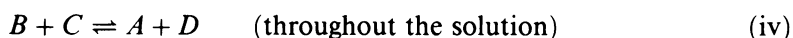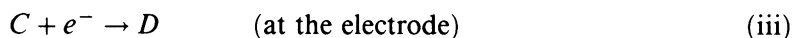# ECE VERSUS DISP ELECTROCHEMICAL COMPETITION*

By

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Abstract. The ECE (Electrochemical, Chemical, Electrochemical) and DISP (DISProportionation) mechanisms describe electrochemical reactions between four species in a diffusive solution. The general set of reactions which encompass both mechanisms is modelled by:

$$A + e^- \to B \qquad \text{(at the electrode)} \qquad \text{(i)}$$

$$B \rightleftharpoons C \qquad \text{(throughout the solution)} \qquad \text{(ii)}$$

$$C + e^- \to D \qquad \text{(at the electrode)} \qquad \text{(iii)}$$

$$B + C \rightleftharpoons A + D \qquad \text{(throughout the solution)} \qquad \text{(iv)}$$

in the case when the applied overpotential is large enough that only the forward steps in (i) and (iii) are present. The ECE mechanism follows the pathway (i), (ii), (iii). The DISP mechanism follows the pathway (i), (ii), (iv). These electrochemical mechanisms play an important role in many organic reactions such as cleavage processes and in inorganic reactions such as the production of forms of technicium used as a radiopharmaceutical. It is important to understand these mechanisms in order to better predict product synthesis and performance. This paper uses asymptotic expansion and perturbation techniques to provide rigorous, relatively simple analytic/numerical solutions for the (linear) ECE mechanism, the (weakly nonlinear) DISP mechanism and a (weakly nonlinear) "competition" mechanism involving all four pathway steps. It is shown that for large dimensionless time, the ECE mechanism evolves to a state with only two species present in order one quantities. Yet, the DISP mechanism retains all four species in order one amounts when step (iv) is reversible. The competition mechanism behaves like the ECE mechanism for small time yet evolves for large time to a form more similar to the DISP mechanism showing that nonlinear effects eventually dominate the mechanistic behavior.

1. Introduction. The ECE and DISP mechanisms are modelled by a coupled set of four reaction diffusion equations. The main difficulty in solving these problems is the nonlinearity and the algebraic complexity that arises from the coupling. Several authors have investigated these mechanisms under heuristic or limiting conditions. Alberts and Shain (1963) solved an ECE problem analytically assuming a diffusion

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limited electrode process ($A = C = 0$ at the surface). Nicholson and Shain (1965) assumed a forward process only in step (ii) ($B \rightarrow C$) and converted the ECE problem into an integral formulation and solved that numerically. Saveant, Andrieux, and Nadjo (1973) assumed a Nernstian electrode process (the ratios A/B and C/D at the surface are fixed constants) and solved that ECE problem analytically. Amatore and Saveant (1977, 1979) assumed a Nernstian electrode process and that the concentration profiles of B and C are independent of time in the DISP problem then solved that numerically using an integral formulation/finite differences. Many authors have used finite difference techniques to solve the ECE and DISP problems. Notable examples are the papers by Hawley and Feldberg (1966), Marcoux, Adams, and Feldberg (1969), Feldberg (1971), and Feldberg and Jeftic (1972). Wilder (1988) solved the full ECE problem (for arbitrary rate constants) analytically. The solution, however, is rather cumbersome in that it requires several pages just to express the answer. It is algebraically infeasible to extend his method to these more complicated problems.

2. Problem formulation. The basic partial differential equations governing the diffusion and chemical reactions (ii) and (iv) are (in dimensional form)

$$
\begin{aligned}
A_{t^*}^* &= d^* A_{x^*x^*}^* + k_7^* C^* B^* - k_8^* A^* D^* \\
B_{t^*}^* &= d^* B_{x^*x^*}^* - k_3^* B^* + k_4^* C^* - k_7^* C^* B^* + k_8^* A^* D^* \\
C_{t^*}^* &= d^* C_{x^*x^*}^* + k_3^* B^* - k_4^* C^* - k_7^* C^* B^* + k_8^* A^* D^* \\
D_{t^*}^* &= d^* D_{x^*x^*}^* + k_7^* C^* B^* - k_8^* A^* D^*
\end{aligned}
\tag{1}
$$

where A^*, B^*, C^*, and D^* are the species concentrations (defined in units of moles/cm^3), d^* is the diffusion coefficient (defined in units of cm^2/sec) assumed the same for each species, k_7^* and k_8^* are the nonlinear rate constants (defined in units of cm^3/(sec·mole)) and k_3^* and k_4^* are the linear rate constants (defined in units of 1/sec). The boundary conditions given by (i) and (iii) and the assumption that the electrode processes follow the Eyring condition are (for a semi-infinite solution)

$$
\begin{aligned}
d^* A_{x^*}^*(0, t^*) &= k_1^* A^*(0, t^*) \\
B_{x^*}^*(0, t^*) &= -A_{x^*}^*(0, t^*) \\
d^* C_{x^*}^*(0, t^*) &= k_5^* C(0, t^*) \\
D_{x^*}^*(0, t^*) &= -C_{x^*}^*(0, t^*)
\end{aligned}
\tag{2}
$$

where k_1^* and k_5^* are the heterogeneous (surface) rate constants (defined in units of cm/sec). The initial conditions are taken to be

$$
\begin{aligned}
A^*(x^*, 0) &= A_0^* \qquad (A_0^* \text{ constant}) \\
B^*(x^*, 0) &= C^*(x^*, 0) = D^*(x^*, 0) = 0.
\end{aligned}
\tag{3}
$$

This problem can be put in nondimensional form by rescaling according to the mass density A_0^*, the length d^*/k^* and the time d^*/k^{*2} where $k^* = \max\{k_1^*, k_5^*\}$. Substituting

$$
\begin{aligned}
A = A^*/A_0^*, \qquad B = B^*/A_0^*, \qquad C &= C^*/A_0^*, \qquad D = D^*/A_0^* \\
k_1 = k_1^*/k^*, \qquad k_5 &= k_5^*/k^* \\
k_3 = k_3^* d^*/k^{*2}, \qquad k_4 &= k_4^* d^*/k^{*2} \\
k_7 = k_7^* A_0^* d^*/k^{*2}, \qquad k_8 &= k_8^* A_0^* d^*/k^{*2}
\end{aligned}
$$

into Eqs. (1), (2), and (3) gives the nondimensional form

$$A_t = A_{xx} + k_7 CB - k_8 AD$$
$$B_t = B_{xx} - k_3 B + k_4 C - k_7 CB + k_8 AD$$
$$C_t = C_{xx} + k_3 B - k_4 C - k_7 CB + k_8 AD \tag{4}$$
$$D_t = D_{xx} + k_7 CB - k_8 AD$$

with the boundary conditions

$$A_x(0,t) = k_1 A(0,t)$$
$$B_x(0,t) = -A_x(0,t)$$
$$C_x(0,t) = k_5 C(0,t) \tag{5}$$
$$D_x(0,t) = -C_x(0,t)$$

and the initial conditions

$$A(x,0) = 1$$
$$B(x,0) = C(x,0) = D(x,0) = 0. \tag{6}$$

Note that by defining $S = A + B + C + D$ to be the total amount of solution present as a function of x and t, Eqs. (4), (5), and (6) imply

$$S_t = S_{xx}$$

with

$$S_x(0,t) = 0$$

and

$$S(x,0) = 1.$$

This problem has the unique solution $S(x,t) = 1$ which is to be expected based on physical arguments since the system is conservative. Therefore, the partial differential equation and boundary and initial conditions for the production of D may be replaced by the relation

$$D = 1 - A - B - C.$$

In both the ECE and the DISP mechanisms, k_3 and k_4 are assumed to be order 1. For the sake of computational simplicity k_3 and k_4 are taken to be 1 in this paper. In the ECE mechanism, k_7 and k_8 are zero. In the weakly nonlinear DISP mechanism, k_7 and k_8 are both considered small; k_7 is, by definition, the small nondimensional parameter ε and $k_8 = \gamma \varepsilon$ ($\gamma \geq 0$). In both the ECE and DISP mechanisns, k_1 is an order 1 constant (often equal to 1 by definition). For simplicity, k_1 is taken to be 1 in this paper. In the ECE mechanisms $k_5 = \delta$, an order one parameter. In the DISP mechanism, $k_5 = 0$. The extension for arbitrary rate constants (of the same order) is straightforward.

3. Justification of the weakly nonlinear approximation. The small nondimensional parameter in this problem is ε which represents the size of the nonlinear rate constants. By definition,

$$\varepsilon = k_7 = k_7^* A_0^* d^* / k^{*2}.$$

Typically, $A_0^* \sim O(10^{-6})$ mole/cm^3 and $d^* \sim O(10^{-5})$ cm^2/sec. k^* and k_7^* are quite variable but typically $k^* \sim O(1)$ to $O(10^{+2})$ cm/sec or larger and $k_7^* \sim O(10^{-5})$ to $O(10^{+5})$ cm^3/(sec·mole). This implies $\varepsilon \sim O(10^{-6})$ or smaller in most laboratory situations. Thus, the weakly nonlinear approximation is a physically realistic assumption.

4. ECE mechanism. The basic equations of the ECE mechanism to be considered are

$$
\begin{aligned}
A_t &= A_{xx} \\
B_t &= B_{xx} - B + C \\
C_t &= C_{xx} + B - C \\
D &= 1 - A - B - C
\end{aligned}
\tag{7}
$$

with

$$
\begin{aligned}
A_x(0, t) &= A(0, t) \\
B_x(0, t) &= -A_x(0, t) \\
C_x(0, t) &= \delta C(0, t)
\end{aligned}
\tag{8}
$$

and

$$
\begin{aligned}
A(x, 0) &= 1 \\
B(x, 0) &= C(x, 0) = 0.
\end{aligned}
\tag{9}
$$

This is a set of linear equations which can be solved (first for A and then for the coupled B and C) by Laplace transforms. The solutions are rather messy. However, the inversion integrals can be evaluated asymptotically for large time to give the much simpler expressions (where $W = B + C$ and $Y = B - C$):

$$A \underset{\substack{t \text{ large} \\ \xi = x/t^{1/2}}}{\sim} \frac{1}{\sqrt{\pi}} \int_0^{\xi} e^{-\lambda^2/4} \, d\lambda + \frac{e^{-\xi^2/4}}{\sqrt{\pi t}}$$

$$W \underset{\substack{t \text{ large} \\ \xi = x/t^{1/2}}}{\sim} \sqrt{\frac{2}{\pi t}} \left(1 + \frac{\sqrt{2}}{\delta}\right) e^{-\xi^2/4}
\tag{10}$$

$$Y \underset{t \text{ large}}{\sim} \sqrt{\frac{2}{\pi t}} e^{-\sqrt{2}x}$$

$$D = 1 - A - W.$$

An equivalent though less obvious derivation is obtained by noting from physical arguments that as t tends to infinity, A and C tend to zero at $x = 0$ since both are destroyed at the electrode and only replaced through diffusion far from the electrode. This means that the boundary conditions (8) can be written in a perturbation expansion which yields the coupled system of solutions (10) directly.

Equation (10) shows that as t tends to infinity for fixed x, the ECE mechanism produces a solution with only the D species present. As t tends to infinity and x tends to infinity along similarity curves with $x/t^{1/2}$ constant, the ECE mechanism produces a solution with species A and D present in order 1 quantities. A plot of the leading order terms for A and D is given in Fig. 1.
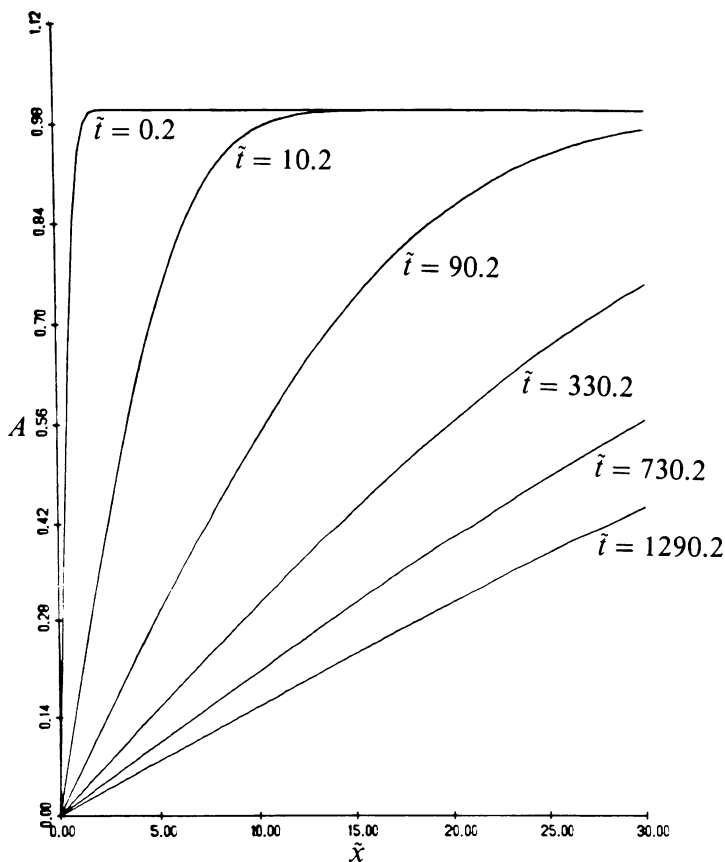

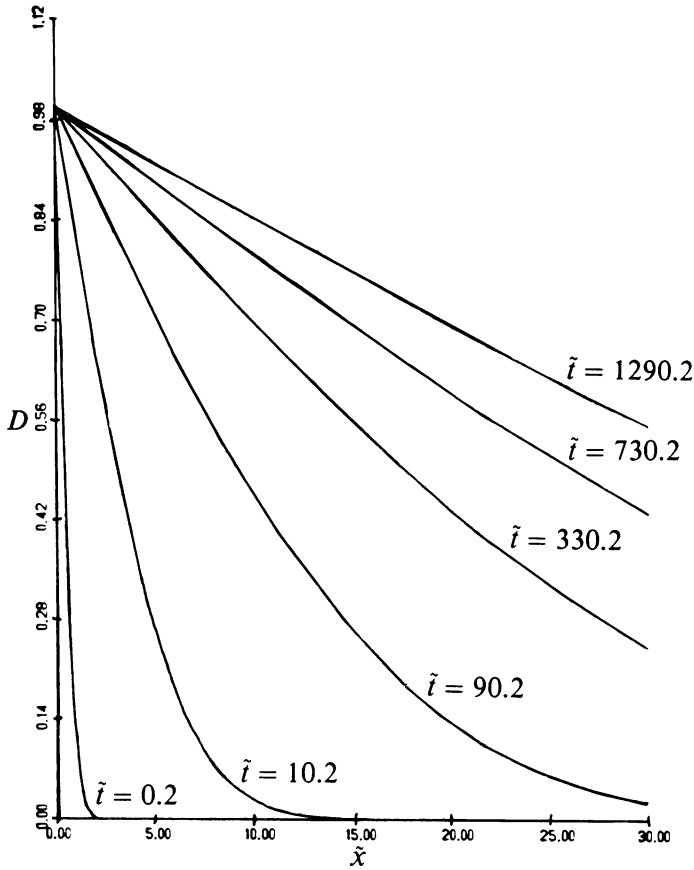FIG. 1a. Concentration profile of species A for ECE mechanism.

FIG. 1b. Concentration profile of species D for ECE mechanism.

5. DISP mechanism. The basic equations of the weakly nonlinear DISP mechanism to be considered are

$$
\begin{aligned}
A_t &= A_{xx} + \varepsilon BC - \varepsilon\gamma AD \\
B_t &= B_{xx} - B + C - \varepsilon BC + \varepsilon\gamma AD \\
C_t &= C_{xx} + B - C - \varepsilon BC + \varepsilon\gamma AD \\
D_t &= D_{xx} + \varepsilon BC - \varepsilon\gamma AD
\end{aligned}
\tag{11}
$$

with

$$
\begin{aligned}
A_x(0,t) &= A(0,t) \\
B_x(0,t) &= -A_x(0,t) \\
C_x(0,t) &= D_x(0,t) = 0
\end{aligned}
\tag{12}
$$

and

$$
\begin{aligned}
A(x,0) &= 1 \\
B(x,0) &= C(x,0) = D(x,0) = 0.
\end{aligned}
\tag{13}
$$

For time not too large, the solution can be written in terms of the regular perturbation expansion

$$A(x, t; \varepsilon) = A_0(x, t) + \varepsilon A_1(x, t) + \cdots$$
$$B(x, t; \varepsilon) = B_0(x, t) + \varepsilon B_1(x, t) + \cdots$$
$$C(x, t; \varepsilon) = C_0(x, t) + \varepsilon C_1(x, t) + \cdots \qquad (14)$$
$$D(x, t; \varepsilon) = D_0(x, t) + \varepsilon D_1(x, t) + \cdots .$$

The leading order terms satisfy the linear equations

$$A_{0_t} = A_{0_{xx}}$$
$$B_{0_t} = B_{0_{xx}} - B_0 + C_0$$
$$C_{0_t} = C_{0_{xx}} + B_0 - C_0 \qquad (15)$$
$$D_{0_t} = D_{0_{xx}}$$

with the boundary conditions

$$A_{0_x}(0, t) = A_0(0, t)$$
$$B_{0_x}(0, t) = -A_{0_x}(0, t) \qquad (16)$$
$$C_{0_x}(0, t) = D_{0_x}(0, t) = 0$$

and initial conditions

$$A_0(x, 0) = 1$$
$$B_0(x, 0) = C_0(x, 0) = D_0(x, 0) = 0. \qquad (17)$$

As in the ECE mechanism these equations have a rather complicated Laplace transform solution. The asymptotic solution of these equations (for $W_0 = B_0 + C_0$ and $Y_0 = B_0 - C_0$) which is valid for time large but not too large (where this statement will be made more precise later) is

$$A_0 \underset{\substack{t \text{ large} \\ \xi = x/t^{1/2}}}{\sim} \frac{1}{\sqrt{\pi}} \int_0^{\xi} e^{-\lambda^2/4} \, d\lambda + \frac{e^{-\xi^2/4}}{\sqrt{\pi t}} + \cdots$$

$$W_0 \underset{\substack{t \text{ large} \\ \xi = x/t^{1/2}}}{\sim} \frac{1}{\sqrt{\pi}} \int_{\xi}^{\infty} e^{-\lambda^2/4} \, d\lambda + \cdots \qquad (18)$$

$$Y_0 \underset{t \text{ large}}{\sim} \frac{1}{\sqrt{2\pi t}} e^{-\sqrt{2}x} + \cdots .$$

$$D_0 \equiv 0.$$

As in the ECE mechanism, an equivalent derivation can be obtained by writing the boundary conditions (16) in perturbation form and solving for the coupled system of solutions (18) directly.

The first correction terms satisfy the nonhomogeneous equations

$$A_{1_t} = A_{1_{xx}} + B_0 C_0$$
$$B_{1_t} = B_{1_{xx}} - B_1 + C_1 - B_0 C_0$$
$$C_{1_t} = C_{1_{xx}} + B_1 - C_1 - B_0 C_0 \qquad (19)$$
$$A_1 + B_1 + C_1 + D_1 = 0$$

with boundary conditions

$$A_{1_x}(0, t) = A_1(0, t)$$
$$B_{1_x}(0, t) = -A_{1_x}(0, t) \tag{20}$$
$$C_{1_x}(0, t) = 0$$

and initial conditions

$$A_1(x, 0) = B_1(x, 0) = C_1(x, 0) = 0. \tag{21}$$

This is a linear problem and so, in theory, the solution can be constructed for all time using Laplace transforms. However, the full expression for $B_0 C_0$ (which is valid for small time) gives rise to a sufficiently messy nonhomogeneous term so as to frustrate such an attempt. The asymptotic form of the solution for $B_0 C_0$ can be used to construct the large time solutions relatively simply as follows. Noting that

$$B_0 C_0 = \frac{W_0^2 - Y_0^2}{4} \underset{t \text{ large}}{\sim} \frac{W_0^2}{4} \tag{22}$$

and substituting $W_1 = B_1 + C_1$ and $Y_1 = B_1 - C_1$ into Eqs. (19) gives the asymptotic set

$$A_{1_t} = A_{1_{xx}} + \frac{1}{4\pi} \left(\int_\xi^\infty e^{-\lambda^2/4} \, d\lambda \right)^2$$

$$W_{1_t} = W_{1_{xx}} - \frac{1}{2\pi} \left(\int_\xi^\infty e^{-\lambda^2/4} \, d\lambda \right)^2 \tag{23}$$

$$Y_{1_t} = Y_{1_{xx}} - 2Y_1$$

$$A_1 + W_1 + D_1 = 0.$$

For t large

$$A_1 \underset{\substack{t \text{ large} \\ \xi = x/t^{1/2}}}{\sim} t f(\xi) + t^{1/2} f_1(\xi) + \cdots$$

where

$$f''(\xi) + \frac{\xi}{2} f'(\xi) - f(\xi) = -\frac{1}{4\pi} \left(\int_\xi^\infty e^{-\lambda^2/4} \, d\lambda \right)^2.$$

The boundary condition $A_{1_x}(0, t) = A_1(0, t)$ implies $f(0) = 0$ since $A_{1_x}(0, t) = t^{1/2} f'(0) + \cdots$ cannot equal the term $A_1(0, t) = t f(0) + t^{1/2} f_1(0) + \cdots$ unless $f(0) = 0$. Then the boundary condition is satisfied through the lower order terms in the expansion for A_1. The initial condition $A_1(x, 0) = 0$ is incorporated into the large time solution by requiring $f(\xi)$ to tend to zero as ξ tends to infinity since, for any fixed time, the solution must tend to the initial condition for x large enough. The problem for f is well-defined. The numerical solution is given in Fig. 2a.

Similarly W_1 has a solution of the form

$$W_1 \underset{\substack{t \text{ large} \\ \xi = x/t^{1/2}}}{\sim} t g(\xi) + \cdots$$

where

$$g''(\xi) + \frac{\xi}{2} g'(\xi) - g(\xi) = \frac{1}{2\pi} \left(\int_\xi^\infty e^{-\lambda^2/4} \, d\lambda \right)^2.$$
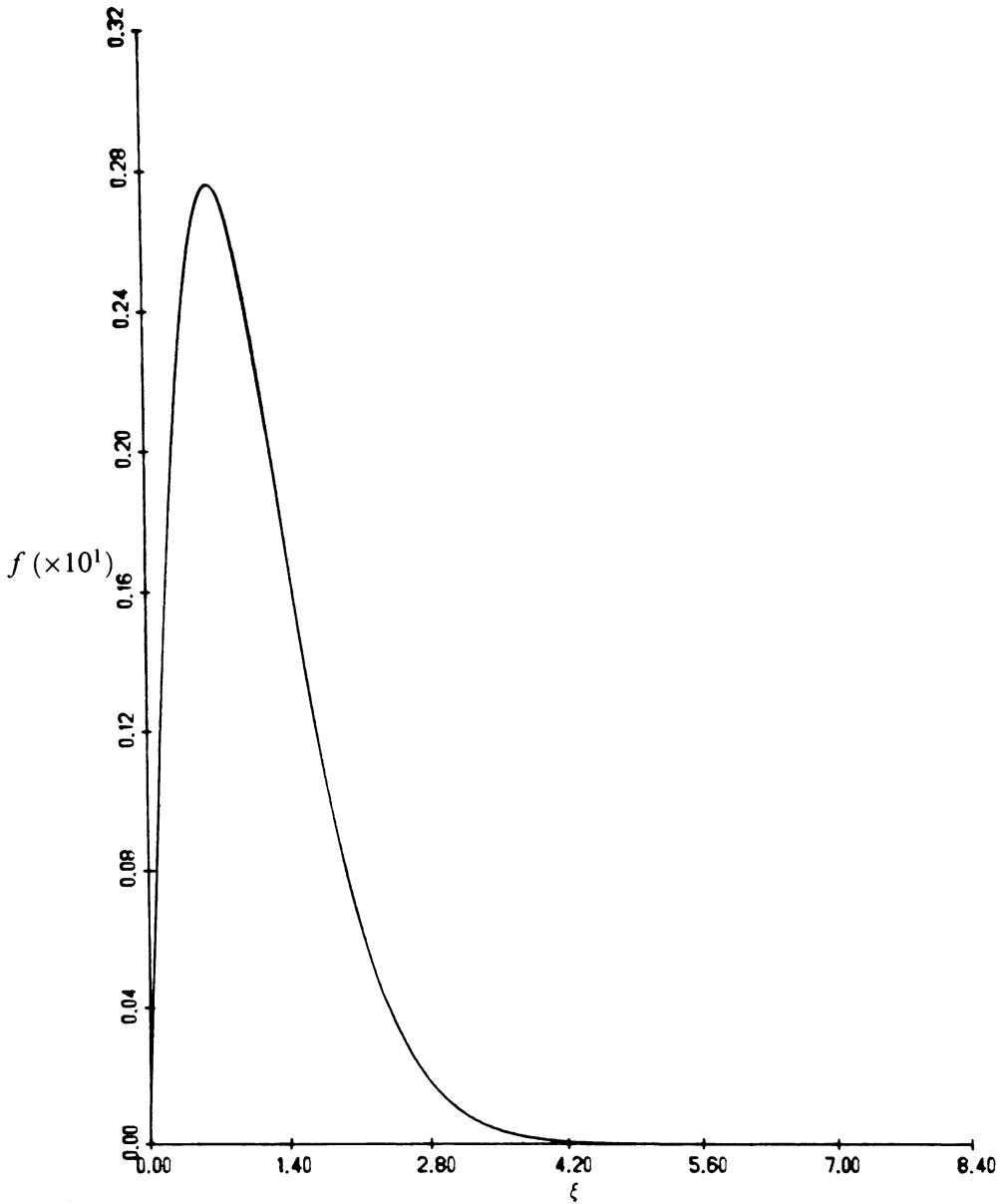
FIG. 2a. Plot of $f(\xi)$ for $A_1 \sim t f(\xi) + \cdots$ in DISP mechanism.

The boundary condition $W_{1_x}(0, t) = -A_{1_x}(0, t)$ implies $g'(0) = -f'(0)$. The initial condition (again recovered as x tends to infinity for fixed t) implies $g(\xi)$ tends to zero as ξ tends to infinity. The problem for g is also well-defined. The numerical solution is given in Fig. 2b.
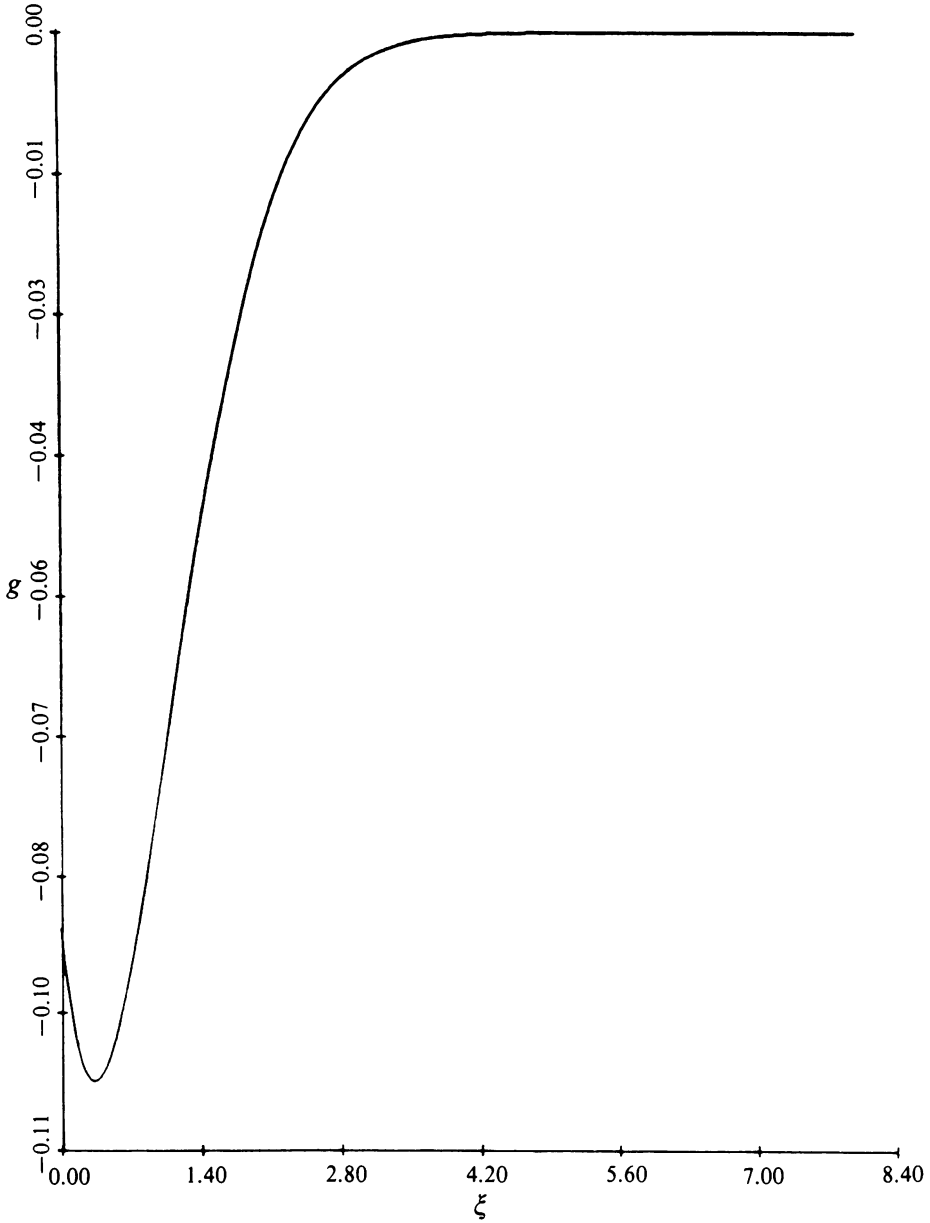
FIG. 2b. Plot of $g(\xi)$ for $W_1 \sim t g(\xi) + \cdots$ in DISP mechanism.

Equation (23) and the boundary conditions $Y_{1_x}(0, t) = -A_{1_x}(0, t) = -t^{1/2} f'(0) + \cdots$ and $Y_1 \to 0$ as $x \to \infty$ implies

$$Y_1 \underset{t \text{ large}}{\sim} \frac{t^{1/2}}{\sqrt{2}} f'(0) e^{-\sqrt{2} x} + \cdots .$$

The regular perturbation expansion breaks down (in the sense that the first order term is the same size as the leading order term) for A, W, and Y when $t \sim O(1/\varepsilon)$. Thus, the regular perturbation solution is valid for $t \sim o(1/\varepsilon)$ and the large time
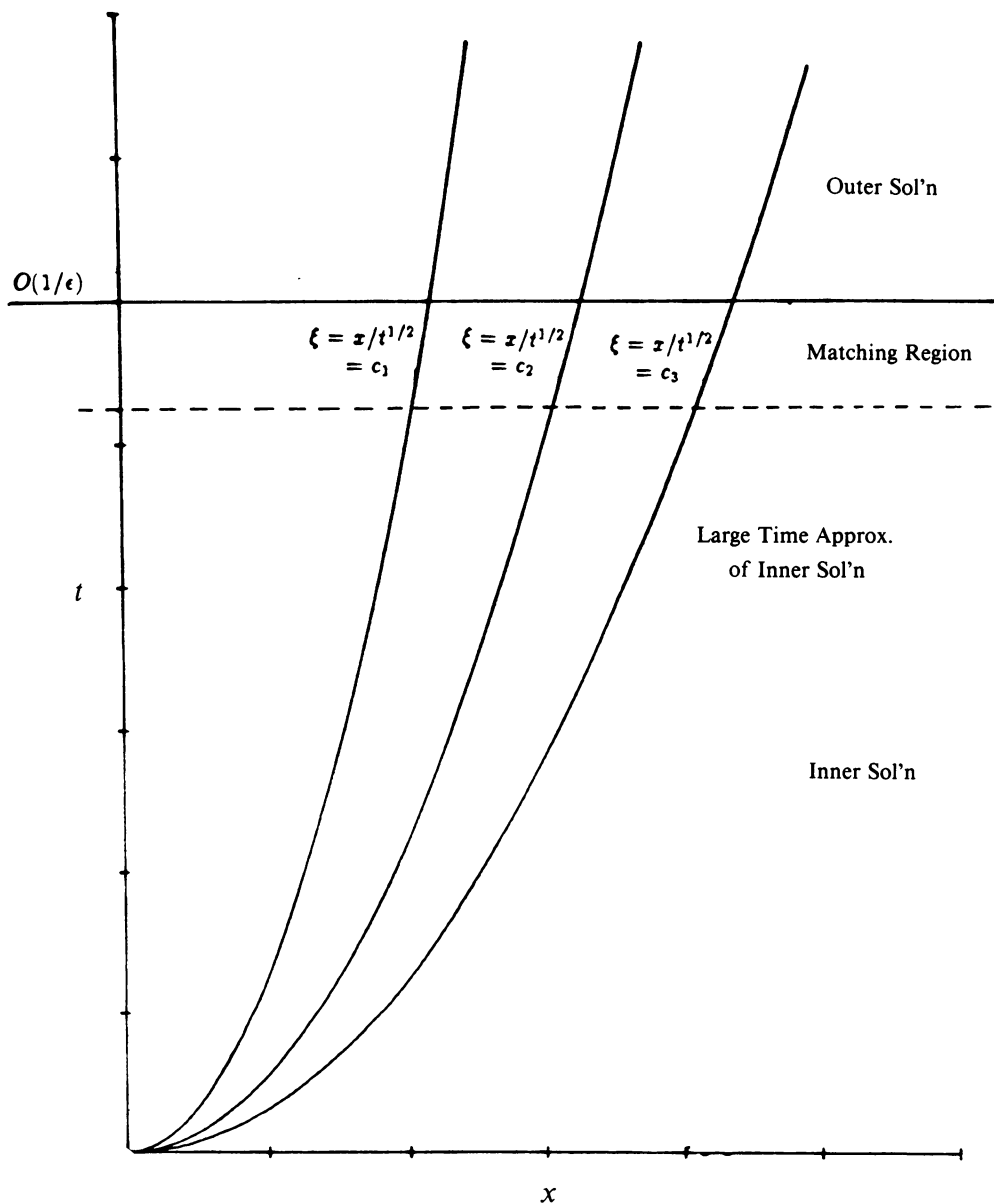
FIG. 3. Regions of validity for the DISP solutions.

approximation for the regular perturbation expansion is valid for $t \gg 1$ but still much smaller than $O(1/\varepsilon)$. A large time solution (valid for t extending to infinity) is given next. The regions of validity for the regular perturbation solution, the matching region and the large time outer solution are shown in Fig. 3.

The breakdown of the regular perturbation theory implies the nonlinear chemical reaction terms are of the same size as the diffusive terms when $t \sim O(1/\varepsilon)$. The large time (outer) solution is constructed by substituting the stretched variables $\tilde{t} = \varepsilon t$ and $\tilde{x} = \varepsilon^{1/2} x$ and $Y \sim O(\varepsilon^{1/2})$ into Eqs. (11), (12), and (13) to give

$$
\begin{aligned}
A_{\tilde{t}} &= A_{\tilde{x}\tilde{x}} + \frac{W^2}{4} - \gamma A D \\
W_{\tilde{t}} &= W_{\tilde{x}\tilde{x}} - \frac{W^2}{2} + 2\gamma A D \\
D &= 1 - A - W
\end{aligned}
\tag{24}
$$

with

$$
\begin{aligned}
A(0, \tilde{t}) &= 0 \\
W_{\tilde{x}}(0, \tilde{t}) &= -A_{\tilde{x}}(0, \tilde{t})
\end{aligned}
\tag{25}
$$

and the matching conditions

$$
\begin{aligned}
A(\tilde{x}, \tilde{t}) &\underset{\substack{\tilde{t} \to 0 \\ \xi = \tilde{x}/\tilde{t}^{1/2} \text{ fixed}}}{\sim} \frac{1}{\sqrt{\pi}} \int_0^{\xi} e^{-\lambda^2/4} \, d\lambda \\
W(\tilde{x}, \tilde{t}) &\underset{\substack{\tilde{t} \to 0 \\ \xi = \tilde{x}/\tilde{t}^{1/2} \text{ fixed}}}{\sim} \frac{1}{\sqrt{\pi}} \int_{\xi}^{\infty} e^{-\lambda^2/4} \, d\lambda.
\end{aligned}
\tag{26}
$$

Note that matching is accomplished along similarity curves. While the outer problem (24)–(26) has to be solved numerically, it is much simpler than the original system (11)–(13). There are only two coupled equations instead of three and ε does not enter explicitly. Thus, the outer solution need only be computed once for all values of ε. Both the outer problem and the original system have an infinite second derivative at their origin. However, because the matching conditions (26) give the solution for $\tilde{t}$ small, as opposed to the initial conditions (13) for $t = 0$ only, the difficulty of using finite differences near the origin could be easily avoided for the outer problem by taking the matching data as the solution out to a small time Δt large enough so that the derivatives were well behaved but small enough to still be valid. The results of such computations for $\gamma = 0$ (an irreversible step (iv)) and $\gamma = 1$ (a reversible step (iv)) are given in Fig. 4. These computations show that for $\gamma = 0$ (the irreversible step), the system tends to a state with only species D present as t tends to infinity. This is to be expected from physical arguments since any D that is produced never enters into a reaction again. Yet, A is continually producing B at the electrode, step (i), B is continually producing C throughout the solution, step (ii), and B and C are continually producing A and D throughout the solution, step (iv). The computations for $\gamma = 1$ (the reversible step) show a more complicated behavior.
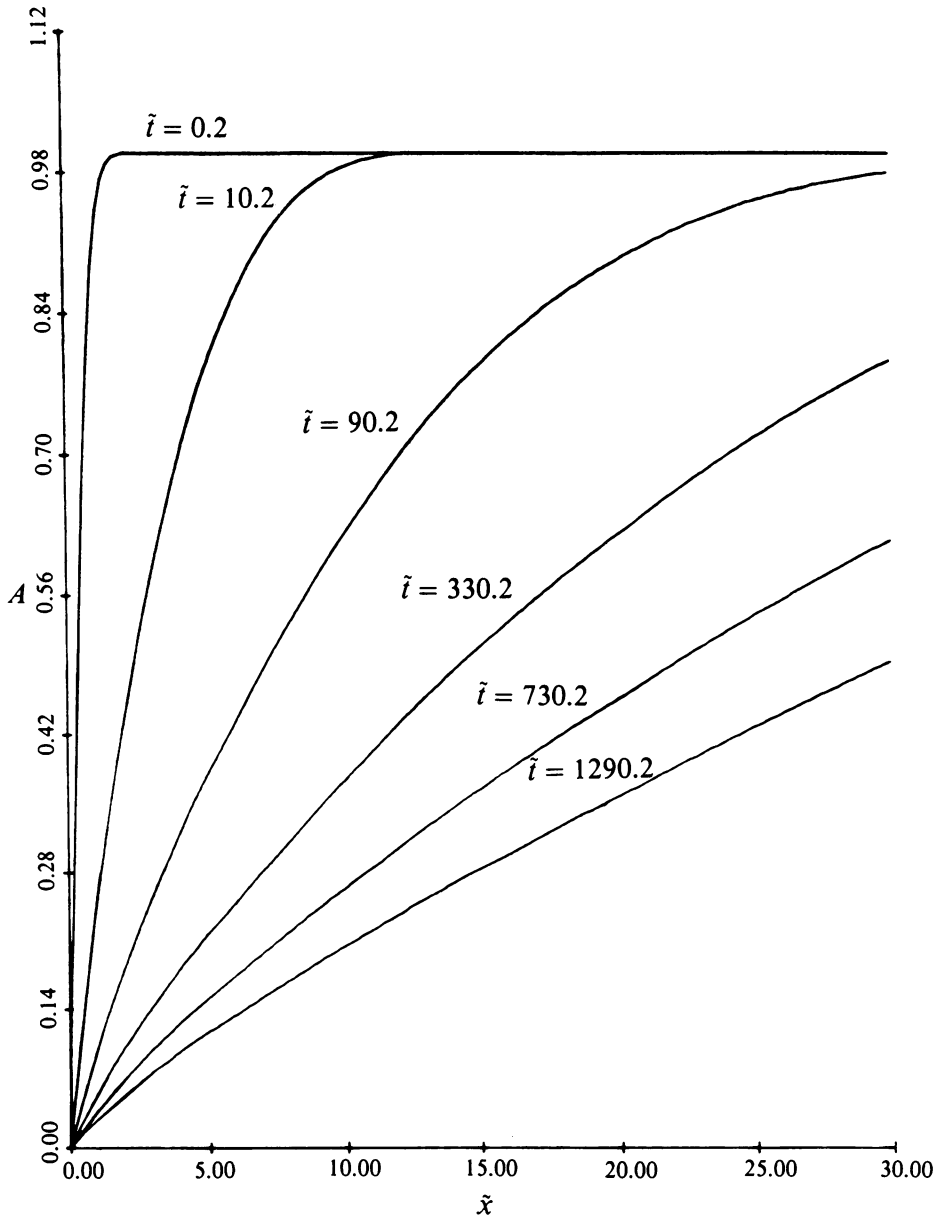
FIG. 4a. Concentration profile of species A for $\gamma = 0$ in DISP mechanism.
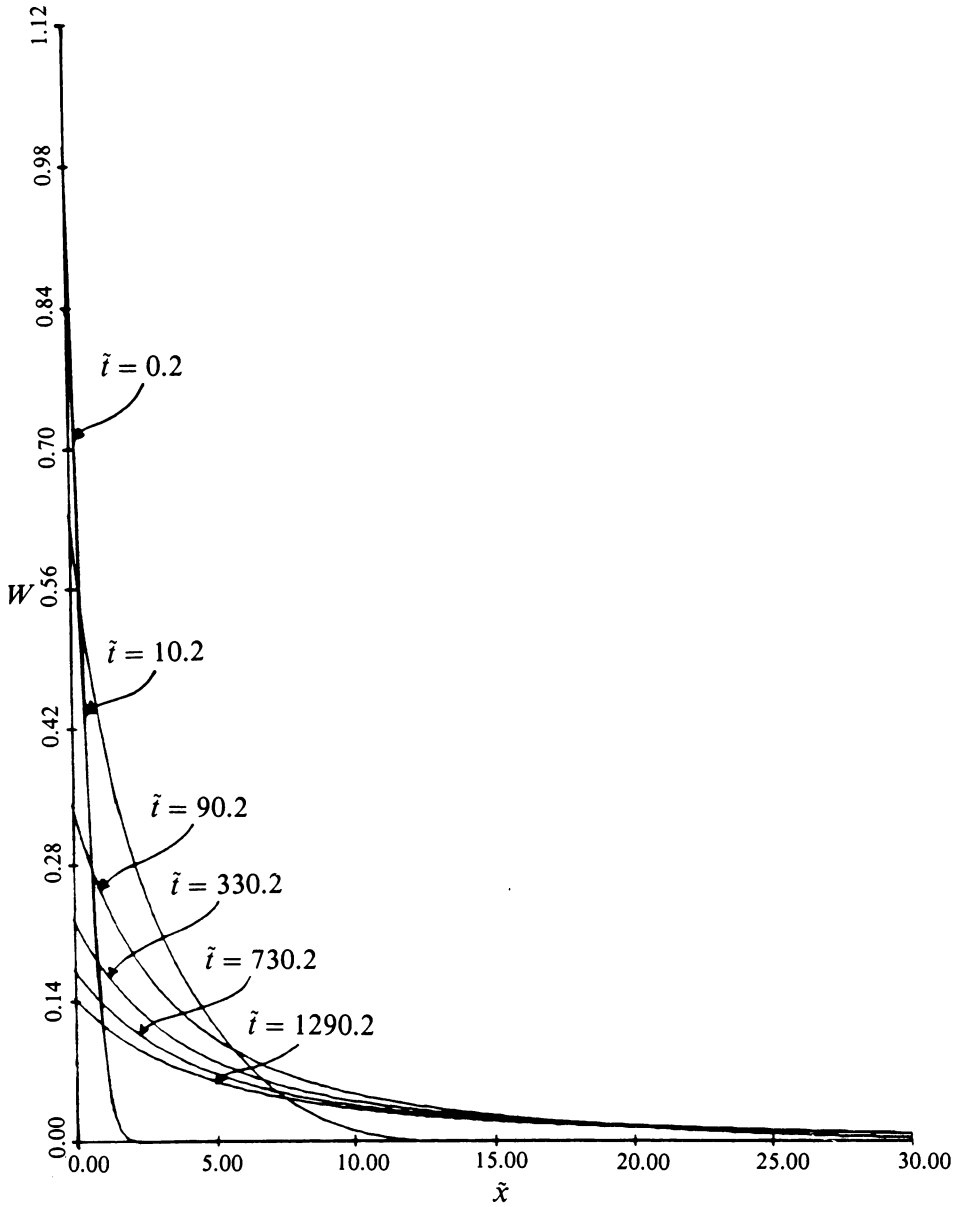
FIG. 4b. Concentration profile of species $W = B + C$ for $\gamma = 0$ in DISP mechanism.
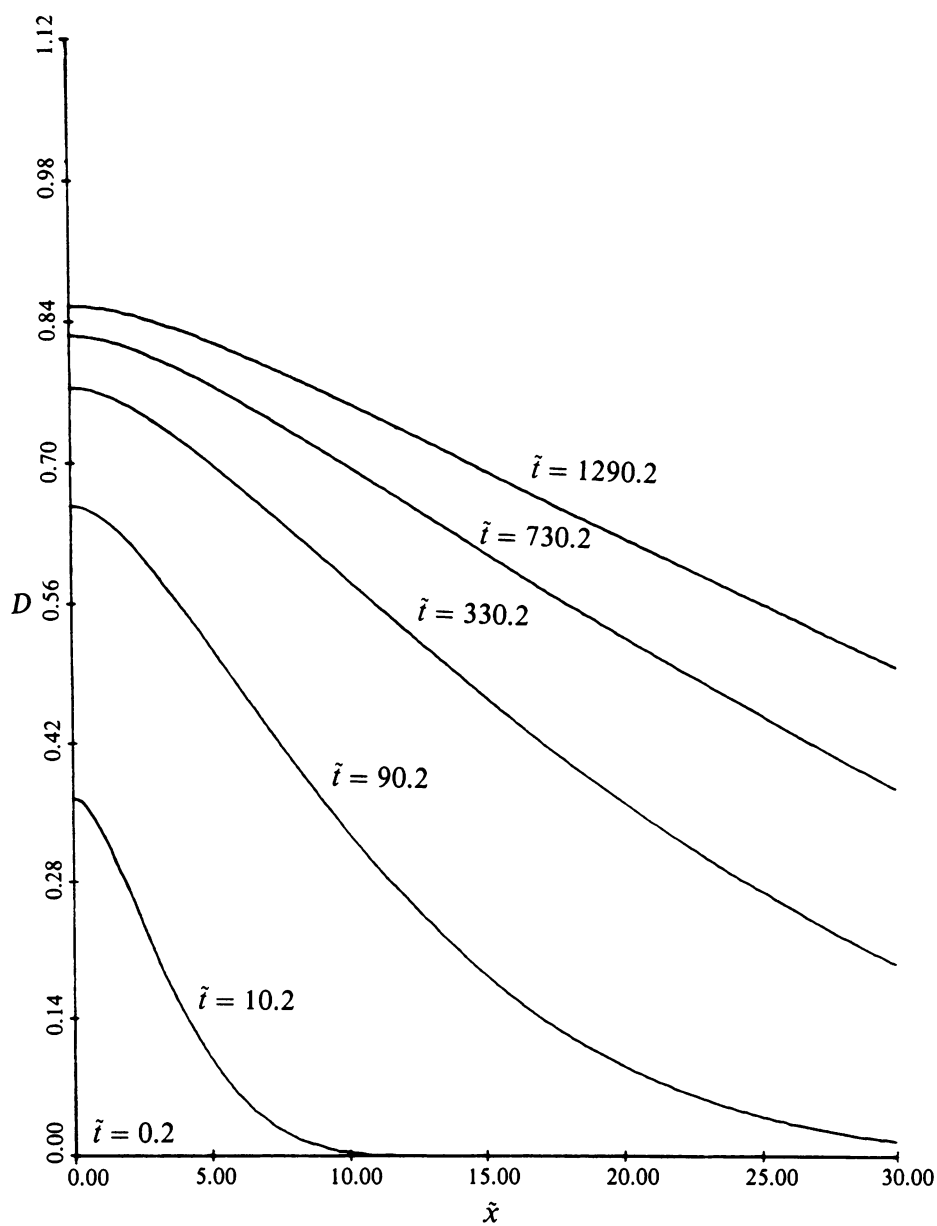
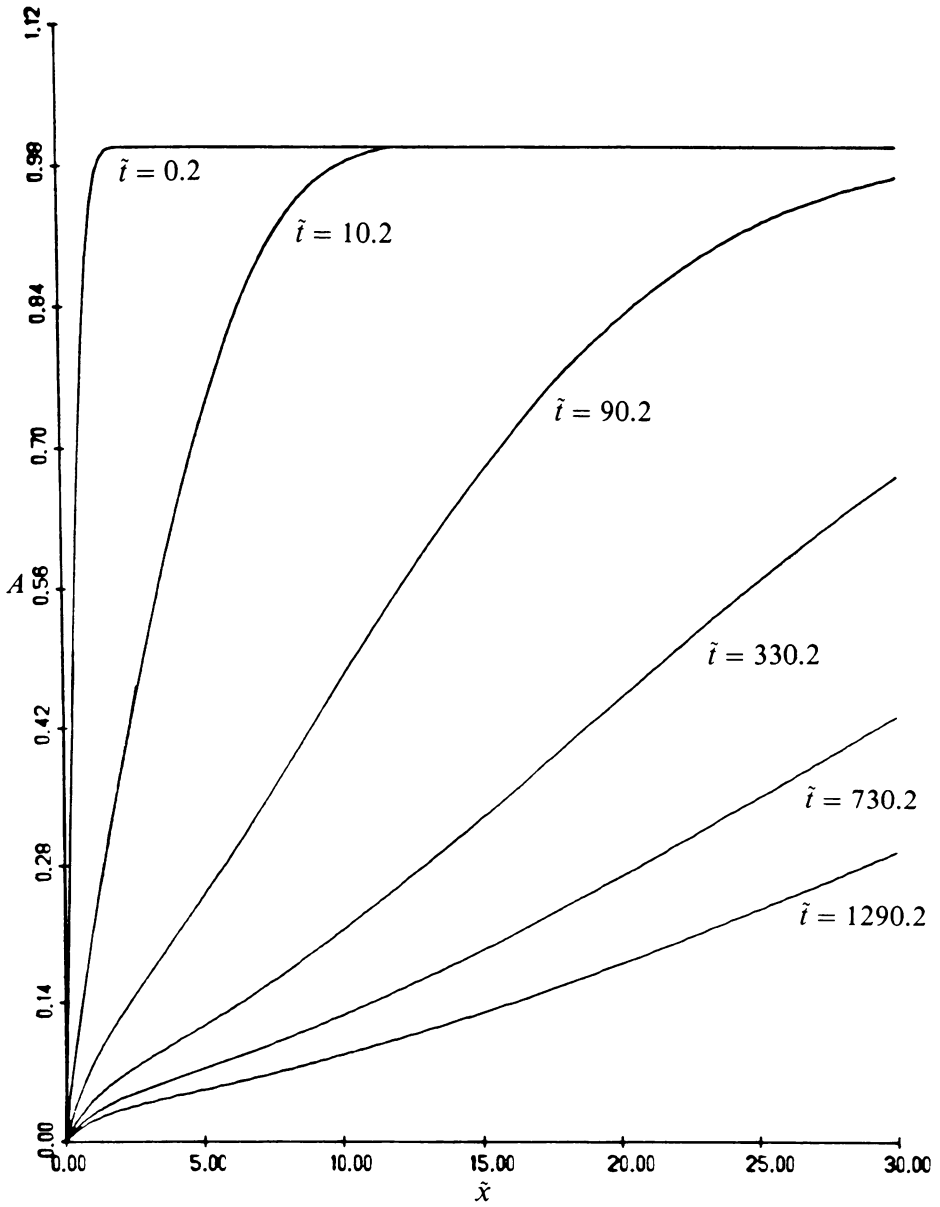FIG. 4c. Concentration profile of species D for $\gamma = 0$ in DISP mechanism.

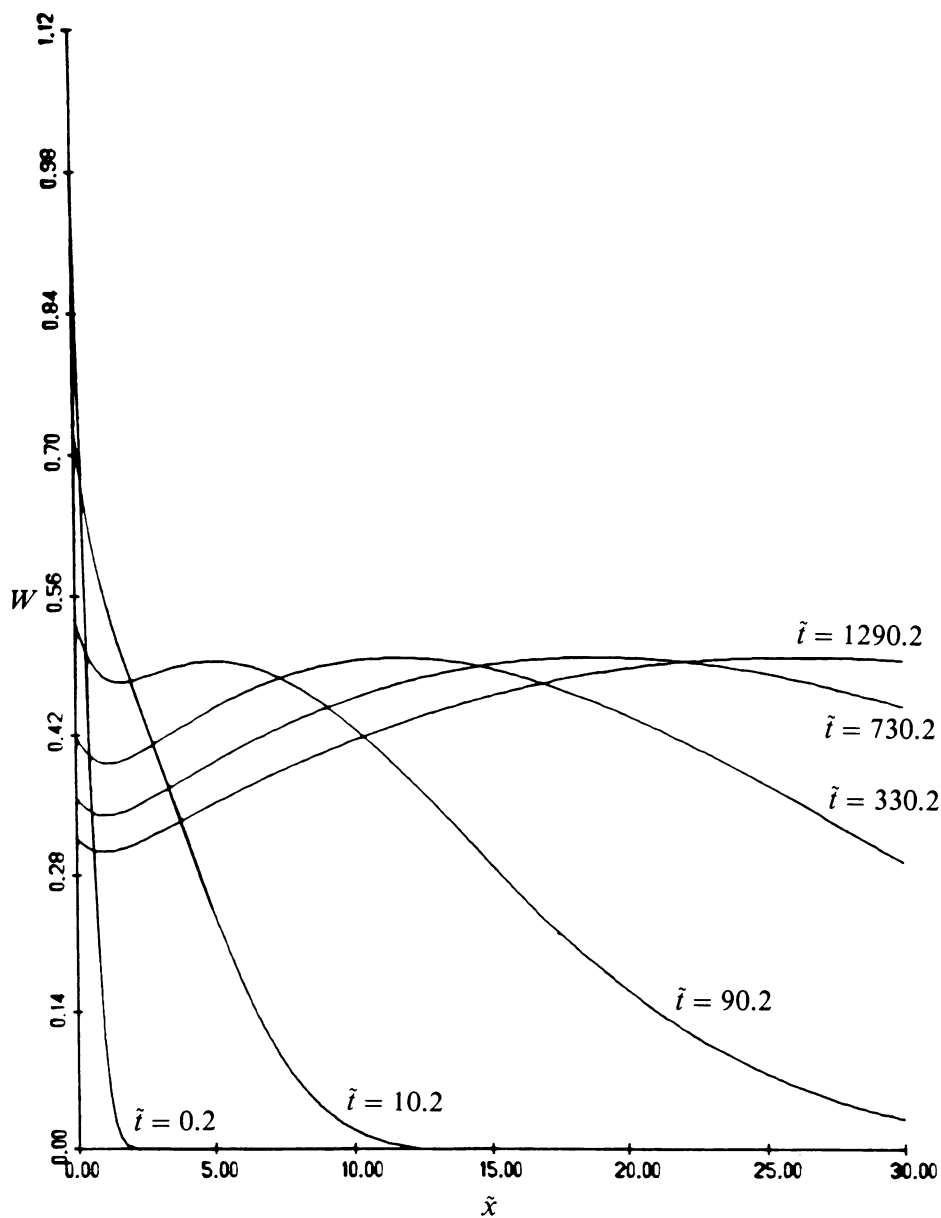FIG. 4d. Concentration profile of species A for $\gamma = 1$ in DISP mechanism.

FIG. 4e. Concentration profile of species $W = B + C$ for $\gamma = 1$ in DISP mechanism.
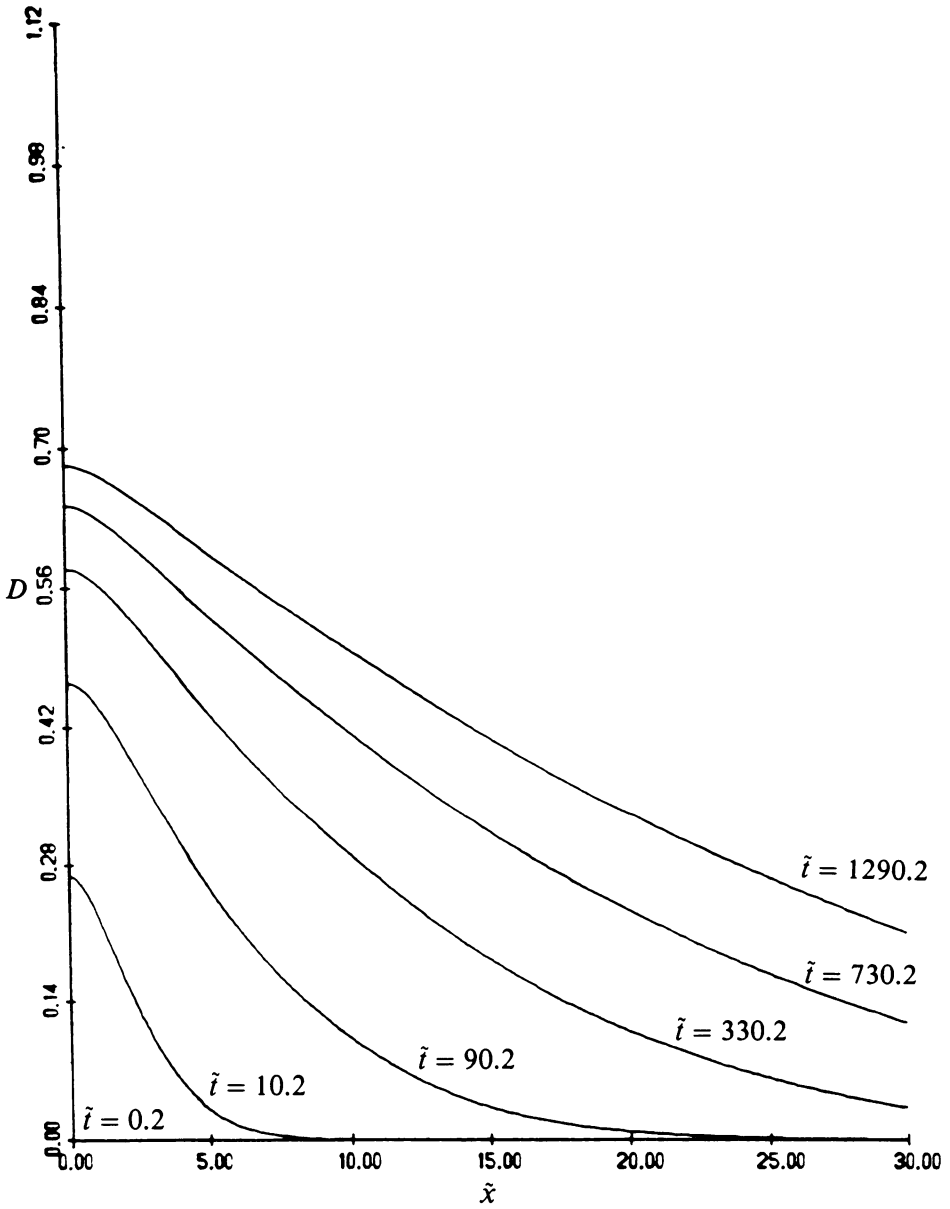
FIG. 4f. Concentration profile of species D for $\gamma = 1$ in DISP mechanism.

6. The competition equations. The competition equations include all four pathway steps and thus represent an intermediary between the ECE and DISP processes. The basic equations to be considered are (for $\gamma = 1$)

$$
\begin{aligned}
A_t &= A_{xx} + \varepsilon BC - \varepsilon AD \\
B_t &= B_{xx} - B + C - \varepsilon BC + \varepsilon AD \\
C_t &= C_{xx} + B - C - \varepsilon BC + \varepsilon AD \\
D &= 1 - A - B - C
\end{aligned}
\tag{27}
$$

with

$$
\begin{aligned}
A_x(0, t) &= A(0, t) \\
B_x(0, t) &= -A_x(0, t) \\
C_x(0, t) &= \delta C(0, t)
\end{aligned}
\tag{28}
$$

and

$$
\begin{aligned}
A(x, 0) &= 1 \\
B(x, 0) &= C(x, 0) = 0.
\end{aligned}
\tag{29}
$$

As in the DISP mechnism, the competition solution can be written in terms of a regular perturbation expansion for time not too large:

$$
\begin{aligned}
A(x, t; \varepsilon) &= A_0(x, t) + \varepsilon A_1(x, t) + \cdots \\
B(x, t; \varepsilon) &= B_0(x, t) + \varepsilon B_1(x, t) + \cdots \\
C(x, t; \varepsilon) &= C_0(x, t) + \varepsilon C_1(x, t) + \cdots \\
D(x, t; \varepsilon) &= D_0(x, t) + \varepsilon D_1(x, t) + \cdots
\end{aligned}
\tag{30}
$$

where the leading order terms satisfy the ECE equations

$$
\begin{aligned}
A_{0_t} &= A_{0_{xx}} \\
B_{0_t} &= B_{0_{xx}} - B_0 + C_0 \\
C_{0_t} &= C_{0_{xx}} + B_0 - C_0 \\
D_0 &= 1 - A_0 - B_0 - C_0
\end{aligned}
\tag{31}
$$

with

$$
\begin{aligned}
A_{0_x}(0, t) &= A_0(0, t) \\
B_{0_x}(0, t) &= -A_{0_x}(0, t) \\
C_{0_x}(0, t) &= \delta C_0(0, t)
\end{aligned}
\tag{32}
$$

and

$$
\begin{aligned}
A_{0_x}(x, 0) &= 1 \\
B_0(x, 0) &= C_0(x, 0) = 0.
\end{aligned}
\tag{33}
$$

The asymptotic solution of these equations (for $W_0 = B_0 + C_0$ and $Y_0 = B_0 - C_0$) which is valid for time large but not too large (where again this statement will be

made more precise later) is

$$
A_0 \underset{\substack{t \text{ large} \\ \xi = x/t^{1/2}}}{\sim} \frac{1}{\sqrt{\pi}} \int_0^\xi e^{-\lambda^2/4}\, d\lambda + \frac{e^{-\xi^2/4}}{\sqrt{\pi t}} + \cdots
$$

$$
W_0 \underset{\substack{t \text{ large} \\ \xi = x/t^{1/2}}}{\sim} \sqrt{\frac{2}{\pi t}} \left(1 + \frac{\sqrt{2}}{\delta}\right) e^{-\xi^2/4} + \cdots
$$

$$
Y_0 \underset{t \text{ large}}{\sim} \sqrt{\frac{2}{\pi t}} e^{-\sqrt{2}x} + \cdots
$$

$$
D_0 \underset{\substack{t \text{ large} \\ \xi = x/t^{1/2}}}{\sim} \frac{1}{\sqrt{\pi}} \int_\xi^\infty e^{-\lambda^2/4}\, d\lambda + \cdots .
$$

(34)

The regular perturbation solutions for A_0, W_0, and D_0 in the competition mechanism are exactly the same as A, W, and D in the ECE mechanism. In the DISP mechanism $W_0 \sim O(1)$ and $D_0 \equiv 0$ for t large. In the competition case $W_0 \sim O(1/t^{1/2})$ and $D_0 \sim O(1)$ for t large. Note that one cannot simply recover the DISP solution from the competition solution as a uniform limit as $\delta \to 0$ since the competition solution for W_0 blows up. This is to be expected since W_0 is of smaller order in the competition solution than in the DISP solution.

The first correction terms satisfy

$$
\begin{aligned}
A_{1_t} &= A_{1_{xx}} + B_0 C_0 - A_0 D_0 \\
B_{1_t} &= B_{1_{xx}} - B_1 + C_1 - B_0 C_0 + A_0 D_0 \\
C_{1_t} &= C_{1_{xx}} + B_1 - C_1 - B_0 C_0 + A_0 D_0
\end{aligned}
$$

(35)

$$
A_1 + B_1 + C_1 + D_1 = 0
$$

with

$$
\begin{aligned}
A_{1_x}(0,t) &= A_1(0,t) \\
B_{1_x}(0,t) &= -A_{1_x}(0,t) \\
C_{1_x}(0,t) &= \delta C_1(0,t)
\end{aligned}
$$

(36)

and

$$
A_1(x,0) = B_1(x,0) = C_1(x,0) = 0.
$$

(37)

For large time, Eqs. (35) are asymptotically equivalent to (for $W_1 = B_1 + C_1$ and $Y_1 = B_1 - C_1$)

$$
A_{1_t} = A_{1_{xx}} - \left(\frac{1}{\sqrt{\pi}} \int_0^\xi e^{-\lambda^2/4}\, d\lambda\right)\left(\frac{1}{\sqrt{\pi}} \int_\xi^\infty e^{-\lambda^2/4}\, d\lambda\right)
$$

$$
W_{1_t} = W_{1_{xx}} + 2\left(\frac{1}{\sqrt{\pi}} \int_0^\xi e^{-\lambda^2/4}\, d\lambda\right)\left(\frac{1}{\sqrt{\pi}} \int_\xi^\infty e^{-\lambda^2/4}\, d\lambda\right)
$$

(38)

$$
Y_{1_t} = Y_{1_{xx}} - 2Y
$$

$$
A_1 + W_1 + D_1 = 0
$$

and the boundary conditions are equivalent to

$$W_{1_x} = -A_{1_x} + \frac{\delta}{2}(W_1 - Y_1)|_{x=0}$$

$$Y_{1_x} = -A_{1_x} - \frac{\delta}{2}(W_1 - Y_1)|_{x=0}. \tag{39}$$

A_1 has a solution of the form

$$A_1 \underset{\substack{t \text{ large} \\ \xi = x/t^{1/2}}}{\sim} tf(\xi) + t^{1/2}f_1(\xi) + \cdots$$

where

$$f''(\xi) + \frac{\xi}{2}f'(\xi) - f(\xi) = \left(\frac{1}{\sqrt{\pi}}\int_0^\xi e^{-\lambda^2/4}\,d\lambda\right)\left(\frac{1}{\sqrt{\pi}}\int_\xi^\infty e^{-\lambda^2/4}\,d\lambda\right)$$

with $f(0) = 0$ and $f \to 0$ as $\xi \to \infty$. Similarly, W_1 has a solution of the same form

$$W_1 \underset{\substack{t \text{ large} \\ \xi = x/t^{1/2}}}{\sim} tg(\xi) + t^{1/2}g_1(\xi) + \cdots$$

where

$$g''(\xi) + \frac{\xi}{2}g'(\xi) - g(\xi) = -2\left(\frac{1}{\sqrt{\pi}}\int_0^\xi e^{-\lambda^2/4}\,d\lambda\right)\left(\frac{1}{\sqrt{\pi}}\int_\xi^\infty e^{-\lambda^2/4}\,d\lambda\right)$$

with

$$g(0) = 0 \quad \text{and} \quad g \to 0 \quad \text{as } \xi \to \infty.$$

Y_1 remains bounded for all t, $Y_1 \sim ce^{-\sqrt{2}x} + \cdots$ where the constant c is determined from (39) through the lower order terms in the expansions for A and W.

The numerical solution for f is given in Fig. 5; $g = -2f$.

The regular perturbation expansion breaks down (in the sense that the first order correction is the same size as the leading order term) for A when $t \sim O(1/\varepsilon)$ and for W when $t \sim O(1/\varepsilon^{2/3})$. Thus, the regular perturbation expansion is valid for $t \gg 1$ but much smaller then $O(1/\varepsilon^{2/3})$.

The regular perturbation breakdown suggests that two outer problems are required to extend the solution for t out to infinity. The first outer solution is constructed by substituting the stretched variables $\hat{t} = \varepsilon^{2/3}t$ and $\hat{x} = \varepsilon^{1/3}x$ and the scaled variable $W = \varepsilon^{1/3}w$ with $Y \sim O(\varepsilon^{1/3})$ into Eqs. (27), (28), and (29). Assuming A, W, and D can be written in terms of a regular perturbation expansion, the equations for the leading order terms for A and D remain unchanged. The equation for w becomes

$$w_{\hat{t}} = w_{\hat{x}\hat{x}} + 2A_0D_0. \tag{40}$$

The boundary conditions (from (28)) are

$$W_x = -A_z + \frac{\delta}{2}(W - Y)|_{x=0}$$

$$Y_x = -A_x - \frac{\delta}{2}(W - Y)|_{x=0}. \tag{41}$$
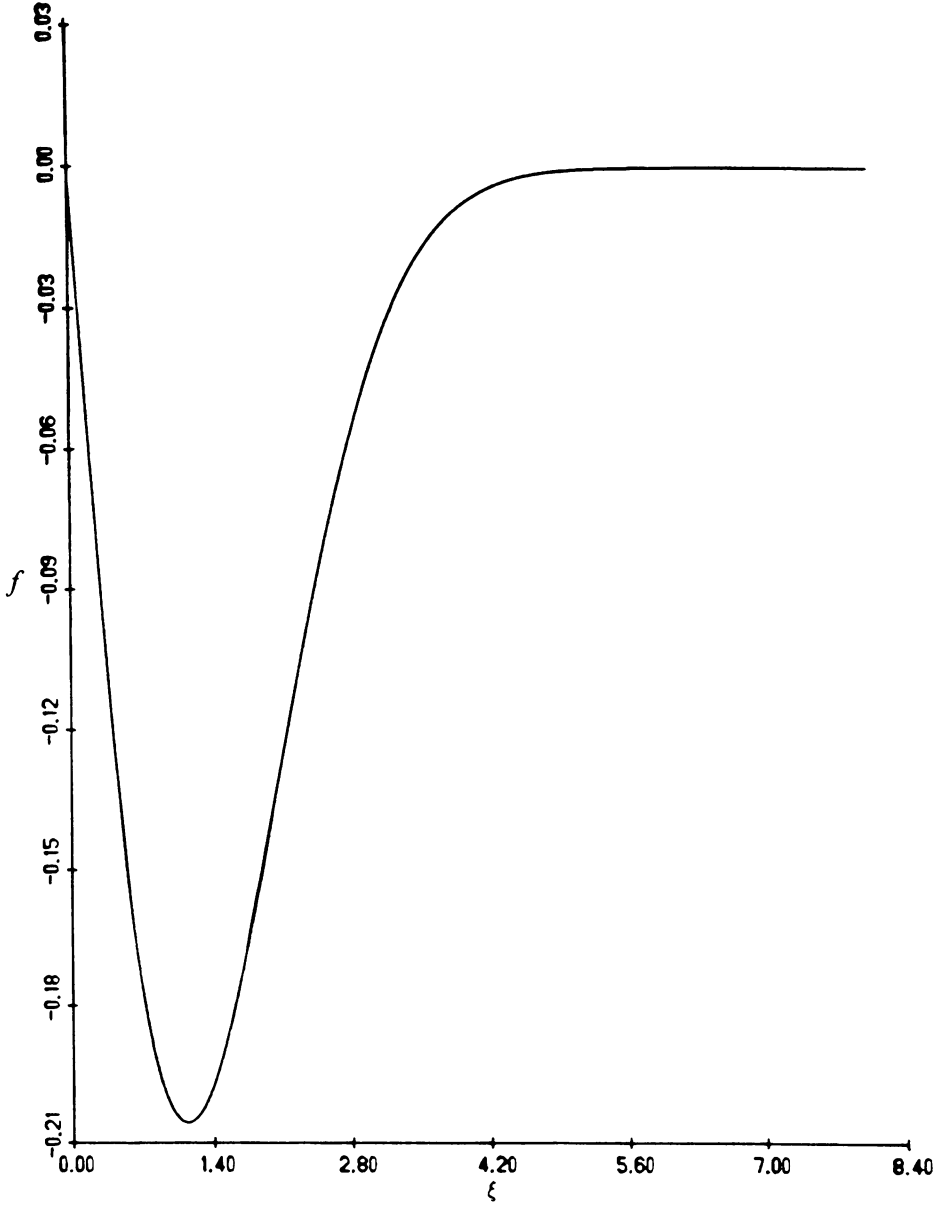
FIG. 5. Plot of $f(\xi)$ for $A_1 \sim t f(\xi) + \cdots$ in competition case.

The initial conditions (from (29)) become

$$W \xrightarrow[x \to \infty]{} 0$$
$$Y \xrightarrow[x \to \infty]{} 0. \tag{42}$$

The solution for w can be decomposed into a particular solution and a homogeneous solution $w = \hat{i}G(\xi) + w_h$ where

$$G''(\xi) + \frac{\xi}{2}G'(\xi) - G(\xi) = -2\left(\frac{1}{\sqrt{\pi}}\int_0^{\xi} e^{-\lambda^2/4}\,d\lambda\right)\left(\frac{1}{\sqrt{\pi}}\int_{\xi}^{\infty} e^{-\lambda^2/4}\,d\lambda\right)$$

with

$$G(0) = 0 \quad \text{and} \quad G \to 0 \quad \text{as } \xi \to \infty$$

and

$$w_{h_i} - w_{h_{\tilde{x}\tilde{x}}}$$

with the boundary conditions for w_h yet to be determined.

Y has a solution of the form

$$Y = \frac{b}{t^{1/2}}e^{-\sqrt{2}x} + \cdots$$

where b is a constant to be determined from the boundary conditions at $x = 0$. These boundary conditions (Eqs. (41)) imply (to the leading order)

$$0 = \left\{-\frac{1}{\sqrt{\pi \hat{i}}} + \frac{\delta}{2}\left(w_h - \frac{b}{\sqrt{\hat{i}}}\right)\right\}_{\hat{x}=0}$$

$$-\frac{\sqrt{2}b}{\sqrt{\hat{i}}} = \left\{-\frac{1}{\sqrt{\pi \hat{i}}} - \frac{\delta}{2}\left(w_h - \frac{b}{\sqrt{\hat{i}}}\right)\right\}_{\hat{x}=0}$$

(since $G(0) = 0$). Thus,

$$w_h = \sqrt{\frac{2}{\pi}}\left(1 + \frac{\sqrt{2}}{\delta}\right)\frac{e^{-\xi^2/4}}{\hat{i}^{1/2}}$$

and

$$Y = \sqrt{\frac{2}{\pi}}\frac{e^{-\sqrt{2}x}}{t^{1/2}}.$$

This solution is valid for $t \sim O(1/\varepsilon^{2/3})$ but breaks down for $t \sim O(1/\varepsilon)$. Then, the nonlinear chemical terms are the same size as the diffusive terms for A, W, and D. Although $W \sim O(\varepsilon^{2/3})$ in the first outer region, the term $\varepsilon^{1/3}\hat{i}G(\xi)$ grows with time to become $O(1)$ in the second outer region. Y remains asymptotically small. Thus, the first outer region acts as a switching region in which the competition solution changes from the ECE form to one more similar to the DISP mechanism. The regions of validity for the inner solution, two outer solutions, and matching regions are shown in Fig. 6.

The solution in the second outer region is constructed by substituting the stretched variables $\tilde{t} = \varepsilon t$ and $\tilde{x} = \varepsilon^{1/2}x$ with the assumption that $Y \sim O(\varepsilon^{1/2})$ into Eqs. (27) and (28) to give

$$A_{\tilde{i}} = A_{\tilde{x}\tilde{x}} - AD + \frac{W^2}{4}$$

$$W_{\tilde{i}} = W_{\tilde{x}\tilde{x}} + 2AD - \frac{W^2}{2} \tag{43}$$
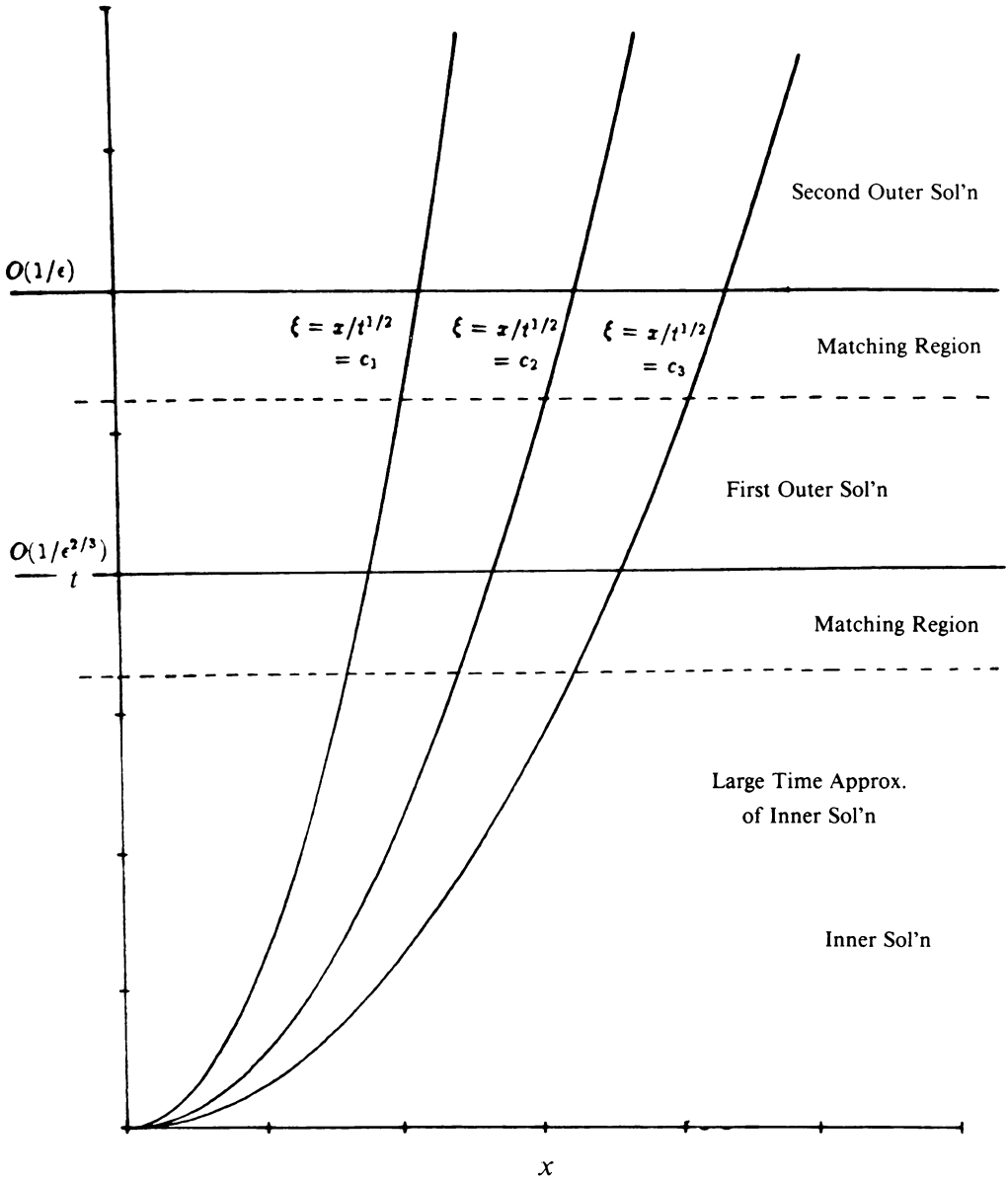
$$D = 1 - A - W$$

FIG. 6. Regions of validity for the competition solutions.

with the boundary conditions

$$A(0, \tilde{t}) = 0$$
$$W(0, \tilde{t}) = 0$$

(44)

since all the other terms for the boundary conditions involving W are of lower order.

The matching conditions imply

$$A \underset{\substack{\tilde{t}\to 0 \\ \xi=\tilde{x}/\tilde{t}^{1/2}\ \text{fixed}}}{\sim} \frac{1}{\sqrt{\pi}} \int_0^{\xi} e^{-\lambda^2/4}\, d\lambda \qquad W(\tilde{x},0) = 0. \tag{45}$$

The finite difference solution to this problem is given in Fig. 7. It is interesting to note that while the competition problem is theoretically more complicated than the DISP problem (since it has two outer solution regions instead of one), the large time concentration profiles are very similar.
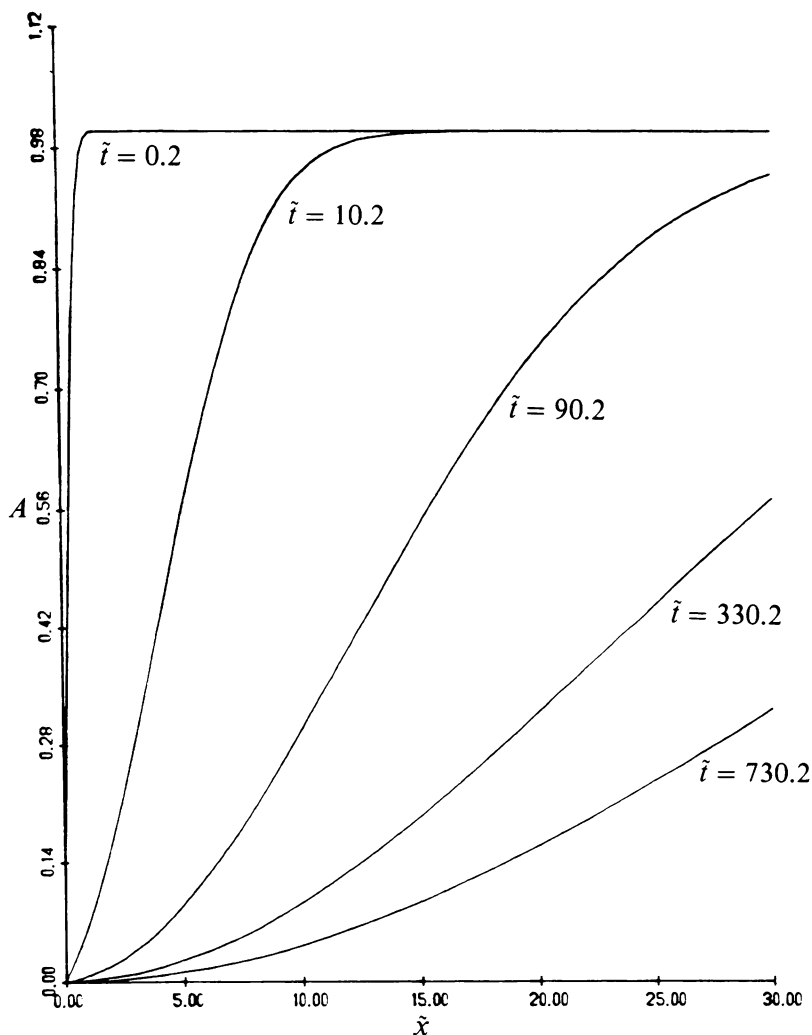

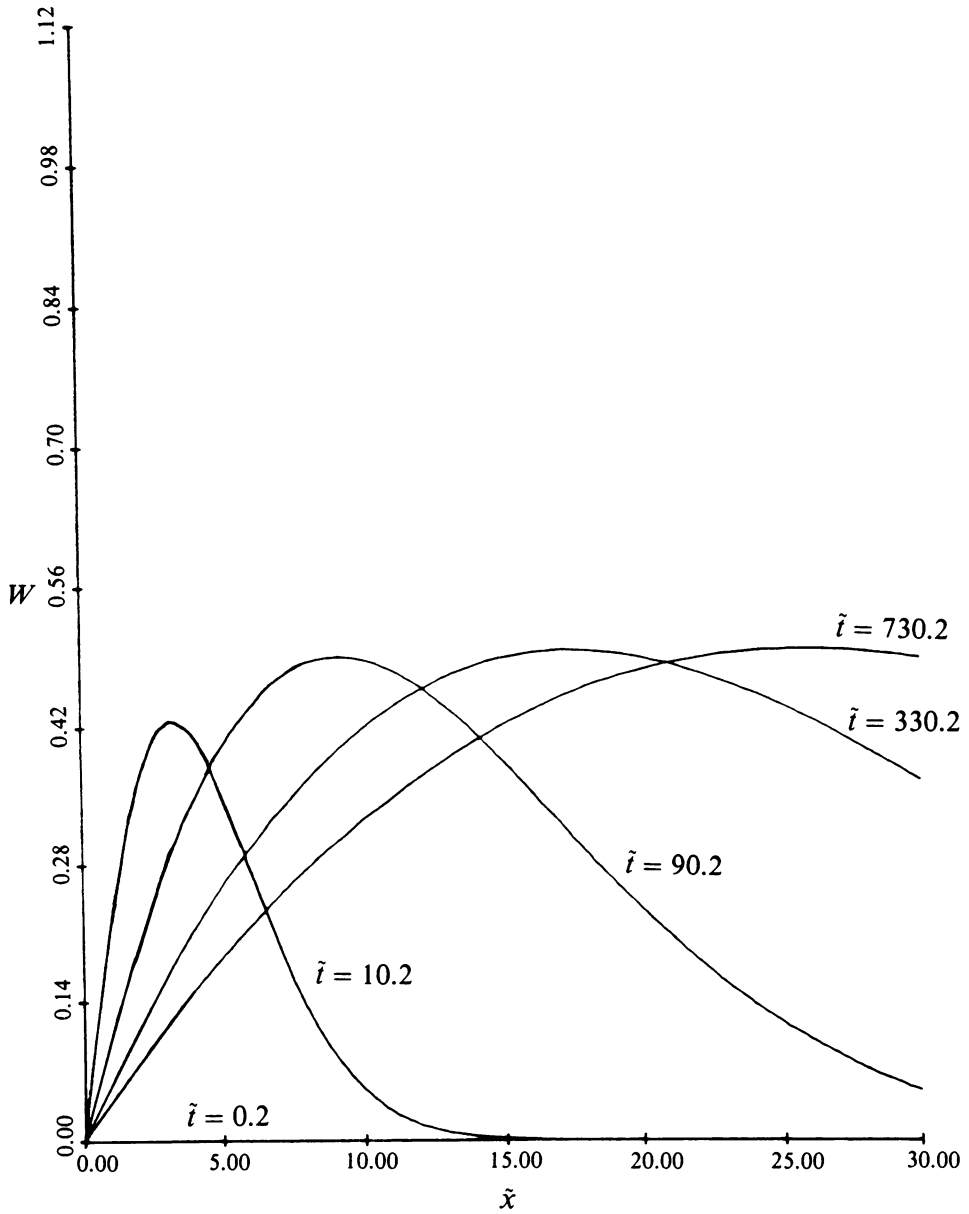FIG. 7a. Concentration profile of species A for competition case.

FIG. 7b. Concentration profile of species $W = B + C$ for competition case.
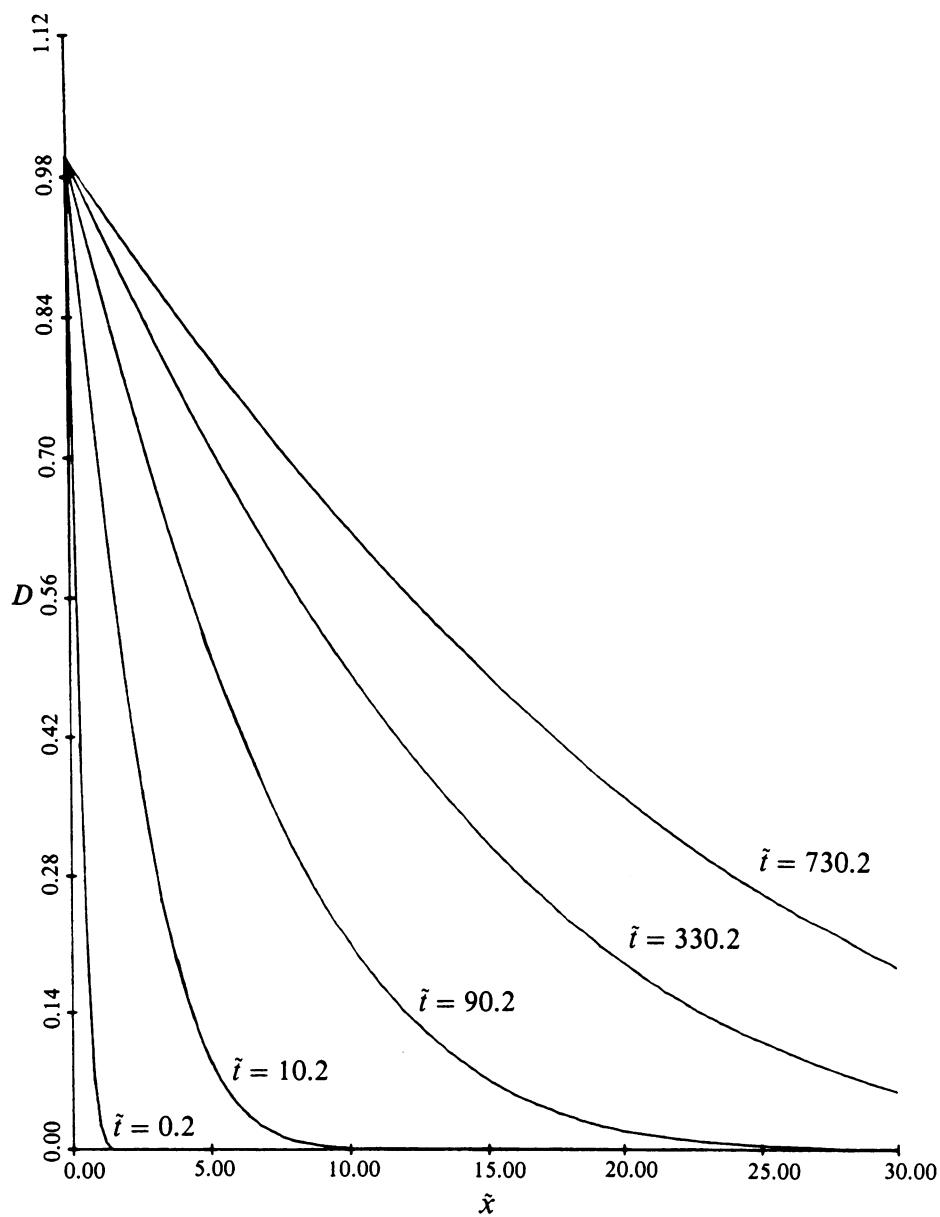
FIG. 7c. Concentration profile of species D for competition case.

7. Conclusions. Current experimental techniques attempt to distinguish between reaction mechanisms based on the flux $A_x|_{x=0}$ which is shown here to be small and similar for all three cases considered when the dimensionless time is large (such as typical in experimental conditions). Because complicated variations in the fluxes are introduced when the rate constants are arbitrary, flux techniques have not always proven adequate to distinguish product pathways. This paper shows that species profiles as can be determined by spectro-electrochemical techniques are very useful because there is a large variation in the gross behavior of the species concentration of the three mechanisms. The ECE mechanism tends to a state with only species A and D present in order one quantities. The DISP mechanism tends to a state with all four species present. The competition case initially behaves like the ECE mechanism but evolves with time to a state more like the DISP mechanism with all four species present in order one quantities.

REFERENCES

[1] G. S. Alberts and I. Shain, *Electrochemical study of kinetics of a chemical reaction coupled between two charge transfer reactions*, J. Anal. Chem. **35**, 1859–1866 (1963)
[2] C. Amatore and J. M. Saveant, *ECE and disproportionation, part V. Stationary state general solution application to linear sweep voltammetry*, J. Electroanal. Chem. **85**, 27–46 (1977)
[3] C. Amatore and J. M. Saveant, *ECE and disproportionation, part VI. General resolution. Application to potential step chronoamperometry*, J. Electroanal. Chem. **102**, 21–40 (1979)
[4] S. W. Feldberg, *Nuances of the ECE mechanism. III. Effects of homogeneous redox equilibrium in cyclic voltammetry*, J. Phys. Chem. **75**, 2377–2380 (1971)
[5] S. W. Feldberg and L. Jeftic, *Nuances of the ECE mechanism. IV. Theory of cyclic voltammetry and chronoamperometry and the electrochemical reduction of hexacyanochromate* (III), J. Phys. Chem. **76**, 2439–2446 (1972)
[6] J. Galvez and A. Molina, *Pulse polarography, part V. On the theory for the kinetic currents with an ECE mechanism*, J. Electroanal. Chem. **107**, 87–94 (1980)
[7] M. D. Hawley and S. W. Feldberg, *Nuances of the ECE mechanism. I. Development of the theoretical relationships for chronoamperometry*, J. Phys. Chem. **70**, 3459–3464 (1966)
[8] L. S. Marcoux, R. N. Adams, and S. W. Feldberg, *Dimerization of triphenylamine cation radicals. Evaluation of kinetics using the rotating disk electrode*, J. Phys. Chem. **73**, 2611–2614 (1969)
[9] R. S. Nicholson and I. Shain, *Theory of stationary electrode polarography for a chemical reaction coupled between two charge transfers*, J. Anal. Chem. **37**, 178–190 (1965)
[10] J. M. Saveant, C. P. Andrieux, and L. Nadjo, *Disproportionation and ECE mechanisms*, J. Electroanal. Chem. **41**, 137–141 (1973)
[11] J. W. Wilder, *Analytic solutions for electrochemical mechanisms involving coupled homogeneous and heterogeneous chemistry*, Ph.D. Dissertation, Rensselaer Polytechnic Institute, Troy, NY, (1988)