$, and $\xi'_p - \xi'_{p/2} = 1.41$, thus establishing equations (5.6) to (5.8).

6.5.2. Catalysis and Inhibition in Homogeneous Systems

Derivation of Equation (5.10) The equation governing the space and time variation of the reduced cosubstrate concentration is written, in the framework of Scheme 5.3,

$$\begin{aligned}\frac{\partial[\mathrm{Q}]}{\partial t} &= D_{\mathrm{P}}\frac{\partial^2[\mathrm{Q}]}{\partial x^2} - (k_{2,1}[\mathrm{Q}][\mathrm{E_1}] - k_{2,-1}[\mathrm{E_1Q}])\\ &\quad - (k_{3,1}[\mathrm{Q}][\mathrm{E_2}] - k_{3,-1}[\mathrm{E_2Q}]) - k_5[\mathrm{Q}][\mathrm{E_3}] \qquad (6.243)\end{aligned}$$

calling for an evaluation of the various forms of the enzyme. These can be expressed as follows under the steady-state assumption, which applies in this range of substrate concentrations:

$$\mathrm{ES}: \quad k_{1,1}[\mathrm{S}][\mathrm{E}] = (k_{1,-1} + k_{1,2})[\mathrm{ES}] \quad \left(\text{i.e., } [\mathrm{E}] = \frac{k_{1,-1} + k_{1,2}}{k_{1,1}[\mathrm{S}]}[\mathrm{ES}]\right.$$

$$\mathrm{E_1}: \quad k_{1,2}[\mathrm{ES}] + k_{2,-1}[\mathrm{E_1Q}] + k_5[\mathrm{Q}][\mathrm{E_3}] = k_{2,1}[\mathrm{Q}][\mathrm{E_1}]$$

$$\left(\text{i.e., } [\mathrm{E_1}] = \frac{k_{2,-1} + k_{2,2}}{k_{2,1}[\mathrm{Q}]}[\mathrm{E_1Q}]\right.$$

$$\mathrm{E_1Q}: \quad k_{2,1}[\mathrm{Q}][\mathrm{E_1}] = (k_{2,-1} + k_{2,2})[\mathrm{E_1Q}]$$

$$(\text{i.e., } k_{1,2}[\mathrm{ES}] + k_5[\mathrm{Q}][\mathrm{E_3}] = k_{2,2}[\mathrm{E_1Q}])$$

$$\mathrm{E_2}: \quad k_{2,2}[\mathrm{E_1Q}] + k_{3,-1}[\mathrm{E_2Q}] = k_{3,1}[\mathrm{Q}][\mathrm{E_2}] + k_4[\mathrm{S}][\mathrm{E_2}]$$

$$(\text{i.e., } k_{2,2}[\mathrm{E_1Q}] = k_{3,2}[\mathrm{E_2Q}] + k_4[\mathrm{S}][\mathrm{E_2}])$$

$$\mathrm{E_2Q}: \quad k_{3,1}[\mathrm{Q}][\mathrm{E_2}] = (k_{3,-1} + k_{3,2})[\mathrm{E_2Q}]$$

$$\left(\text{i.e., } [\mathrm{E_2}] = \frac{k_{3,-1} + k_{3,2}}{k_{3,1}[\mathrm{Q}]}[\mathrm{E_2Q}]\right.$$

$$\mathrm{E_3}: \quad k_4[\mathrm{S}][\mathrm{E_2}] = \{k_5[\mathrm{Q}] + k_6\}[\mathrm{E_3}]$$

It follows that equation (6.243) may be rewritten as

$$\frac{\partial[\mathrm{Q}]}{\partial t} = D_{\mathrm{P}}\frac{\partial^2[\mathrm{Q}]}{\partial x^2} - \left\{2\frac{k_{3,1}k_{3,2}}{k_{3,-1} + k_{3,2}}[\mathrm{Q}][\mathrm{E_2}] + k_5[\mathrm{Q}][\mathrm{E_3}] + k_4[\mathrm{S}][\mathrm{E_2}]\right\}$$

Because the primary catalytic loop is much faster than reactivation of the enzyme through pathway 5, the two last kinetic terms are negligible in front of the first, thus leading to

$$\frac{\partial[\mathrm{Q}]}{\partial t}=D_{\mathrm{P}}\frac{\partial^2[\mathrm{Q}]}{\partial x^2}-\left\{2k_3[\mathrm{Q}]+k_4[\mathrm{S}]\left(1+\frac{k_5[\mathrm{Q}]}{k_5[\mathrm{Q}]+k_6}\right)\right\}[\mathrm{E}_2] \tag{6.244}$$

Introduction of the following dimensionless variables and parameters:

$$e=\frac{[\mathrm{E}]}{C_{\mathrm{E}}^0}\qquad e_1=\frac{[\mathrm{E}_1]}{C_{\mathrm{E}}^0}\qquad e_2=\frac{[\mathrm{E}_2]}{C_{\mathrm{E}}^0}\qquad e_3=\frac{[\mathrm{E}_3]}{C_{\mathrm{E}}^0}$$

$$\tau=\frac{Fv}{\mathcal{R}T}t\qquad y=x\sqrt{\frac{Fv}{\mathcal{R}TD_{\mathrm{P}}}}\qquad q=\frac{[\mathrm{Q}]}{C_P^0}\qquad \lambda=\frac{\mathcal{R}T}{F}\frac{2k_3C_{\mathrm{E}}^0}{v}$$

$$\sigma=k_3C_{\mathrm{P}}^0\left(\frac{1}{k_{3,2}}+\frac{1}{k_{1,2}}+\frac{1}{k_1C_{\mathrm{S}}^0}\right)$$

$$\frac{1}{\chi}=C_{\mathrm{P}}^0\left[\frac{1}{K_{3,\mathrm{M}}}+k_3\left(\frac{1}{k_{1,2}}+\frac{1}{k_1C_{\mathrm{S}}^0}\right)\right]$$

$$\rho_e=\frac{k_4C_{\mathrm{S}}^0}{k_5C_{\mathrm{P}}^0}\quad\text{and}\quad\varepsilon=\frac{k_6}{k_5C_{\mathrm{P}}^0}$$

leads to

$$\frac{\partial q}{\partial\tau}=\frac{\partial^2 q}{\partial y^2}-\lambda q e_2 \tag{6.245}$$

Since reactions E/E_1 and E_2/E jointly govern the kinetics of the primary catalytic loop, $[\mathrm{E}_1]$ and $[\mathrm{E}_1\mathrm{Q}]$ are negligible. The forms remaining into play are thus E, ES, E_2, $\mathrm{E}_2\mathrm{Q}$, and E_3. The following expression of the E_2 concentration follows from the steady-state expression of the concentrations of the various forms of the enzyme, taking into account that $k_3[\mathrm{Q}]\gg k_4[\mathrm{S}]$:

$$e_2=\frac{1}{1+q\left\{\frac{k_{3,1}C_{\mathrm{P}}^0}{k_{3,-1}+k_{3,2}}+k_3C_{\mathrm{P}}^0\left(\frac{1}{k_{1,2}}+\frac{1}{k_1C_{\mathrm{S}}^0}\right)\right\}+\frac{k_4C_{\mathrm{S}}^0}{k_5C_{\mathrm{P}}^0q+k_6}}$$

Thus,

$$e_2=\frac{1}{1+\frac{q}{\chi}+\frac{\rho_e}{q+\varepsilon}}$$

Introduction of this expression into equation (6.245) leads to

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial y^2} - \lambda \frac{\chi q^2}{q^2 + (\chi + \varepsilon)q + \chi(\rho_e + \varepsilon)} + \frac{\varepsilon \chi q}{q^2 + (\chi + \varepsilon)q + \chi(\rho_e + \varepsilon)}$$

Taking into account the fact that a pure kinetic situation prevails, the equation above becomes

$$\frac{\partial^2 q}{\partial y^2} = \lambda \frac{\chi q^2}{q^2 + (\chi + \varepsilon)q + \chi(\rho_e + \varepsilon)} + \frac{\varepsilon \chi q}{q^2 + (\chi + \varepsilon)q + \chi(\rho_e + \varepsilon)}$$

Changing y into $y^* = y\sqrt{\lambda}$ and introducing

$$\varphi = \left(\frac{\partial q}{\partial y^*}\right)_{y^*=0} = \frac{i}{FSC_{\mathrm{P}}^0 \sqrt{D_{\mathrm{P}}} \sqrt{\frac{Fv}{RT}} \sqrt{\lambda}} = \frac{i}{FSC_{\mathrm{P}}^0 \sqrt{D_{\mathrm{P}}} \sqrt{2k_3 C_{\mathrm{E}}^0}}$$

integration of the previous partial derivative equation, according to the same procedure as in Section 2, leads to

$$\varphi = \sqrt{2} \sqrt{\int_0^1 \frac{\chi q^2 dq}{q^2 + (\chi + \varepsilon)q + \chi(\rho_e + \varepsilon)} + \int_0^1 \frac{\varepsilon \chi q dq}{q^2 + (\chi + \varepsilon)q + \chi(\rho_e + \varepsilon)}}$$

$$= \sqrt{2} \sqrt{I_1 + I_2}$$

$\varphi = 1$ corresponds to the maximal plateau current that can be obtained when E_2/E is the rate-determining step of the primary catalytic loop:

$$i_{pl} = FSC_{\mathrm{P}}^0 \sqrt{D_{\mathrm{P}}} \sqrt{2k_3 C_{\mathrm{E}}^0}$$

that is, the plateau current in the absence of inhibition and of Michaelis–Menten saturation. φ thus expresses a normalization of the current vs. this maximal value.

We now proceed to the integration of the foregoing expression of φ, introducing the function $\mathrm{lms}(\chi, \rho_e, \varepsilon)$ defined as follows: If $\Delta = (\chi + \varepsilon)^2 - 4\chi(\rho_e + \varepsilon) < 0$,

$$I_1 = \chi \left\{ 1 - \frac{\chi + \varepsilon}{2} \ln \frac{1 + \chi + \varepsilon + \chi(\rho_e + \varepsilon)}{\chi(\rho_e + \varepsilon)} + \frac{(\chi + \varepsilon)^2 - 2\chi(\rho_e + \varepsilon)}{\sqrt{-\Delta}} \right.$$
$$\left. \times \left[\tan^{-1} \frac{2 + \chi + \varepsilon}{\sqrt{-\Delta}} - \tan^{-1} \frac{\chi + \varepsilon}{\sqrt{-\Delta}} \right] \right\}$$

$$I_2 = \varepsilon\chi\left\{\frac{1}{2}\ln\frac{1+\chi+\varepsilon+\chi(\rho_e+\varepsilon)}{\chi(\rho_e+\varepsilon)} - \frac{\chi+\varepsilon}{\sqrt{-\Delta}}\left[\tan^{-1}\frac{2+\chi+\varepsilon}{\sqrt{-\Delta}} - \tan^{-1}\frac{\chi+\varepsilon}{\sqrt{-\Delta}}\right]\right\}$$

If $\Delta = (\chi+\varepsilon)^2 - 4\chi(\rho_e+\varepsilon) > 0$,

$$\begin{aligned} I_1 = \chi\Bigg[1 &- \frac{\chi+\varepsilon}{2}\ln\frac{1+\chi+\varepsilon+\chi(\rho_e+\varepsilon)}{\chi(\rho+\varepsilon)} \\ &+ \frac{(\chi+\varepsilon)^2 - 2\chi(\rho_e+\varepsilon)}{2\sqrt{\Delta}}\ln\left(\frac{2+\chi+\varepsilon-\sqrt{\Delta}}{2+\chi+\varepsilon+\sqrt{\Delta}}\frac{\chi+\varepsilon+\sqrt{\Delta}}{\chi+\varepsilon-\sqrt{\Delta}}\right)\Bigg] \end{aligned}$$

$$I_2 = \varepsilon\chi\left[\frac{1}{2}\ln\frac{1+\chi+\varepsilon+\chi(\rho_e+\varepsilon)}{\chi(\rho_e+\varepsilon)} - \frac{\chi+\varepsilon}{2\sqrt{\Delta}}\ln\left(\frac{2+\chi+\varepsilon-\sqrt{\Delta}}{2+\chi+\varepsilon+\sqrt{\Delta}}\frac{\chi+\varepsilon+\sqrt{\Delta}}{\chi+\varepsilon-\sqrt{\Delta}}\right)\right]$$

If $\Delta = (\chi+\varepsilon)^2 - 4\chi(\rho_e+\varepsilon) = 0$,

$$I_1 = \chi\left\{1 - (\chi+\varepsilon)\ln\frac{1+\dfrac{\chi+\varepsilon}{2}}{\dfrac{\chi+\varepsilon}{2}} - \frac{(\chi+\varepsilon)^2}{4}\left(\frac{1}{1+\dfrac{\chi+\varepsilon}{2}} - \frac{1}{\dfrac{\chi+\varepsilon}{2}}\right)\right\}$$

$$I_2 = \varepsilon\chi\left\{\ln\frac{1+\dfrac{\chi+\varepsilon}{2}}{\dfrac{\chi+\varepsilon}{2}} + \frac{\chi+\varepsilon}{2}\left(\frac{1}{1+\dfrac{\chi+\varepsilon}{2}} - \frac{1}{\dfrac{\chi+\varepsilon}{2}}\right)\right\}$$

Thus, $\mathrm{lms}(\chi,\rho_e,\varepsilon) = \sqrt{2}\sqrt{I_1+I_2}$, leading to equation (5.10).

Control by Substrate Diffusion At low concentrations of H_2O_2 and when the pure kinetic conditions are fulfilled, the diffusion–reaction equations pertaining to Q and S are written

$$0 = \frac{\partial[\mathrm{Q}]}{\partial t} = D_{\mathrm{P}}\frac{\partial^2[\mathrm{Q}]}{\partial x^2} - 2C_{\mathrm{E}}^0\frac{k_1[\mathrm{S}]k_3[\mathrm{Q}]}{k_1[\mathrm{S}]+k_3[\mathrm{Q}]}$$

$$\frac{\partial[\mathrm{S}]}{\partial t} = D_{\mathrm{S}}\frac{\partial^2[\mathrm{S}]}{\partial x^2} - C_{\mathrm{E}}^0\frac{k_1[\mathrm{S}]k_3[\mathrm{Q}]}{k_1[\mathrm{S}]+k_3[\mathrm{Q}]}$$

Subtracting the first of these equations to the second leads to

$$\frac{\partial\left(2[\mathrm{S}] - \dfrac{D_{\mathrm{P}}}{D_{\mathrm{S}}}[\mathrm{Q}]\right)}{\partial t} = D_{\mathrm{S}}\frac{\partial^2\left(2[\mathrm{S}] - \dfrac{D_{\mathrm{P}}}{D_{\mathrm{S}}}[\mathrm{Q}]\right)}{\partial x^2}$$

with as initial and boundary conditions,

$$t = 0,\ x \geq 0 \text{ and } x = \infty,\ t \geq 0: \qquad [\mathrm{Q}] = 0, \quad [\mathrm{S}] = C_S^0$$

$$x = 0,\ t \geq 0: \qquad [\mathrm{Q}] = \frac{C_P^0}{1 + \exp[(F/\mathcal{R}T)(E - E^0_{\mathrm{P/Q}}]}, \quad \frac{\partial[\mathrm{S}]}{\partial x} = 0$$

The current is given by $i = FSD_{\mathrm{P}}(\partial[\mathrm{Q}]/\partial x)_{x=0}$. In dimensionless terms, after introduction of $s = [\mathrm{S}]/C_P^0$ and of the excess factor $\gamma = C_{\mathrm{S}}^0/C_{\mathrm{P}}^0$, we obtain

$$\frac{\partial\left(2s - \dfrac{D_{\mathrm{P}}}{D_{\mathrm{S}}}q\right)}{\partial \tau} = \frac{D_{\mathrm{P}}}{D_{\mathrm{S}}}\frac{\partial^2\left(2s - \dfrac{D_{\mathrm{P}}}{D_{\mathrm{S}}}q\right)}{\partial y^2}$$

Integration leads to

$$s_{y=0} = \gamma\left(1 + \frac{1}{2}\frac{D_{\mathrm{P}}C_{\mathrm{P}}^0}{D_{\mathrm{S}}C_{\mathrm{S}}^0}q_{y=0} - I\psi'\right)$$

with

$$\psi' = \sqrt{\frac{D_{\mathrm{P}}}{D_{\mathrm{S}}}}\frac{C_{\mathrm{P}}^0}{C_{\mathrm{S}}^0}\frac{\psi}{2} = \frac{i}{2FS\sqrt{D_{\mathrm{S}}}C_{\mathrm{S}}^0\sqrt{\dfrac{Fv}{\mathcal{R}T}}}$$

and

$$I\psi' = \frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi' d\eta}{\sqrt{\tau - \eta}} = \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\xi}\frac{\psi' d\eta}{\sqrt{\xi - \eta}}$$

Since, as seen next, $q_{y=0}$ is small compared to 1 because the wave occurs at a more positive potential than the standard potential of the P/Q couple. It follows that $s_{y=0} \approx \gamma(1 - I\psi')$.

The dimensionless expression of the catalytic current may be recast from Section 6.5.1 as

$$\frac{\sigma^2\psi^2}{2\lambda\left(s_{y=0}\right)^2} = \sigma\frac{q_{y=0}}{s_{y=0}} - \ln\left(1 + \sigma\frac{q_{y=0}}{s_{y=0}}\right)$$

taking into account the fact that because the substrate concentration is small, the expression of the parameter σ simplifies to $\sigma = k_3C_{\mathrm{P}}^0/k_1C_{\mathrm{S}}^0$. Kinetic control by reaction (1) and by the diffusion of the substrate requires large values of σ. It follows that in the expression of the current above, the log term may be neglected, leading to

$$\frac{\sigma\psi^2}{2\lambda q_{y=0}} = s_{y=0} = \gamma[1 - I\psi']$$

and therefore,

$$\frac{\psi'^2[1 + \exp(-\xi)]}{\dfrac{\lambda}{2\gamma\sigma}\dfrac{D_\mathrm{P}}{D_\mathrm{S}}} = [1 - I\psi']$$

Introducing a new potential variable:

$$\xi' = \xi + \ln\left(\frac{D_\mathrm{P}}{D_\mathrm{S}}\frac{\mathcal{R}T}{F}\frac{k_1 C_\mathrm{E}^0}{v}\right) = -\frac{F}{\mathcal{R}T}(E - E')$$

with

$$E' = E^0_{\mathrm{P/Q}} + \frac{\mathcal{R}T}{F}\ln\left(\frac{D_\mathrm{P}}{D_\mathrm{S}}\frac{\mathcal{R}T}{F}\frac{k_1 C_\mathrm{E}^0}{v}\right)$$

It follows since the kinetic term is large that the equation of the wave becomes $\psi'^2 \exp(-\xi') = 1 - I\psi'$, leading to a wave that is under complete control of the substrate diffusion and is shifted toward positive potentials as compared to the standard potential of the P/Q couple. The peak characteristics are $\psi'_p = 0.609$, $\xi'_p = 0.409$, and $\xi'_p - \xi'_{p/2} = 1.41$. Thus,

$$i_p = 2 \times 0.609 FS\sqrt{D_S}C_\mathrm{S}^0\sqrt{\frac{Fv}{\mathcal{R}T}}$$

reflecting a total control by substrate diffusion under the conditions of total catalysis (see Section 2.2.6).

6.5.3. Catalysis at Multilayered Electrode Coatings

For the simple system that contains a single active layer at a distance L from the electrode surface and separated from it by a series of inactivated monolayers, the current is given by the following equation adapted from equation (5.13), in which $[\mathrm{Q}]_{x=0}$ is replaced by $[\mathrm{Q}]_{x=L_-}$ and $[\mathrm{S}]_{x=0}$ by $[\mathrm{S}]_{x=L_-} = C_\mathrm{S}^0$:

$$\frac{2FS\Gamma_\mathrm{E}^0}{i} = \frac{1}{k_1 C_\mathrm{S}^0} + \frac{1}{k_{1,2}} + \frac{1}{k_{2,2}} + \frac{1}{k_2[\mathrm{Q}]_{x=L_-}}$$

From the electrode to the film–solution interface, the following boundary conditions apply:

$$\begin{aligned}\frac{i}{FS} &= D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{x=0} = -D_{\mathrm{Q}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{x=0}\\ &= D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{x=L_-} = -D_{\mathrm{Q}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{x=L_-}\\ &= D_{\mathrm{PQ}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{x=L_+} = -D_{\mathrm{PQ}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{x=L_+}\end{aligned}$$

$$[\mathrm{P}]_{x=L_-} = [\mathrm{P}]_{x=L_+} \quad \text{and} \quad [\mathrm{Q}]_{x=L_-} = [\mathrm{Q}]_{x=L_+}$$

In the solution

$$[\mathrm{P}]_{x=L_+} = C_{\mathrm{P}}^0 - \sqrt{\frac{D_{\mathrm{PQ}}}{\pi}}\int_0^t \left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{x=L_+} \frac{d\eta}{\sqrt{t-\eta}}$$

$$[\mathrm{Q}]_{x=L_+} = -\sqrt{\frac{D_{\mathrm{PQ}}}{\pi}}\int_0^t \left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{x=L_+} \frac{d\eta}{\sqrt{t-\eta}}$$

Thus,

$$[\mathrm{P}]_{x=L_-} + [\mathrm{Q}]_{x=L_-} = [\mathrm{P}]_{x=L_+} + [\mathrm{Q}]_{x=L_+} = C_{\mathrm{P}}^0$$

On the plateau of the wave, $[\mathrm{P}]_{x=0} = 0$, and therefore

$$\frac{[\mathrm{P}]}{C_{\mathrm{P}}^0} = \frac{i}{FSD_{\mathrm{P}}C_{\mathrm{P}}^0}x$$

In particular,

$$\frac{[\mathrm{P}]_{x=L_-}}{C_{\mathrm{P}}^0} = \frac{i}{FSD_{\mathrm{P}}C_{\mathrm{P}}^0}L$$

and

$$\frac{[\mathrm{Q}]_{x=L_-}}{C_{\mathrm{P}}^0} = 1 - \frac{i}{FSD_{\mathrm{P}}C_{\mathrm{P}}^0}L$$

Equations (5.31) to (5.33) ensue.

The diffusion–reaction problem in the more general case occurs in a system containing $n-1$ inactivated enzyme layers adjacent to the electrode surface on top of which $N-n$ active layers have been deposited. Table 6.9 lists the equations that govern the fluxes of the two forms of the cosubstrate in such systems.

Proper combination of the equations in Table 6.9 results in the following

TABLE 6.9. Fluxes Equations in an Enzyme Film Containing $n-1$ Inactive and $N-n$ Active Layers

	x
el: $\frac{i}{FS}=D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{el}=-D_{\mathrm{Q}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{el}, [\mathrm{Q}]_{el}=[\mathrm{P}]_{el}\exp\left[\frac{F}{\mathcal{R}T}(E-E^{0}_{\mathrm{P/Q}})\right]$	0
$\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{-1}=\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{\mathrm{el}}, \left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{-1}=\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{\mathrm{el}}=\cdots$	l_0
1: $\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{+1}=\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{-1}, \left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{+1}=\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{-1}$	l_0+l
$\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{+1}=\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{-n}, \left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{+1}=\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{-n}$	
n: $D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{-n}-D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{+n}=2k_2\Gamma_{\mathrm{E}_2}, [\mathrm{Q}]_n=D_{\mathrm{Q}}\left(\frac{\partial \mathrm{Q}}{\partial x}\right)_{+n}-D_{\mathrm{Q}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{-n}$	$l_0+(n-1)l$
$\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{-(n+1)}=\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{+n}, \left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{-(n+1)}=\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{+n}$	
m − 1: $D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{-(m-1)}-D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{+(m-1)}=D_{\mathrm{Q}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{+(m-1)}-D_{\mathrm{Q}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{-(m-1)}=2k_2\Gamma_{\mathrm{E}_2}[\mathrm{Q}]_{(m-1)}$	$l_0+(m-2)l$
$\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{-m}=\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{+(m-1)}, \left(\frac{\partial \mathrm{Q}}{\partial x}\right)_{-m}=\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{+(m-1)}$	
m: $D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{-m}-D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{+m}=D_{\mathrm{Q}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{+m}-D_{\mathrm{Q}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{-m}=2k_2\Gamma_{\mathrm{E}_2}[\mathrm{Q}]_m$	$l_0+(m-1)l$

flux relationships:

$$D_{\mathrm{PQ}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{fs}+D_{\mathrm{PQ}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{fs}=0$$

$$D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{m\pm}+D_{\mathrm{Q}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{m\pm}=0$$

$$D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{el}+D_{\mathrm{Q}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{el}=0$$

TABLE 6.9. (*Continued*)

	x
$\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{-(m+1)}=\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{+m},\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{-(m+1)}=\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{+m}$	
$m+1$: $D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{-(m+1)}-D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{+(m+1)}=D_{\mathrm{Q}}\left(\frac{\partial \mathrm{Q}}{\partial x}\right)_{+(m+1)}-D_{\mathrm{Q}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{-(m+1)}=2k_2\Gamma_{\mathrm{E}_2}[\mathrm{Q}]_{(m+1)}$	l_0+ml
$N-1$: $D_{\mathrm{PQ}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{-(N-1)}-D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{+(N-1)}=D_{\mathrm{PQ}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{+(N-1)}-D_{\mathrm{Q}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{-(N-1)}=2k_2\Gamma_{\mathrm{E}_2}[\mathrm{Q}]_N$	$l_0+(N-2)l$
$\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{-N}=\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{+(N-1)},\left(\frac{\partial \mathrm{Q}}{\partial x}\right)_{-N}=\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{+(N-1)}$	
N: $D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{-N}-D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{+N}=D_{\mathrm{Q}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{+N}-D_{\mathrm{Q}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{-N}=2k_2\Gamma_{\mathrm{E}_2}[\mathrm{Q}]_N$	$l_0+(N-1)l$
fs: $D\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{fs}=D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{+N},D\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{fs}=D_{\mathrm{P}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{+N}$ $[\mathrm{P}]_N=\kappa_{\mathrm{P}}[\mathrm{P}]_{fs},[\mathrm{Q}]_N=\kappa_{\mathrm{Q}}[\mathrm{Q}]_{fs}$ $[\mathrm{P}]_{fs}=C_{\mathrm{P}}^0-\sqrt{\frac{D}{\pi}}\int_0^t\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{fs},\frac{d\eta}{\sqrt{t-\eta}}[\mathrm{Q}]_{fs}=\sqrt{\frac{D}{\pi}}\int_0^t\left(-\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{fs}\frac{d\eta}{\sqrt{t-\eta}}$	

from which one infers, using the two integral equations, that

$$[\mathrm{P}]_{fs} + [\mathrm{Q}]_{fs} = C^0_{\mathrm{P}} \quad \text{and therefore} \quad [\mathrm{P}]_N + [\mathrm{Q}]_N = C^0_{\mathrm{P}}$$

The second space derivative of the concentration at each enzyme layer may be approximated by the difference between the two gradients on each side of the layer:

$$\frac{\partial^2[\mathrm{P}]}{\partial x^2} = \frac{\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_+ - \left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_-}{l} \qquad \frac{\partial^2[\mathrm{Q}]}{\partial x^2} = \frac{\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_+ - \left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_-}{l}$$

It thus follows from what precedes that

$$\frac{\partial^2 D_{\mathrm{P}}[\mathrm{P}] + D_{\mathrm{Q}}[\mathrm{Q}]}{\partial x^2} = 0$$

and therefore,

$$D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right) + D_{\mathrm{Q}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right) = D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_0 + D_{\mathrm{Q}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_0 = 0$$

$$D_{\mathrm{P}}[\mathrm{P}]_0 + D_{\mathrm{Q}}[\mathrm{Q}]_0 = D_{\mathrm{P}}[\mathrm{P}] + D_{\mathrm{Q}}[\mathrm{Q}] = D_{\mathrm{P}}[\mathrm{P}]_N + D_{\mathrm{Q}}[\mathrm{Q}]_N$$

Within this finite difference framework the following approximations are also valid:

$$\left(\frac{\partial^2[\mathrm{P}]}{\partial x^2}\right)_m = \frac{\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{+m} - \left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{-m}}{l} = \frac{[\mathrm{P}]_{m+1} - 2[\mathrm{P}]_m + [\mathrm{P}]_{m-1}}{l^2}$$

A consequence of the fact that the diffusion layer is much thicker than the enzyme film is that the fluxes in the solution are negligible compared to the fluxes in the film. The two time-dependent integral equations relating the fluxes and the concentrations at the film–solution interface may be thus be replaced by

$$0 = D\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{fs} = D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{N+} \quad \text{and} \quad 0 = D\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{fs} = D_{\mathrm{P}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{N+}$$

which allows the equations pertaining to the enzyme layer N to be simplified as:

$$D_{\mathrm{P}}\left(\frac{\partial[\mathrm{P}]}{\partial x}\right)_{N-}=2k_2\Gamma_{\mathrm{E}_2}\qquad[\mathrm{Q}]_{N-}=-D_{\mathrm{Q}}\left(\frac{\partial[\mathrm{Q}]}{\partial x}\right)_{N-}$$

Γ_{RE} is the surface concentration of the reduced form of the enzyme in each of the active enzyme layers. As seen earlier,

$$\Gamma_{\mathrm{E}_2}=\frac{\Gamma_{\mathrm{E}}^0}{1+k_2[\mathrm{Q}]\left(\dfrac{1}{k_{2,2}}+\dfrac{1}{k_{1,2}}+\dfrac{1}{k_1[\mathrm{S}]}\right)}$$

The exact number and nature of independent factors that the system depends on may be obtained after introduction of the following dimensionless variables and parameters:

$$q=\frac{[\mathrm{Q}]}{C_{\mathrm{P}}^0}\qquad p=\frac{[\mathrm{P}]}{C_{\mathrm{P}}^0}\qquad \lambda=\frac{lk_2\Gamma_{\mathrm{E}}^0}{\delta_{\mathrm{Q}}C_{\mathrm{P}}^0D_{\mathrm{PQ}}}\qquad f_0=\frac{l}{l_0}$$

$$\sigma=k_2C_{\mathrm{P}}^0\left(\frac{1}{k_{2,2}}+\frac{1}{k_{1,2}}+\frac{1}{k_1[\mathrm{S}]}\right)$$

$$\psi=\frac{i}{FS}\frac{l}{C_{\mathrm{P}}^0D}\quad\text{with}\quad\delta_{\mathrm{Q}}=\frac{D_{\mathrm{Q}}}{D_{\mathrm{PQ}}},\qquad\delta_{\mathrm{P}}=\frac{D_{\mathrm{P}}}{D_{\mathrm{PQ}}}$$

The concentrations of Q and P are normalized to the values they would have if the film were exposed to a concentration of Q or P equal to the bulk concentration of cosubstrate, C_{P}^0, taking into account the two partition coefficients, κ_{P} and κ_{Q}. The kinetic parameter λ measures the competition within the enzyme film between diffusion represented by the term $\delta_{\mathrm{Q}}D/l$ and the rate term $k_2\Gamma_{\mathrm{E}}^0$. The current is normalized toward the parameters of the diffusional transport of the cosubstrate in the solution in the solution. The set of equations listed in Table 6.10 ensues.

The system thus obtained involves $N-n+1$ variables, including ψ, related by the same number of equations. Since $N-n$ of these are nonlinear equations because of the σq term, an iteration procedure is needed. One starts from a set of q values obtained for $\sigma=0$. The equations then become linear and the Gauss elimination method may thus be used to obtain these starting q values. In a second round, these values are used in the σq term and a new set of q values are obtained by

TABLE 6.10. Dimensionless Equations

$$q_n - q_{n-1} + f_0\psi = 0$$

$$q_{n+1} - q_n + f_0\psi = \frac{2\lambda q_n}{1 + \sigma q_n}$$

$$q_{n+2} - 2q_{n+1} + q_n = \frac{2\lambda q_{n+1}}{1 + \sigma q_{n+1}}$$

$$q_m - 2q_{m-1} + q_{m-2} = \frac{2\lambda q_{m-1}}{1 + \sigma q_{m-1}}$$

$$q_{m+1} - 2q_m + q_{m-1} = \frac{2\lambda q_m}{1 + \sigma q_m}$$

$$q_{m+2} - 2q_{m+1} + q_m = \frac{2\lambda q_{m+1}}{1 + \sigma q_{m+1}}$$

$$q_N - 2q_{N-1} + q_{N-2} = \frac{2\lambda q_{N-1}}{1 + \sigma q_{N-1}}$$

$$-q_N + q_{N-1} = \frac{2\lambda q_N}{1 + \sigma q_N}$$

$$\frac{\delta_P}{\delta_Q} q_N + (n - 1 + f_0)\psi = \frac{\delta_P}{\delta_Q}$$

means of the Gauss elimination method. The procedure is repeated until the desired accuracy has been reached. The current and the concentration profiles may thus be obtained in this manner. The procedure also applies to the case where the amount of enzyme is not the same in each layer. It suffices to enter each value in the parameter λ and proceed with the calculation in the same way.

Each of these calculations requires inputting four independent parameters: λ, σ, f_0, and δ_P/δ_Q. Thus, if an estimate of l is to be derived from experimental values of the plateau current obtained with known values of the cosubstrate and substrate bulk concentrations, one ought to know from independent sources the three rate constants; the surface concentration of enzyme in each layer; the ratio of the distance between the electrode and the first enzyme layer to the distance between two successive layers, f_0, in case it differs from 1; the diffusion coefficient of the cosubstrate in the solution; D_{PQ}, the ratio of the diffusion coefficients of the active form of the cosubstrate in the film and in the solution; δ_Q; and δ_P.

REFERENCES AND NOTES

1. Bateman, H. *Tables of Integral Transforms*, McGraw-Hill: New York, 1954, Vol. 1, Chaps. IV and V.
2. Subtraction of the self-potential before computing the charging work is equivalent to the more traditional procedure for estimating the Born solvation free energy which involves subtracting the charging work in vacuum from the charging work in the solvent.
3. Bockriss, J. O'M.; Reddy, A. K. N. *Modern Electrochemistry*, Plenum Press: New York, 1970, Vol. 1, Chap. 2.