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Polynomial Approximation Techniques for Differential Equations in Electrochemical Problems.

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A complete listing of the techniques of weighted residuals and their use in electrochemistry is given, Solutions include those by orthogonal collocation, and direct application to a number of electrochemical techniques, electrode geometrics, and kinetic mechanism are given.

Polynomial Approximation Techniques for Differential Equations in Electrochemical Problems

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I. INTRODUCTION

Stephen Feldberg's finite difference methods [1] for digital simulation has been the primary method of approximating the solutions to second order partial differential equations found in electrochemistry. The intensity of usage of digital simulations by these finite difference methods has increased markedly, and it has become apparent in some cases that there is a need for faster techniques capable of delivering accurate results as well as being able to simulate extremely "fast" systems more efficiently. As a result, several groups [2] have made significant contributions toward improving finite difference methods for electrochemical problems. But instability and lengthy computational times under certain conditions still manifests itself as a primary drawback.

The methods described in this chapter provide some of the answers to these problems. The mathematics involved in these polynomial approximation methods are only slightly more complicated than the finite difference equations, but the accuracy of the results, stability limits, and speed of execution of the computer programs make their use well worth the small extra effort needed to implement them.

It is not intended to imply that the methods described are the "ultimate" electrochemical differential equation simulations. The rapid convergence of low approximation order solutions to the exact solutions has been proven mathematically for many types of problems, but certainly not all. However, it is this type of convergence in a method that urges us to seek general theorems that may lead to faster, even more effective methods of approximation.

The interest in the use of new highly efficient numerical methods for the solution of complex mathematical problems is further evidenced by the overwhelming number of publications on the subject that have appeared in the recent mathematics and engineering literature [3]. The success of these techniques may be attributed to: a) the impressive degree of accuracy that is obtainable;

b) the fact that many of the methods may be constructed from only a few basic principles;

c) the consideration that many methods are "modular" in construction, and the "modules" are available as highly efficient algorithms amenable to digital computer implementation.

Harrison and Gray [4] used Chebyshev polynomial approximations some years ago for an electrochemical simulation. More recently, Whiting and Carr [5] introduced an advanced and highly efficient method (orthogonal collocation) into the simulation of electrode reactions. Their work outlines the theory of orthogonal collocation and its application to several electrochemical mechanisms occurring during chronoamperometric experiments. Bewick, Mellor, and Pons [6] applied the technique to some actual complicated systems and extended the method to simulate modulated specular reflectance transient responses of the intermediates formed during the reaction. More recently, Rieker and Speiser [7] have used orthogonal collocation to simulate a full spectrum of cyclic voltammetric responses.

The methods that will be discussed in this chapter are suitable in nature to the solution of a great many types of differential equations. As Whiting and Carr [5] pointed out, it is usually just a matter of changing a few steps in the program to switch from one problem to one of a completely different nature, e.g., the chronoamperometric response of an e.c.e. mechanism in electrochemistry to a dynamic model of a differential scanning calorimeter. With this in mind, it is also important to remember that even highly efficient methods may be improved by using certain techniques to treat peculiar situations that arise in specific problems. I have, however, tried to keep the methods as general as possible.

Special attention has been given to the integration of "stiff" differential equations, since it is with this type that electrochemists are most often confronted in their routine work. Equations of this type are of considerable interest in engineering research presently, and new, more efficient methods are being developed rapidly.

Some simple approximation methods are also described that may be solved on a calculator. These methods are of acceptable accuracy in many types of experiments, and some are of accuracy approaching the more sophisticated methods.

II. THE METHOD OF WEIGHTED RESIDUALS

A. Introduction

Consider the boundary value problem

$$\emptyset_t = \emptyset_{xx} \qquad (1)$$

where

$$\emptyset_t = \frac{\delta\emptyset(x,t)}{\delta t} \qquad (2)$$

and

$$\emptyset_{xx} = \frac{\delta^2\emptyset(x,t)}{\delta x^2} \qquad (\ 3)$$

We assume that $\emptyset$ is defined and continuous in the domain W. We also define $\emptyset_0(x) = \emptyset(x,0)$ as the initial condition of $\emptyset$, and $\emptyset_Z(x,t)$ are the values of $\emptyset$ at the boundaries Z of the domain. We choose an approximate solution, $\emptyset_A$ to the problem in the form:

$$\emptyset_A = \emptyset_{Z=0}(x,t)+\emptyset_{Z=L}(x,t)+\sum_{i=1}^{n} \alpha_i(t)\emptyset_i(x) \qquad (\ 4)$$

where $\emptyset_A$ is the approximate solution, $\emptyset_{Z=0}$ and $\emptyset_{Z=L}$ are the solutions at the boundaries 0 and L, and the $\emptyset_i$ are the basis functions (which may be polynomial, trigonometric, or other types). Various techniques would prescribe whether the basis functions satisfy the differential equation, the boundary conditions, or both.

The *residual* of equation (1) is defined as

$$R(\emptyset) = \emptyset_{xx} - \emptyset_t \qquad (\ 5)$$

so that if $\emptyset_A$ is an accurate approximation to the actual $\emptyset$, then $R(\emptyset_A)$ will equal zero. It is the purpose in the weighted residual methods to pick the $\alpha_i(t)$ such that the residual tends to zero. The $\alpha_i(t)$ are chosen by specifying that the integral of the residual times some weighting function w is equal to zero. Thus it is the "weighted average" of the residual that is specified to be zero over the whole domain:

$$\int_W w_j R(\phi_A)dx \equiv 0 \qquad (6)$$

The choice of the weighting function w_j determines which method of weighted residuals is being utilized. Some of the more popular methods are listed here [8].

1. Integral Method (method of moments, 1st order subdomain)

   The w_j are chosen to be x^j, j=0,1,2,3,----- So for the first order approximation problem, $x^j=1$, the integral

   $$\int_W R(\phi_A)dx = 0 \qquad (7)$$

   is evaluated. The result, for time dependent α_i, is a first order differential equation in ϕ_A.

2. Galerkin Method

   In this, a most widely used and highly accurate method, the basis functions for the ϕ_A are chosen as the weighting function, i.e.,

   $$w_j = \phi_j(x) \qquad (8)$$

   Because of this choice, and the completeness of the basis set, the method can be made *exact* as j → ∞.

3. Variational Methods

   Using the calculus of variations, certain problems may be approximated similar to weighted residual methods. The solutions, when accessible, compare in accuracy to the Galerkin method. However, the method is not directly applicable to all general second order partial differential equations, and is mentioned here for reference only.

4. Least Squares Method

Here, the weighting functions are chosen to be

$$w_j = \frac{\delta R(\emptyset_A)}{\delta \alpha_i(t)} \qquad (9)$$

The $\alpha_i(t)$ are provided by n equations from the set of equations

$$\frac{\delta Q}{\delta \alpha_i(t)} = 2\int R(\emptyset_A)\frac{\delta R(\emptyset_A)}{\delta \alpha_i(t)}\, dx = 0, \; i = 1,2,---n \qquad (10)$$

for a one dimensional situation.

5. General Collocation

The weighting functions are given by

$$w_j = \delta(x-x_j) \;, \qquad (11)$$

δ being the Dirac delta function, which is defined as follows:

$$\begin{aligned} &\delta(r) = 0 \;,\; r \neq 0 \\ &\int f(r)\delta(r)d\tau = f(0) \end{aligned} \qquad (12)$$

Note that if $f(r) = 1$, $\int \delta(r)d\tau = 1$. Also, it is true that $\delta(r)$ is only defined during an integration.

It is then immediately obvious that this choice of weighting function leads to

$$0 \equiv \int_W w_j R(\emptyset_A)dx = \int \delta(x-x_j)R(\emptyset_A)dx = R(\emptyset_A(x_j)) \qquad (13)$$

so that the residual is given in terms of a fixed set of x_j only. The x_j are any set of points in the integration interval.

6. Orthogonal Collocation Method

This highly accurate method, which is used in this work for accurate simulations of complicated systems, is the same as method (5) above with the collocation points x_j chosen as the real roots of an orthogonal polynomial.

7. Subdomain Method

The integration domain W is subdivided into subdomains W/n, n=1,2,3,----. The weighting functions are equal to 1 when x is in a particular subdomain, and equal to zero when it is not. If the number of subdomains is increased, the residual approximates zero closely in more regions, and eventually approximates zero over the entire region.

In the following section, a very useful approximation is made to the general diffusion problem. Several weighted residual methods are then used to provide the concentration profiles, and a comparison is made of the results.

B. The Diffusion Boundary Layer Approximation

As an example of one method that may be used on a hand calculator, we develop an approximation for the EC mechanism using a boundary layer approach. We have:

$$A \underset{}{\overset{ne-}{\rightleftharpoons}} B \xrightarrow{k} C \qquad (14)$$

at a planar electrode under conditions of semi infinite linear diffusion, and the conditions:

$$[A]_{X,0} = [A]_{\infty,T} = [A°] \qquad (15)$$

$$[B]_{X,0} = [C]_{X,0} = [A]_{0,T} = [B]_{\infty,T} = [C]_{\infty,T} = 0 \qquad (16)$$

$$\left(\frac{d[A]}{dX}\right)_{X=0} = - \left(\frac{d[B]}{dX}\right)_{X=0} \qquad (17)$$

This problem is one of a potential step applied to the electrode of such magnitude that the surface concentration of species A is reduced immediately to zero. We wish to determine the concentration profile of species B as a function of time. The differential equation to be solved is

$$\frac{\delta[B]}{\delta T} = D_B \frac{\delta^2[B]}{\delta X^2} - k[B] \qquad (18)$$

Assume that L is some distance from the electrode such that at the end of the experiment, there has been no diffusion of any species to L. In this case, we define the dimensionless parameters

$$t = \frac{TD_B}{L^2} \quad x = \frac{X}{L} \quad \beta = \frac{kL^2}{D_B} \quad c_B = \frac{[B]}{[A°]} \qquad (19)$$

Inserting these parameters into (18), we obtain

$$\frac{\delta c_B}{\delta t} = \frac{\delta^2 c_B}{\delta x^2} - \beta c_B \qquad (20)$$

The initial and boundary conditions are also changed to

$$c_B(x,0) = c_B(1,t) = 0 \tag{21}$$

$$c_A(0,t) = 1 \tag{22}$$

Now consider the diffusion boundary layer. When the potential step is applied, B immediately starts diffusing into the solution toward the cell wall which we assume to be no closer than L. Assume that the concentration of B ahead of this boundary, whose distance from the electrode we shall call b, is equal to zero. We also assume that behind the boundary, B is represented by a continuous gradient. We note that b is a function of t only. We may, under this supposition, treat distance from the electrode surface as some fraction of the parameter b(t). We now define a dimensionless distance transformation, which is simply a fraction of the diffusion boundary thickness:

$$\mu = \frac{x}{b(t)} \tag{23}$$

Since the concentration is to be expressed as a function of distance from the electrode surface, we have

$$c_B = c_B(\mu) = c_B\left(\frac{x}{b(t)}\right) \tag{24}$$

Note that we have combined distance and time into one new independent variable μ.

From the nature of the model, the following general boundary conditions must be imposed:

(1) The dimensionless concentration at the electrode surface is 1, i.e.

$$c_B = f(\mu)=f(0)=1 \tag{25}$$

(2) At the edge of the moving boundary (μ=1), the concentration is 0, i.e.

$$c_B = f(\mu)=f(1)=0 \tag{26}$$

(3) There is no flux of material across the moving boundary, i.e.

$$f'(1)=0 \tag{27}$$

(4) The moving boundary initially is located at the electrode surface, i.e.

$$b(0)=0 \tag{28}$$

Now we rewrite the differential equation in terms of the new single independent variable μ.

$$c_B = f(\mu)=f(\frac{x}{b(t)}) \tag{29}$$

$$\frac{\delta c_B}{\delta t} = \frac{\delta f(\mu)}{\delta t} = \frac{\delta f(\frac{x}{b(t)})}{\delta t} = \frac{\delta f(\frac{x}{b(t)})}{\delta(\frac{x}{b(t)})} \quad \frac{\delta(\frac{x}{b(t)})}{\delta t}$$

$$= -f'(\frac{x}{b(t)})(\frac{x}{b(t)})(\frac{1}{b(t)}) \quad \frac{db(t)}{dt}$$

$$= =f'(\mu) \ \mu \ b(t)^{-1} b'(t) \tag{30}$$

$$\frac{\delta c_B}{\delta x} = \frac{\delta f(\frac{x}{b(t)})}{\delta x} = \frac{\delta f(\frac{x}{b(t)})}{\delta (\frac{x}{b(t)})} \frac{\delta (\frac{x}{b(t)})}{\delta x} = f'(\mu)(\frac{1}{b(t)}) = f'(\mu)b^{-1}(t) \qquad (31)$$

$$\frac{\delta^2 c_B}{\delta x^2} = \frac{\delta (f'(\frac{x}{b(t)})b^{-1}(t)}{\delta (\frac{x}{b(t)})} \frac{\delta (\frac{x}{b(t)})}{\delta x} = \frac{1}{b(t)} f''(\mu)(\frac{1}{b(t)}) = f''(\mu)b(t)^{-2} \qquad (32)$$

The differential equation (20) now reads:

$$-f'(\mu)\ \mu\ b(t)^{-1}b'(t) - b^{-2}f''(\mu) - \beta f(\mu) \qquad (33)$$

The residual of (33) is simply the left hand side minus the right hand side. Now we choose an approximating function for f(μ). The simplist *polynomial* approximation that satisfies all of the boundary conditions (25-28) is:

$$f(\mu) = (1-\mu)^2 = 1-2\mu + \mu^2 \qquad (34)$$

We have:

$$f'(\mu) = 2\mu - 2 \qquad (35)$$

and

$$f''(\mu) = 2 \qquad (36)$$

So:

$$R_E = -\mu(2\mu-2)b'(t)b(t)^{-1} - 2b(t)^{-2} + \beta(1-2\mu+\mu^2) \qquad (37)$$

or $$b(t)^2 R_E = (2\mu-2\mu^2)b'(t)b(t) - 2 + \beta b^2(t)(1-2\mu+\mu^2) \qquad (38)$$

Now we shall apply various MWR to solve for the moving boundary position b. Insertion of this value into equation (34) will give the concentration profiles for species B. The results for each method are then compared to the exact solution.

Method (1): The integral method (w_j=1)

For the highest accuracy, we demand that the residual be equal to zero in the weighted average sense:

$$b^2\int_0^1 w_j R_E d\mu = \int_0^1 R_E d\mu = 0 \tag{39}$$

i.e.

$$\int_0^1 (2\mu-2\mu^2)b'(t)b(t) - 2 + \beta b(t)^2(1-2\mu+\mu^2)d\mu = 0 \tag{40}$$

$$\int_0^1 R_E d\mu = \frac{b'(t)b(t)}{3} - 2 + \frac{\beta b^2(t)}{3} = 0 \tag{41}$$

The first order differential equation is solved for b(t):

$$b(t)b'(t) - 6 + \beta b^2(t) = 0 \tag{42}$$

and since $b'(t) = \frac{db(t)}{dt}$, we have

$$\frac{b(t)db(t)}{(\beta b^2-6)} = -dt \tag{43}$$

which is integrated to give

$$b(t) = \left[\frac{6}{\beta}(1-\exp(-2\beta t))\right]^{1/2} \tag{44}$$

This approximation describes the movement of the diffusion boundary layer in time.

The approximate concentration change with distance and time is obtained by substitution of (44) into (34):

$$c_B = f(\mu) = (1-\mu)^2 = (1-\frac{x}{b(t)})^2 = \left(1 - \frac{x}{\frac{6}{\beta}(1-\exp(-2\beta t))\ ^{1/2}}\right)^2 \qquad (45)$$

The solution is valid until the moving diffusion boundary layer reaches the outer boundary limit b=1:

$$\frac{6}{\beta}(1-\exp(-2\beta t))^{1/2} = 1 \qquad (46)$$

or until

$$t = -\frac{1}{2\beta}\ln(1-\frac{\beta}{6}) \qquad (47)$$

<u>Method (2)</u>: The method of moments with j=2.

Using j=2 (a second order approximation),

$$w_2(\mu) = \mu^{j-1} = \mu \qquad (48)$$

The residual integral is then

$$\int_0^1 w_2 R_E d\mu = \int_0^1 \mu R_E d\mu$$

$$= \int_0^1 \mu[(2\mu-2\mu^2)b'(t)b(t) - 2 + \beta b^2(t)(1-2\mu+\mu^2)]d\mu = 0 \qquad (49)$$

The solution is

$$\int_0^1 w_2 R_E d\mu = \frac{1}{6}b'(t)b(t) - 1 + \beta b^2(t)(\frac{1}{12}) = 0 \qquad (50)$$

The differential equation is solved easily to give the new approximation for b(t)

$$b(t) = \left[\frac{12}{\beta}(1-\exp(-\beta t))\right]^{1/2} \qquad (51)$$

and substitution into (34) gives the new approximate concentration profile:

$$c_B = f(\mu) = \left[1 - \frac{x}{\left[\frac{12}{\beta}(1-\exp(-\beta t))\right]^{1/2}}\right]^2 \qquad (52)$$

<u>Method (3a)</u>: Single point collocation, $w_j(\mu) = (\mu-\mu_j)$, $j-1,2,---N$ where the μ are N points in the integral $(0,b(t))$.

Let us arbitrarily pick 1/2 as a collocation point because of symmetry. Thus we have from (38):

$$b^2R_E = (1-1/2)b(t)b'(t)-2 + \beta b^2(t)(1/4) = 0 \qquad (53)$$

or

$$\frac{b(t)b'(t)}{2} - 2 + \frac{\beta b^2(t)}{4} = 0 \qquad (54)$$

This equation yields

$$b(t) = \left[\frac{8}{\beta}(1-\exp(-\beta t))\right]^{1/2} \qquad (55)$$

and thus

$$c_B = f(\mu) = \left[1 - \frac{x}{\left[\frac{8}{\beta}(1-\exp(-\beta t))\right]^{1/2}}\right]^2 \qquad (56)$$

<u>Method (3b)</u>: Other collocation points might have been chosen. As an example, if we had chosen $\mu = 1/3$ (a highly effective choice in Galerkin collocation methods), we would have the result:

$$c_B = f(\mu) = \left[1 - \frac{x}{\left[\frac{9}{2\beta}(1-\exp(-2\beta t))\right]^{1/2}}\right]^2 \tag{57}$$

Method (4): The Galerkin Method $w_j(\mu) = f\ (\mu) = 1-2\mu+\ \mu^2$

$$\int_0^1 w_j R_E d\mu = \int_0^1 (1-2\mu-\mu^2)[(2\mu-2\mu^2)b(t)b'(t)-2+\beta b^2(t)(1-2\mu+\mu^2)]d\mu=0 \tag{58}$$

Integration and solution of the resulting differential equation yields

$$c_B = f(\mu) = \left[1-\frac{x}{\left[\frac{10}{3\beta}(1-\exp(-4\beta t))\right]^{1/2}}\right]^2 \tag{59}$$

Method (5): Integral method, j=1, but choose as an approximation polynomial the function

$$c_B = f(\mu) = 1-\sin\frac{\pi\mu}{2} \tag{60}$$

instead of equation (34).

Thus

$$f'(\mu) = -\frac{\pi}{2}\cos\frac{\pi}{2}\mu \text{ and } f''(\mu) = \frac{\pi^2}{4}\sin\frac{\pi}{2}\mu \tag{61}$$

so that since

$$R_E = -\mu f'(\mu)b(t)b^{-1}(t)-f''(\mu)b^{-2}(t) + \beta f(\mu) \tag{62}$$

we have

$$R_E=-\mu(-\frac{\pi}{2}\cos\frac{\pi}{2}\mu)b(t)b^{-1}(t)-(\frac{\pi^2}{4}\sin\frac{\pi}{2}\mu)b^{-2}(t)+\beta(1-\sin\frac{\pi}{2}\mu) \tag{63}$$

and

$$\int_0^1 w_j R_E d\mu = \int_0^1 (\frac{\mu\pi}{2}\cos\frac{\pi}{2}\mu)b(t)b^{-1}(t) - (\frac{\pi^2}{4}\sin\frac{\pi}{2}\mu)b^{-2}(t) + \beta$$

$$- \beta\sin\frac{\pi}{2}\mu = 0 \qquad (64)$$

Integration and solution of the resulting differential equation leads to

$$b(t) - \left[\frac{1.571}{0.3634\ \beta}(1-\exp(-2\beta t))\right]^{1/2} \qquad (65)$$

and since $\mu = \frac{x}{b(t)}$,

$$c_B = 1 - \sin\left[\frac{\pi x}{2}\ [\frac{1.571}{0.3634\ \beta}(1-\exp(-2\beta t))]^{-1/2}\right] \qquad (66)$$

Exact solution:

The exact solution to the catalytic boundary value problem has been given by Joslin and Pletcher [9] as

$$[B] = \frac{[A^\circ]}{2}\exp(-X\sqrt{\frac{k}{D}})\operatorname{erfc}(\frac{X}{2\sqrt{DT}} - \sqrt{kT}) + \frac{[A^\circ]}{2}\exp(X\sqrt{\frac{k}{D}})\operatorname{erfc}(\frac{X}{2\sqrt{DT}} + \sqrt{kT}) \quad (67)$$

For comparison of the exact solution with the approximations, we choose $k = 100\ s^{-1}$, $T = 10^{-2}$ s, $D = 10^{-5}\ cm^2 s^{-1}$ and $[A^\circ] = 10^{-3}$ moles 1^{-1}.

We find that if we choose, under these conditions, the boundary $X=L \geq 3 \times 10^{-3}$ cm, that there are no diffusion effects at the boundary under these conditions, therefore the approximate solutions are valid using $L = 3 \times 10^{-3}$ cm. This leads (using the relations in (19)) to the following values of the dimensionless parameters:

$$t = 0.0111 \qquad \beta = 90 \qquad x = \frac{X}{3\times10^{-3}} \qquad c_B = \frac{[B]}{1\times10^{-3}} \qquad (68$$

Table 1 lists the results of each of the approximation methods and the exact solution at various distances from the electrode-solution interface. The accuracy of the collocation method 3b is impressive for regions close to the electrode (or at short times). This method is particularly interesting because of the low order (j=1) of polynomials used for the basis functions. It will be seen in the next section that the use of the more sophisticated orthogonal collocation method leads to continuation of rapid convergence as the approximation order is increased. The approximation is thus capable of giving highly accurate results with little computational effort.

III. ORTHOGONAL COLLOCATION

A. Introduction

The method of orthogonal collocation has as its basis the existence of what is known as interpolating polynomials. If we have a real function $\emptyset(x)$, and we choose n points x_1,x_2---x_n in the interval $[x_1,x_n]$ then it may be shown [10] that there exists some polynomial of degree n-1 which equates to $\emptyset(x)$ at each of the points x_n. If the number of points x_n is increased, a new polynomial may thus be found which describes $\emptyset(x)$ at these new points. Therefore, in the limit, $\emptyset(x)$ can be described at every point. Certain techniques may be used, however, to use a relatively small number of x_n (interpolation points) and still describe $\emptyset(x)$ accurately at all points in the interval. This is most readily accomplished by choosing the proper type of polynomial. The interpolation points are defined by the polynomial chosen, and are usually the roots of that polynomial.

The purpose of orthogonal collocation solutions to partial differential equations is to supply time dependent coefficients to the

Table 1. Comparison of results of the several MWR for the catalytic mechanism. Parameters: $T = 10^{-2}$ s, $[A°] = 10^{-3}$ M, $k = 100$ s^{-1}, $D = 10^{-5}$ $cm^2 s^{-1}$, $\beta = 90$.

	Concentration, species B, $M/10^{-3}$						
ℓ/cm	EXACT	1	2	3a	3b	4	5
2×10^{-6}	.9934	.9944	.9954	.9944	.9936	.9930	.9949
4	.9868	.9889	.9908	.9888	.9872	.9861	.9897
6	.9802	.9834	.9863	.9832	.9808	.9791	.9846
8	.9738	.9779	.9817	.9776	.9745	.9722	.9794
1×10^{-5}	.9673	.9724	.9772	.9721	.9682	.9653	.9743
2	.9355	.9452	.9546	.9445	.9369	.9313	.9486
4	.8749	.8920	.9103	.8906	.8758	.8650	.8974
6	.8177	.8403	.8670	.8383	.8169	.8012	.8464
8	.7639	.7902	.8247	.7876	.7699	.7398	.7959
1×10^{-4}	.7133	.7416	.7835	.7385	.7015	.6809	.7459
2	.4930	.5218	.5934	.5165	.4615	.4230	.5085
4	.2343	.1977	.2924	.1913	.1287	.0906	.2118

various powers of x in the polynomial, thereby providing $\emptyset(x)$ at the interpolation points x_n. In the method described herein, the polynomials chosen are orthogonal shifted Jacobi polynomials, and the interpolation or collocation points are the roots of those polynomials. These choices have been shown [11] to be sufficient to describe solutions to the types of systems of equations that appear in electrochemical diffusion-kinetic problems.

The advantages over finite difference methods are:

(1) Inherent stability of solutions.

(2) Greatly increased savings in computational effort.

(3) Ease in changing programs from one mechanism to another.

A given polynomial of degree n-1, i.e. $P_{n-1}(x)$, may be found if it is possible to solve a set of simultaneous equations in the x_n interpolation points, i.e.

$$\begin{array}{l} \alpha_{n-1}x_1^{n-1} + \alpha_{n-2}x_1^{n-2} + ---- + \alpha_1 x_1 + \alpha_0 = \emptyset(x_1) \\ \alpha_{n-1}x_2^{n-1} + \alpha_{n-2}x_2^{n-2} + ---- + \alpha_1 x_2 + \alpha_0 = \emptyset(x_2) \\ \vdots \qquad\qquad \vdots \qquad\qquad\qquad \vdots \qquad \vdots \qquad \vdots \\ \alpha_{n-1}x_n^{n-1} + \alpha_{n-2}x_n^{n-2} + ---- + \alpha_1 x_n + \alpha_0 = \emptyset(x_n) \end{array} \tag{69}$$

If the determinate in the x^j of the above system is nonzero, then a unique solution exists. Since the x_n are known, and the orthogonal collocation technique will supply the α_j, the solution of the $\emptyset(x_n)$ is straightforward.

It was mentioned above that as the number of interpolation points are increased in the interval, the more accurately the polynomial interpolates to $\emptyset(x)$ at every point. The exact error bound at a point x_m, where $x_m \neq x_n$ is given by the relation

$$\text{Error } [\emptyset;m] \le \frac{1}{n!} \mid Y_n(m) \mid Z_n \qquad (70)$$

where $Y_n(x) = (x-x_1)(x-x_2)---(x-x_n)$, and Z_n is defined if we know that $|\emptyset^{(n)}(x)| < Z_n$ for all x in $[x_1,x_n]$. This assumes that $\emptyset(x)$ has continuous derivatives $\emptyset^{(n)}$ in the interval. It is obvious that as the number n of interpolation points is increased, there is a rapid decrease in the error bounds.

The individual reacting species' spectrochemical absorbances and the total charge consumed during the reaction may be obtained by the time integration of the appropriate concentration profile and the current, respectively. For polynomials, a class of formulas called quadrature formulas [12] exist such that their solutions yield exact values of the integral of the polynomial over the designated interval. With respect to a specified weight function (w(x), the formula

$$\int_{x_1}^{x_n} w(x)\emptyset(x)dx = \sum_{i=1}^{n} Q_i\emptyset(x_i) \qquad (71)$$

represents an exact quadrature formula for the integral of $\emptyset(x)$ with respect to the weight function w(x) over the interval $[x_1,x_n]$. The Q_i are constants that are determined once again by methods dependent on the type of polynomial that has been used to simulate $\emptyset(x)$ in the interval $[x_1,x_n]$. Certain of these quadrature formulas lead to the well known Newton-Cotes, trapezoidal, and Simpsons' rule integration formulas. We will be concerned here with the highly accurate Gauss-Jacobi, Lobatto, and Radau types of quadrature formulas.

B. Discretization of the Differential Equations

We are interested in solving an equation describing electrochemical diffusion phenomenon such as the type

$$\phi_t = \phi_{xx} , \tag{72}$$

where

$$\phi_t = \frac{\delta\phi}{\delta t} , \tag{73}$$

and

$$\phi_{xx} = \frac{\delta^2\phi}{\delta x^2} \tag{74}$$

We assume that there is an interpolation polynomial that will describe $\phi(x,t)$ over the interval $[0,L]$. The constants α in the polynomial described in the previous section, are now functions of time $(\alpha(t))$ since we are dealing with a function ϕ of x and t.

As mentioned, the orthogonal polynomial that we shall use to approximate $\phi(x,t)$ is the shifted Jacobi polynomial. These polynomials, $P_N(\gamma,\delta)_{(x)}$ are described by the orthogonality relation

$$\int_0^1 x^\delta (1-x)^\gamma P_N^{(\gamma,\delta)}(x)\ P_M^{(\gamma,\delta)}(x)\ dx = 0 \tag{75}$$

where $x^\delta(1-x)^\gamma$ is the weight function; γ and $\delta > -1$. Letting $\gamma = \delta = 0$, we have polynomials defined that are suitable for the linear diffusion approximation. These are known as the Legendre polynomials. Since the interpolation polynomial will have order (n-1) where n is the number of interpolation points to be used for calculation of the values of $\phi(x,t)$, the highest power of x in the approximation will be (n-1). The trial function for ϕ may thus be written:

$$\phi_T = \sum_{j=1}^{n+2} \alpha_j(t)x^{j-1} \tag{76}$$

The n+2 terms come from the fact that x = 0 and x = 1 are also roots of the polynomial. In terms of the interpolation (collocation) points, equation (76) becomes:

$$\emptyset(x_i,t) = \sum_{j=1}^{n+2} \alpha_j(t)x_i^{j-1} \text{ , } i = 1,2,\text{---}n+2 \tag{77}$$

This represents a set of n+2 simultaneous equations in the unknown $\emptyset$ and α. Since the α_j represent the elements of an n+2 vector of the time dependent coefficients, the $\emptyset(x_i,t)$ represent the elements of a vector in the $\emptyset(t)$, and the x_i^{j-1} are the elements of an (n+2,n+2) matrix. Equation (77) may be represented in matrix/vector notation after Whiting and Carr [5] as:

$$\overline{\emptyset(t)} = \bar{\alpha}\cdot\bar{\bar{Q}} \tag{78}$$

at fixed x_i, where the

$$Q_{ij} = x_i^{j-1} \tag{79}$$

We now differentiate (77) with respect to x to get the terms in the original equation (76):

$$\frac{d}{dx}(\emptyset(x,t)) = \sum_{i=1}^{n+2} \alpha_j(t) \frac{dx^{j-1}}{dx} \tag{80}$$

or in general,

$$\frac{d^{(k)}}{dx^{(k)}}(\emptyset(x,t)) = \sum_{i=1}^{n+2} \alpha_j(t) \frac{d^{(k)}x^{j-1}}{dx^{(k)}} \tag{81}$$

Specifically then, at the collocation points,

$$\left.\frac{d^{(k)}\emptyset}{dx^{(k)}}\right|_{x=x_i} = \sum_{i=1}^{n+2} \alpha_j(t) \left.\frac{d^{(k)}x^{j-1}}{dx^{(k)}}\right|_{x=x_i} \text{ , } i = 1,2,\text{---}n+2 \tag{82}$$

In matrix/vector notation, for k = 1 and k = 2, this is equivalent to

$$\overline{\frac{d\phi(t)}{dx}} = \overline{\alpha(t)}\cdot\overline{\overline{C}} \qquad (83)$$

and

$$\overline{\frac{d^2\phi(t)}{dx^2}} = \overline{\alpha(t)}\cdot\overline{\overline{D}} \qquad (84)$$

where

$$C_{ij} = \frac{dx_i^{j-1}}{dx} \qquad (85)$$

and

$$D_{ij} = \frac{d^2x_i^{j-1}}{dx^2} \qquad (86)$$

The desired quantities are the $\alpha_j(t)$, and follow from matrix algebra: From (78) we have

$$\overline{\alpha}(t) = \overline{\overline{Q}}^{-1}\ \overline{\phi(t)} \qquad (87)$$

such that

$$\overline{\frac{d\phi(t)}{dx}} = \overline{\overline{Q}}^{-1}\overline{\phi(t)}\cdot\overline{\overline{C}} \quad \text{and} \qquad (88)$$

$$\overline{\frac{d^2\phi(t)}{dx^2}} = \overline{\overline{Q}}^{-1}\overline{\phi(t)}\cdot\overline{\overline{D}} \qquad (89)$$

or

$$\overline{\frac{d\phi(t)}{dx}} = \overline{\overline{A}}\ \overline{\phi(t)}\ , \text{ and} \qquad (90)$$

$$\overline{\frac{d^2\phi(t)}{dx^2}} = \overline{\overline{B}}\ \overline{\phi(t)} \qquad (91)$$

where $\overline{\overline{A}} = \overline{\overline{C}}\ \overline{\overline{Q}}^{-1}$ and $\overline{\overline{B}} = \overline{\overline{DQ}}^{-1}$

For a single collocation point, we have

$$\left.\frac{d\emptyset(t)}{dx}\right|_{x_i} = \sum_{j=1}^{n+2} A_{ij}\emptyset(x_j,t) \tag{92}$$

$$\left.\frac{d^2\emptyset(t)}{dx^2}\right|_{x_i} = \sum_{j=1}^{n+2} B_{ij}\emptyset(x_j,t) \tag{93}$$

Equation (93) may be used immediately in the diffusion equation $\emptyset_t = \emptyset_{xx}$ to yield

$$\left.\frac{d\emptyset}{dt}\right|_{x=x_i} = \sum_{j=1}^{n+2} B_{ij}\emptyset(x_j,t) \tag{94}$$

The diffusion equation is reduced to n+2 simultaneous first order differential equations in n+2 unknowns, $\emptyset(x_j,t)$.

C. Integration

There are many standard methods that may be used for the integration of these simultaneous first order differential equations. We have found [13] that the method of Calliaud and Padmanabhan [14] is probably the fastest and most accurate for diffusion/kinetic equations. This method, known as ISI3, has been shown [15] to be highly effective for the integration of stiff coupled differential equations. The reader is referred to the original literature for details of the derivation; the pertinent features are given here.

In a Runge-Kutta method of integration, many derivative approaches may be taken. In the semi-implicit ISI3 variation, the solution y at the n+1 point to a general differential equation

$$\frac{dy}{dq} = f(y) \tag{95}$$

is given by

$$y_{n+1} = y_n + \sum_{i=1}^{r} R_i l_i \tag{96}$$

where r is the approximation order. The l_i for a third order method are given explicitly by:

$$l_1 = \frac{hf(y_n)}{(I-hc_1B(y_n))} \tag{97}$$

$$l_2 = \frac{hf(y_n+c_1l_1)}{(I-hc_1B(y_n))} \tag{98}$$

and

$$l_3 = \frac{hB(y_n)(c_3l_1+c_4l_2)}{(I-hc_1B(y_n))} \tag{99}$$

Here, B is the Jacobian of f(y) at y_n, h is the integration step size, c_i are constants, and the I are elements of the identity matrix. The R_i and c_i are found by comparing Taylor/power series expansions of equation (95) with the Taylor series expansion of y_{n+1}. Using this procedure with the constraint of making the characteristic root at $(-\infty)$ equal to zero (a necessary condition for accurate integration of stiff equations), the values in Table 2 for the c_i and R_i are obtained.

Table 2

c_1	0.43586659
c_2	0.75
c_3	-0.27468397
c_4	-0.10562709
R_1	16/27
R_2	11/27
R_3	1.

Use of these constants in the above equations gives very accurate integrations of differential equations possessing large differences in subsequent eigenvalues ("stiff" equations). This is the primary method used i: this work, and the Fortran program STIFF3 [15] is given in the appendix. Included also are programs for calculating the roots of an orthogonal polynomial (collocation points), the A and B coefficients for the descretized differential equations, and programs to calculate the quadrature coefficients and perform polynomial integration. The examples there demonstrat the use of the programs.

D. Spline Collocation

When dealing with equations containing large homogeneous rate constants and/or trying to solve equations at very short times, it is obvious that the use of a low collocation approximation order will not be sufficient to simulate the response accurately. The rapidly changing response simply might take place before the first interior interpolation point. This is the same problem that presents itself in finite difference schemes and to which Joslin and Pletcher [2] have treated for that technique. In collocation techniques, there are several good ways to eliminate this problem while maintaining the use of only a few collocation points for the simulation. One such method is the automatic choice of the pre-summation factor as discussed in section (F.b.). Here, another simple option is discussed: the method of global splines.

There are techniques for dividing the interval of interest into many subintervals, and then performing a standard collocation technique on each subinterval [15]. The solutions at the outer boundary of each subinterval become the internal boundary conditions for the next subinterval. The procedure continues until the original outer boundary (or last subinterval) has been treated. The number of equations is raised by a factor equal to the number of subintervals. This technique then becomes similar to simply raising the number of mesh points in a finite difference scheme, although one finds that for similar accuracy between the two methods, this spline technique is still significantly faster.

The diffusion boundary concept provides a very simple but highly efficient spline method. Initially, the original spacing between the collocation points is compressed so that their total spanned interval is just slightly larger than the region where the profile is changing most rapidly. As the width of the change increases, the concentration value is tested at the last internal collocation points (N or N+1). As the concentration there begins to become larger (or smaller if appropriate) than the boundary condition for that species, then the distance between the collocation points is expanded, and the procedure repeated. In this new repetition, solutions at all times less than the time at which the expansion was made are discarded as inaccurate. The procedure is continued until the final desired time has been reached. Solutions of exceptional accuracy are obtained. For instance, the maximum relative error in a catalytic mechanism simulation under a chronoamperometric experiment where the rate constant was 100 s^{-1} and the integration was from 10^{-8} s to 20 s, the maximum relative error was 0.07 percent.

The procedure for implementing this "spline point" method is quite simple to execute. The subinterval is normalized to a (0,1) interval by a variable transformation, and the normal integration procedure is followed. However, the value of the concentration at the outer points is tested continuously as mentioned. The test value is dependent on several factors, including the rate constant, time of integration, number of species, etc. It was found empirically that in using 6 internal collocation points (6th order Legendre polynomial) for the ECE/DISP mechanism under a chronoamperometric experiment, that a branch test at the N+1 point of 0.001 concentration units was sufficient to maintain high accuracy even at very high rate constants (up to 10^6 first order and 10^{10} second order) when compared to finite difference schemes taking computing times up to 10^4 times as long and extremely fine mesh sizes (high memory usage).

Consider the general partial differential equation

$$\frac{\delta \phi}{\delta t} = \frac{\delta^2 \phi}{dx^2} \qquad (100)$$

in the interval (0,1). If we desire to insert a spline point at some value x, such that $0 < x_s < 1$, then we would simply make the variable transformation

$$z = \frac{x}{x_s} \qquad (101)$$

in our equation to renormalize the boundaries. The equation then reads

$$\frac{\delta \phi}{\delta t} = \frac{1}{x_s^2} \frac{\delta^2 \phi}{\delta z^2} \qquad (102)$$

Discretization, then, leads to

$$\left.\frac{\delta\phi}{\delta t}\right|_{z_i} = \frac{1}{x_s^{2}}\sum_{j=1}^{N+2} B_{ij}\phi(x_i,t) \qquad (103)$$

Integration of the set of equations (103) is performed as usual. When the branch is made to a wider interval, x_s is changed and the process repeated.

Spline techniques are given in example 3 in section E.

E. Discretization Examples

Example 1: The reversible charge transfer mechanism under a potential step to a region where the kinetics are diffusion controlled.

$$A \overset{ne^-}{\rightleftharpoons} B \qquad (104$$

The descriptive equations and boundary conditions are:

$$\frac{\delta[A]}{\delta T} = D_A\,\frac{\delta^2[A]}{\delta X^2} \qquad (105$$

$$\frac{\delta[B]}{\delta T} = D_B\,\frac{\delta^2[B]}{\delta X^2} \qquad (106$$

$$[A]_{0,T} = [B]_{\infty,T} = [B]_{X,0} = 0 \qquad (107$$

$$[A]_{X,0} = [A]_{\infty,T} = [A^\circ] \qquad (108$$

$$\left.\frac{d[A]}{dX}\right|_{0,T} = -\left.\frac{d[B]}{dX}\right|_{0,T} \qquad (109$$

Inserting the dimensionless parameters

$$t = \frac{DT}{L^2}\ ,\quad x = \frac{\bar{X}}{L}\ ,\quad \text{and } c_A = \frac{[A]}{[A^\circ]}\ ,$$

we have

$$\frac{\delta c_A}{\delta t} = \frac{\delta^2 c_A}{\delta x^2} \tag{110}$$

$$\frac{\delta c_B}{\delta t} = \frac{\delta^2 c_B}{\delta x^2} \tag{111}$$

$$c_A(0,t) = c_B(1,t) = c_B(x,0) = 0 \tag{112}$$

$$c_A(x,0) = c_A(1,t) = 1 \tag{113}$$

$$\left.\frac{dc_A}{dx}\right|_{x_1=0} = - \left.\frac{dc_B}{dx}\right|_{x_1=0} \tag{114}$$

From (93), we then have

$$\left.\frac{dc_A}{dt}\right|_{x_i} = \sum_{j=1}^{N+2} B_{i,j}c_A(x_j,t) \tag{115}$$

$$\left.\frac{dc_B}{dt}\right|_{x_i} = \sum_{j=1}^{N+2} B_{i,j}c_B(x_j,t) \tag{116}$$

After partial expansion, we obtain

$$\left.\frac{dc_A}{dt}\right|_{x_i} = B_{i,1}c_A(0,t) + B_{i,N+2}c_A(1,t) + \sum_{j=2}^{N+1} B_{i,j}c_A(x_j,t) \tag{117}$$

$$\left.\frac{dc_B}{dt}\right|_{x_i} = B_{i,1}c_B(0,t) + B_{i,N+2}c_B(1,t) + \sum_{j=2}^{N+1} B_{i,j}c_B(x_j,t) \tag{118}$$

The known boundary conditions (112) and (113) for $c_A(0,t)$, $c_A(1,t)$ and $c_B(1,t)$ may be entered at this point to give

$$\left.\frac{dc_A}{dt}\right|_{x_i} = B_{i,N+2} + \sum_{j=2}^{N+1} B_{i,j}c_A(x_j,t) \tag{119}$$

$$\left.\frac{dc_B}{dt}\right|_{x_i} = B_{i,1}c_B(0,t) + \sum_{j=2}^{N+1} B_{i,j}c_B(x_j,t) \tag{120}$$

Note that we must use some other means to eliminate $c_B(0,t)$. This may be done by discretizing the boundary condition (114) with (92).

$$\left.\frac{dc_A}{dx}\right|_{x_1=0} = - \left.\frac{dc_B}{dx}\right|_{x_1=0} \tag{121}$$

$$\sum_{j=1}^{N+2} A_{1,j}c_A(x_j,t) = - \sum_{j=1}^{N+2} A_{1,j}c_B(x_j,t) \tag{122}$$

$$-[A_{1,1}c_A(0,t)+A_{1,N+2}c_A(1,t)+\sum_{j=2}^{N+1} A_{i,j}c_A(x_j,t)] = A_{1,1}c_B(0,t)$$

$$+A_{1,N+2}c_B(1,t)+\sum_{j=2}^{N+1} A_{i,j}c_B(x_j,t) \tag{123}$$

Inserting the known boundary conditions (112) and (113) again for $c_A(0,t)$, $c_A(1,t)$ and $c_B(1,t)$ we have

$$-[A_{1,N+2}+\sum_{j=2}^{N+1} A_{i,j}c_A(x_j,t)] = A_{1,1}c_B(0,t)+\sum_{j=2}^{N+1} A_{i,j}c_B(x_j,t) \tag{124}$$

Solving for $c_B(0,t)$,

$$c_B(0,t) = - \frac{1}{A_{1,1}} [A_{1,N+2}+\sum_{j=2}^{N+1} A_{i,j}(c_A(x_j,t)+c_B(x_j,t))] \tag{125}$$

This explicit value may now be substituted in (120) to yield

$$\left.\frac{dc_B}{dt}\right|_{x_i} = - \frac{B_{i,1}}{A_{1,1}} [A_{1,N+2}+\sum_{j=2}^{N+1} A_{i,j}(c_A(x_j,t)+c_B(x_j,t))]$$

$$+ \sum_{j=2}^{N+1} B_{i,j}c_B(x_j,t) \tag{126}$$

Now the problem has been reduced to the simultaneous solution of 2N equations, i.e. (119) and (126) in order to obtain $c_A(t)$ and $c_B(t)$ at each of the collocation points x_i.

We will depart from the normal format at this point to completely develop the program necessary to solve this particular basic example. In the later examples, only the equations necessary to be programmed will be given.

In this example, we use a Legendre polynomial of order six (six *internal* roots or collocation points). We know the concentration at both boundaries for the A species at all times, and we know the concentration of B at the outer boundary at all times. The concentration of B at the electrode surface may be found easily if we know all of the other A and B concentrations at each internal point as one can see from (125). For a large savings in computational time and programming ease, it will be simpler to simply solve for the six internal concentrations of A and B (12 equations) instead of at all 8 points (16 equations). The procedure calls for the writing of 3 short subroutines, FUN, DFUN, and OUT. In this example, FUN consists of defining the differential equations and returning their values as F(I), I = 1 to 6 for the A species (119), and F(I+6), I = 1 to 6 for the B species. We will use Y(I), I = 1 to 6 for the six concentrations of species A at the internal points, and Y (I+6), I = 1 to 6 as the six internal concentrations of species B. From (119), therefore, we have

$$F(1) = \left.\frac{dc_A}{dt}\right|_{x_1} = B_{2,8} + \sum_{j=1}^{6} B_{2,j+1}c_A(x_j,t) \qquad \text{E1}$$

$$F(2) = \left.\frac{dc_A}{dt}\right|_{x_2} = B_{3,8} + \sum_{j=1}^{6} B_{3,j+1}c_A(x_j,t) \qquad \text{E2}$$

$$\vdots \qquad \vdots$$

$$F(6) = \left.\frac{dc_A}{dt}\right|_{x_6} = B_{7,8} + \sum_{j=1}^{6} B_{7,j+1}c_A(x_j,t) \qquad \text{E3}$$

Note that for programming simplicity, we have changed the i and j indices slightly. Since we are considering the *internal* solutions only, the i and j indices on the right hand side of the equations on the A and B coefficients are simply changed to i + 1 and j + 1. We are simply *refering* to

$$F(I) = \left.\frac{dc_A}{dt}\right|_{x_i} \qquad i = 2,7 \qquad \text{E4}$$

as

$$F(I) = \left.\frac{dc_A}{dt}\right|_{x_i} \qquad i = 1,6 \qquad \text{E5}$$

The j index on the summation thus is changed also from j = 2 to 7 to j = 1 to 6 to maintain consistency.

Partially transforming to FORTRAN language, we have

$$F(I) = B(I+1,8) + \sum_{j=1}^{6} B(I+1,J+1)*Y(J) \qquad \text{E6}$$

To get rid of the summation symbol, we use the following loop

```
     DO 1, I = 1,6
     TDDER1 = 0.
     DO 2 J = 1,6
   2 TDDER1 = TDDER1 + B(I+1,J+1)*Y(J)
   1 F(I) = B(I+1,8) + TDDER1
```

Thus the 6 differential equations are defined in subroutine FUN and will be returned to the main program for simultaneous integration.

Programming for the six differential equations F(I+6), I = 1 to 6 for the six *internal* concentrations Y(I+6) for the B species follows a similar line of reasoning. We also "re-index" for programming simplicity in the same manner. (Replace i and j on right hand side of (126) on the collocation coefficients A and B by i + 1 and j + 1 and change the summation index from j = 2 to 7 to j = 1 to 6.)

$$F(7) = \left.\frac{dc_B}{dt}\right|_{x_1} = -\frac{\Sigma_{2,1}}{A_{1,1}}[A_{1,8}+\sum_{j=1}^{6} A_{2,j+1}(c_A(x_j,t)+c_B(x_j,t))$$

$$+\sum_{j=1}^{6} B_{2,j+1}c_B(x_j,t)] \qquad E7$$

•
•
•

$$F(12) = \left.\frac{dc_B}{dt}\right|_{x_6} = -\frac{B_{7,1}}{A_{1,1}}[A_{1,8}+\sum_{j=1}^{6} A_{7,j+1}(c_A(x_j,t)+c_B(x_j,t))$$

$$+\sum_{j=1}^{6} B_{j,j+1}c_B(x_j,t)] \qquad E8$$

Partial transformation to FORTRAN gives

$$F(I+6) = -B(I+1,1)/A(1,1)*(A(1,8)+\sum_{J=1}^{6} A(I+1,J+1)*(Y(J)+Y(J+6))$$

$$+\sum_{J=1}^{6} B(I+1,J+1)*Y(J+6)$$

Again the summation signs may be eliminated by the following loops

```
    DO 1 I = 1,6
    TDDER2 = 0.
    TDDER3 = 0.
    DO 2 J = 1,6
    TDDER2 = TDDER2+A(I+1,J+1)*(Y(J)+Y(J+6))
  2 TDDER3 = TDDER3+B(I+1,J+1)*Y(J+6)
  1 F(I+6) = -B(I+1)/A(1,1)*(A(1,8)+TDDER2)+TDDER3
```

Thus, the entire subroutine defining both sets of differential equations for the A and B species would appear as follows:

```
( 1)  SUBROUTINE FUN (Y,F)

( 2)  IMPLICIT REAL*8(A-H,O-F)
      (Implicitly invoking double precision mathematics for all real
      variables)
( 3)  DIMENSION Y(16), F(16)
( 4)  COMMON A(30,30), B(30,30), ROOT(30)
      (The collocation coefficients A and B and the polynomial roots
      ROOT have been defined by subroutine JCOBI and DFOPR.  They are
      passed to FUN, when needed, by the COMMON block statement.)

( 5)  DO 1 I = 1,6
( 6)  TDDER1 = 0.
( 7)  TDDER2 = 0.
( 8)  TDDER3 = 0.
( 9)  DO 2 J = 1,6
```

```
      TDDER1 = TDDER1+B(I+1,J+1)*Y(J)
      TDDER2 = TDDER2+A(I+1,J+1)*(Y(J)+Y(J+6))
    2 TDDER3 = TDDER3+B(I+1,J+1)*Y(J+6)
      F(I) = B(I+1,8)+TDDER1
    1 F(I+6) = -B(I+1,1)/A(1,1)*(A(1,8)+TDDER2)+TDDER3
      RETURN
      END
```

The next subroutine that must be defined is DFUN. DFUN is used by the integration subroutine. DFUN must return the values of the derivatives of F(I) and F(I+6) at each one of the collocation points x_i as DF(I) and DF(I+6), I = 1 to 6.

The differentiation is seen to be straightforward upon expansion of one of the F(I) terms, say F(1)

$$F(1) = B_{2,8}+B_{2,2}c_A(x_1,t)+B_{2,3}c_A(x_2,t)+B_{2,4}c_A(x_3,t)+B_{2,5}c_A(x_4,t)$$
$$+B_{2,6}c_A(x_5,t)+B_{2,7}c_A(x_6,t) \qquad \text{E9}$$

We desire

$$\frac{d(F(1))}{dc_A(x_j)}\ , \quad j = 1 \text{ to } 6 \qquad \text{E10}$$

We have, by inspection,

$$DF(1,1) = \frac{d(F(1))}{dc_A(x_1,t)} = B_{2,2} \qquad \text{E11}$$

$$DF(1,2) = \frac{d(F(1))}{dc_A(x_2,t)} = B_{2,3} \qquad \text{E12}$$

$$\begin{matrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{matrix}$$

$$DF(1,6) = \frac{d(F(1))}{dc_A(x_6,t)} = B_{2,7} \qquad \text{E13}$$

In general, we have

$$DF(I,J) = \frac{d(F(I))}{dc_A(x_j,t)} = B(I+1,J+1)$$

These are programmed into DFUN as follows

```
  DO 1 I = 1,6
  DO 1 J = 1,6
1 DF(I,J) = B(I+1,J+1)
```

The F(I=6) are differentiated similarly. For instance,

$$F(7) = -\frac{B_{2,1}}{A_{1,1}}[A_{1,8}+A_{2,2}(c_A(x_1,t)+c_B(x_1,t))+A_{2,3}(c_A(x_2,t)+c_B(x_2,t)) + A_{2,4}(c_A(x_3,t)+c_B(x_3,t)) + A_{2,5}(c_A(x_4,t)+c_B(x_4,t)) + A_{2,6}(c_A(x_5,t)+c_B(x_5,t)) + A_{2,7}(c_A(x_6,t)+c_B(x_6,t) + B_{2,2}c_B(x_1,t) + B_{2,3}c_B(x_2,t) + B_{2,4}c_B(x_3,t) + B_{2,5}c_B(x_4,t) + B_{2,6}c_B(x_5,t) + B_{2,7}c_B(x_6,t)] \qquad E14$$

We desire $\frac{d(F(7))}{dc_B(x_j,t)}$, $j = 1,6$ E15

Note that the $c_B(x_j,t)$ are the Y(I+6), so that we use the nomenclature DF(I+6,J+6) for the B species.

$$DF(7,7) = \frac{d(F(7))}{dc_B(x_1,t)} = -\frac{B_{2,1}}{A_{1,1}} A_{2,2} + B_{2,2} \qquad E16$$

$$DF(7,8) = \frac{d(F(7))}{dc_B(x_2,t)} = -\frac{B_{2,1}}{A_{1,1}} A_{2,3} + B_{2,3} \qquad E17$$

$$\vdots \qquad\qquad \vdots$$

$$DF(7,12) = \frac{d(F(7))}{dc_B(x_6,t)} = -\frac{B_{2,1}}{A_{1,1}} A_{2,7} + B_{2,7} \qquad E18$$

or in general,

$$DF(I+6,J+6) = \frac{d(F(I+1))}{dc_B(x_j,t)} = -\frac{B(I+1,1)}{A(1,1)} *A(I+1,J+1)+B(I+1,J+1)$$

This is programmed exactly the same as the DF(I,J) above. The entire subroutine then appears as follows

```
      SUBROUTINE DFUN (Y,DF)
      IMPLICIT REAL * 8 (A-H,O-Z)
      DIMENSION DF(30,30)
      COMMON A(30,30), B(30,30), ROOT(30)
      DO 1 I = 1,6
      DO 1 J = 1,6
      DF(I,J) = B(I+1,J+1)
    1 DF(I+6,J+6) = -B(I+1,1)/A(1,1)*A(I+1,J+1)+B(I+1,J+1)
      RETURN
      END
```

The OUT subroutine is called at predetermined time increments from the integration subroutine STIFF3. When OUT is called, the O values for the concentration profile (Y(I) and Y(I+6), I = 1 to 6) are available for output. Four parameters are transferred:

X = the current value of the time

Y = the current value of the concentration at each collocation point

IH = number of bisections that occurred before successful integration

Q = stepwise acceleration integration factor.

In general, IH and Q are of little interest for our purposes.

One thing that may be done first in OUT is the calculation of the unknown boundary condition--i.e. the value of the B species at the electrode surface $c_B(0,t)$. For convenience we call this value Y(13). From (125), after re-indexing,

$$Y(13) = c_B(0,t) = -\frac{-1}{A_{1,1}} [A_{1,8} + \sum_{j=1}^{6} A_{i+1,j+1}(c_A(x_j,t)+c_B(x_j,t)) \qquad E19$$

We perform this calculation in OUT since all of the c_A and c_B (Y(I) and Y(I+6)) are available. Partial conversion to FORTRAN gives

```
  DO 1 I = 1,6
  TDDER4 = 0.
  DO 2 J = 1,6
2 TDDER4 = TDDER4+A(I+1,J+1)*(Y(J)+Y(J+6)
1 Y(13) = - 1/A(1,1)*(A(1,8)_TDDER4)
```

The rest of the OUT subroutine may be used for calculating the current or spectrochemical absorbance, etc., as well as defining the output format.

For instance, the flux at the electrode surface is given by

$$\frac{dc_A}{dx}\bigg|_{x_i=0} = \sum_{j=1}^{N+2} A_{1,j}c_A(x_j,t) \qquad \text{E20}$$

Partial expansion gives

$$\frac{dc_A}{dx}\bigg|_{x_1=0} = A_{1,1}c_A(0,t)+A_{1,8}c_A(1,t)+\sum_{j=2}^{N+1} A_{1,j}c_A(x_j,t)$$

$$= A_{1,8}+\sum_{j=2}^{N+1} A_{1,j}c_A(x_j,t) \qquad \text{E21}$$

after insertion of $c_A(0,t) = 0$ and $c_A(1,t) = 1$.

Switching to the new index for programming, we have

$$\text{FLUX} = \text{A(1,8)} + \sum_{\text{J}=1}^{6} \text{A(1,J+1)*Y(J)}$$

Eliminating the summation sign, we have

```
  TDX = 0.
  DO 1 J = 1,6
1 TDX = TDX+A(1,J+1)*Y(J)
  FLUX = A(1,8)+TDX
```

So to calculate the surface concentration of the B species at all times, and to calculate and print the flux as well as the profiles for each species, the subroutine would appear as follows:

```
            SUBROUTINE OUT(X,Y,IH,Q)
            IMPLICIT REAL*8(A-H,O-Z)
            DIMENSION Y(30)
            COMMON A(30,30),B(30,30),ROOT(30)
            DO 1 I = 1,6
            TDX=0.
            TDDER4=0.
            DO 2 J =1,6
            TDDER4=TDDER4+A(I+1,J+1)*(Y(J)+Y(J+6))
       2    TDX=TDX+A(1,J+1)*Y(J)
            Y(13)=-1./A(1,1)*(A(1,8)+TDDER4)
       1    FLUX=A(1,8)+TDX
            WRITE(6,100)X,FLUX,(Y(I),I=1,6),Y(13),(Y(I+6),I=1,6)
     100    FORMAT(' TIME=',E20.15,/,' FLUX=',E20.15,/,4X,
          1 '0.00000000000',3(F16.11,1X),/1X,3(F16.11,1X),3X,
          1 '1.00000000000',//,4X,F16.11,1X,3(F16.11,1X),/,
          1 1X,3(F16.11,1X),3x,'0.00000000000')
            RETURN
            END
```

The main program for the solution of these equations would appear, for example, as follows:

```
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION DIF1(30),DIF2(30),DIF3(30),VECT(30),F(30),FOLD(30)
      DIMENSION YOLD1(30),YA(30),YK1(30),YK2(30),YK3(30)
      DIMENSION DF(30,30),DFOLD(30,30),W(30),Y(30),YOLD(30)
            (The above defines the subroutine variable arrays.)
      COMMON A(30,30),B(30,30),ROOT(30)
      EXTERNAL FUN,DFUN,OUT
      N=6
            (Defines order of polynomial used and hence the number of
            internal collocation roots.)
      NØ=1
      N1=1
            (Specifies that the X-0 and X-1 boundaries will also be roots.
            (see JCOB1))
      AL=0
      BE=0
            (Specifies that α=β=0 and hence an orthogonal Legendre poly-
            nomial will be used (see JCOB1).)
      ND=30
            (Indicates maximum vector dimension size for this program - note
            this is the array sizes in the DIMENSION statements.)
      CALL JCOBI(ND,N,NØ,NL,AL,BE,DIF1,DIF2,DIF3,ROOT)
            (Calculates the roots of the Legendre polynomial, i.e. the X_i.)
      DO 4 I = 1,8
    4 A(I,J)=VECT(J)
            (Calculates the A matrix collocation coefficients and places
            them in the A(I,J) matrix.)
      DO 5 I = 1,8
      CALL DFOPR(ND,N,NØ,N1,I,1,DIF1,DIF2,DIF3,ROOT,VECT)
    5 DO 5 J = 1,8
      B(I,J)=BECT(J)
            (Calculates the B matrix collocation coefficients and places
            them in the B(I,J) matrix.)
      XØ=0.DØ
      X1=20.DØ
            (Sets the starting and ending times for integration.)
      EPS=1.D-Ø6
            (Sets integration error limit at 10^-6.)
      DO 6 I = 1,6
      Y(I)=1.DØ
      Y(I+6)=Ø.DØ
            (Sets initial conditions for A and B species.)
      W(I)=1.DØ
    6 W(I+6) = 1.DØ
            (Sets weight factors for results at 1.)
      HØ=1.D=06
            (Sets initial value for integration interval time step at 10^-6
            units.)
      CALLSTIFF3(12,30,10,FUN,DFUN,OUT,XØ,X1,HØ,EPS,
     1W,Y,YOLD,YOLD1,IP,YA,YK1,YK2,YK3,DF,DFOLD,F,FOLD)
            (Begins integration of the equations contained in FUN.  There
            are 12 equations to be integrated and OUT will be called every
            10 integration steps.)
      STOP
      END
```

These four user defined programs (MAIN, FUN, DFUN, OUT) are then compiled with the six library subroutines STIFF3, JCOB1, DFOPR, SIRK, LU, and BACK (which perform the integrations).

Example 2: The ECE/DISP1 mechanism under a potential step to a region where the kinetics are diffusion controlled.

$$
\begin{array}{lll}
A \xrightleftharpoons{n_1e^-} B & & E_1^\circ \\
B \xrightleftharpoons{k_1} C + H^+ & & \\
C \xrightleftharpoons{n_2e-} D & & E_2^\circ << E_1^\circ \\
B{+}C \xrightleftharpoons{k_2} A{+}D & \text{Homogeneous } e^- \text{ transfer, equilibrium constant } K. & \\
D \xrightleftharpoons[k_4]{k_3} E & &
\end{array}
\qquad (127)
$$

The above mechanism has been investigated by Saveant et al. [16] and Bewick et al. [17].

The equations to be solved are:

$$\frac{\delta[A]}{\delta T} = D_A \frac{\delta^2[A]}{\delta X^2} + k_2[B][C] \qquad (128)$$

$$\frac{\delta[B]}{\delta T} = D_B \frac{\delta^2[C]}{\delta X^2} - k_1[B] - k_2[B][C] \qquad (129$$

$$\frac{\delta[C]}{\delta T} = D_C \frac{\delta^2[C]}{\delta X^2} + k_1[B] - k_2[B][C] \qquad (130$$

$$\frac{\delta[D]}{\delta T} = D_D \frac{\delta^2[D]}{\delta X^2} + k_2[B][C] - k_3[D] + k_4[E] \qquad (131$$

$$\frac{\delta[E]}{\delta T} = D_E \frac{\delta^2[E]}{\delta X^2} + k_3[D] - k_4[E] \qquad (132$$

The boundary conditions are:

$$[A]_{0,T} = [B]_{\infty,T} = [C]_{\infty,T} = [D]_{\infty,T} = [E]_{\infty,T} = 0 \qquad (133)$$

$$[B]_{X,0} = [C]_{X,0} = [D]_{X,0} = [E]_{X,0} = 0 \qquad (134)$$

$$\left.\frac{\delta A}{\delta X}\right|_{0,T} = - \left.\frac{\delta B}{\delta X}\right|_{0,T} \quad , \quad \left.\frac{\delta C}{\delta X}\right|_{0,T} = - \left.\frac{\delta D}{\delta X}\right|_{0,T} \qquad (135)$$

Using the dimensionless parameters $t = \frac{DT}{L^2}$, $x = \frac{X}{L}$, $c_I = \frac{[I]}{[A°]}$, and

$$\alpha = \frac{D}{k_1 L^2} \qquad (136)$$

$$\beta = \frac{k_2}{k_1} [A°] \qquad (137)$$

$$\gamma = \frac{k_3}{k_1} \qquad (138)$$

$$\delta = \frac{k_4}{k_1} \qquad (139)$$

the equations (128-132) and boundary conditions (133-135) are converted to the following dimensionless forms:

$$\frac{\delta c_A}{\delta t} = \frac{\delta^2 c_A}{\delta x^2} + \beta c_B c_C \qquad (140)$$

$$\frac{\delta c_B}{\delta t} = \frac{\delta^2 c_B}{\delta x^2} - c_B - \beta c_B c_C \qquad (141)$$

$$\frac{\delta c_C}{\delta t} = \frac{\delta^2 c_C}{\delta x^2} + c_B - \beta c_B c_C \qquad (142)$$

$$\frac{\delta c_D}{\delta t} = \frac{\delta^2 c_D}{\delta x^2} + \beta c_B c_C - \gamma c_D + \delta c_E \qquad (143)$$

$$\frac{\delta c_E}{\delta t} = \alpha \frac{\delta^2 c_E}{\delta x^2} + \gamma c_D - \delta c_E \tag{144}$$

$$c_A(0,t) = c_B(1,t) = c_C(1,t) = c_D(1,t) = c_E(1,t) = 0 \tag{145}$$

$$c_B(x,0) = c_C(x,0) = c_D(x,0) = c_E(x,0) = 0 \tag{146}$$

$$\left.\frac{dc_A}{dx}\right|_{x_1=0} = - \left.\frac{dc_B}{dx}\right|_{x_1=0} \quad , \quad \left.\frac{dc_C}{dx}\right|_{x_1=0} = - \left.\frac{dc_D}{dx}\right|_{x_1=0} \tag{147}$$

Note that the normal assumption of setting all of the diffusion coefficients equal to each other is not necessary in orthogonal collocation simulations, and is simply done here for brevity.

Precisely the same technique is used as in the first example above to discretize the equations. The results are:

$$\left.\frac{dc_A}{dt}\right|_{x_i} = \alpha[B_{i,N+2} + \sum_{j=2}^{N+1} B_{ij} c_A(x_j,t)] + \beta c_B(x_i,t) c_C(x_i,t) \tag{148}$$

$$\left.\frac{dc_B}{dt}\right|_{x_i} = \alpha[- \frac{B_{i,1}}{A_{1,1}} [A_{1,N+2} + \sum_{j=2}^{N+1} A_{1,j}(c_A(x_j,t)+c_B(x_j,t))]$$

$$+ \sum_{j=2}^{N+1} B_{ij} c_B(x_j,t)] - c_B(x_i,t) - \beta c_B(x_i,t) c_C(x_i,t) \tag{149}$$

$$\left.\frac{dc_C}{dt}\right|_{x_i} = \alpha \sum_{j=2}^{N+1} B_{ij} c_C(x_j,t) + c_B(x_j,t) - \beta c_B(x_i,t) c_C(x_i,t) \tag{150}$$

$$\left.\frac{dc_D}{dt}\right|_{x_i} = \alpha[- \frac{B_{i,1}}{A_{1,1}} [\sum_{j=2}^{N+1} A_{1,j}(c_C(x_j,t)+c_D(x_j,t))] + \sum_{j=2}^{N+1} B_{i,j} c_D(x_j,t)]$$

$$+ \beta c_B(x_i,t) c_C(x_i,t) - \gamma c_D(x_i,t) + \delta c_E(x_i,t) \tag{151}$$

$$\left.\frac{dc_E}{dt}\right|_{x_i} = \alpha[-\frac{B_{i,1}}{A_{1,1}}[\sum_{j=2}^{N+1} A_{1,j}c_E(x_j,t)] + \sum_{j=2}^{N+1} B_{i,j}c_E(x_j,t)]$$

$$+ \gamma c_D(x_i,t) - \delta c_E(x_i,t) \qquad (152)$$

This last equation makes use of the fact that the flux of the species E at the electrode surface is zero, i.e.

$$\left.\frac{dc_E}{dx}\right|_{x_1=0} = \sum_{j=1}^{N+2} A_{1,j}c_E(x_j,t) = 0 \qquad (153)$$

$$A_{1,1}c_E(0,t) + A_{1,N+2}c_E(1,t) + \sum_{j=2}^{N+1} A_{1,j}c_E(x_j,t) = 0 \qquad (154)$$

Since $c_E(1,t) = 0$, we have

$$c_E(0,t) = -\frac{1}{A_{1,1}} \Sigma A_{1,j}c_E(x_j,t) \qquad (155)$$

which is substituted into equation (144) after initial discretization.

Spline Modified Collocation Examples

Example 3: Chronoamperometric single pulse

(a) Reversible charge transfer under diffusion controlled kinetics.

$$A \underset{+ne^-}{\overset{-ne^-}{\rightleftharpoons}} B \qquad (156)$$

$$t = \frac{TD}{L^2} \quad x = \frac{X}{L} \quad z = \frac{x}{x_s} \quad c_A = \frac{[A]}{[A^\circ]} \quad c_B = \frac{[B]}{[A^\circ]} \quad D = D_A + D_B \qquad (157)$$

$$c_A(0,t) = c_B(x,0) = c_B(1,t) = 0 \qquad (158)$$

$$c_A(1,t) = c_A(x,0) = 1 \qquad (159)$$

$$\left(\frac{\delta c_A}{\delta x}\right)_{x_1=0} = -\left(\frac{\delta c_B}{\delta x}\right)_{x_1=0} \tag{160}$$

$$\left.\frac{dc_A}{dt}\right|_{z_i} = \frac{1}{x_s^2}\,[B_{i,N+2}+\sum_{j=2}^{N+1} B_{i,j}c_A(z_j,t)] \tag{161}$$

$$\left.\frac{dc_B}{dt}\right|_{z_i} = \frac{1}{x_s^2}\,[B_{i,1}+\sum_{j=2}^{N+1} B_{i,j}c_B(z_j,t)] \tag{162}$$

(b) Reversible Charge Transfer-Reversible Chemical Reaction (EC_{Rev})

$$A \underset{+ne^-}{\overset{-ne^-}{\rightleftharpoons}} B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C \tag{163}$$

$$t = \frac{TD}{L^2} \quad x = \frac{X}{L} \quad z = \frac{x}{x_s} \quad K = \frac{k_b}{k_f} \quad k = k_f+k_b \quad \beta = \left(\frac{k}{1+K}\right)\left(\frac{L^2}{D}\right)$$

$$c_A = \frac{[A]}{[A^\circ]} \quad c_B = \frac{[B]}{[A^\circ]} \quad c_C = \frac{[C]}{[A^\circ]} \quad D = D_A = D_B = D_C \tag{164}$$

$$c_A(0,t) = c_B(1,t) = c_C(1,t) = c_B(X,0) = c_C(X,0) = 0 \tag{165}$$

$$c_A(1,t) = c_A(X,0) = c_{A^\circ} \tag{166}$$

$$\left(\frac{\delta c_A}{\delta x}\right)_{x_1=0} = -\left(\frac{\delta c_B}{\delta x}\right)_{x_1=0} \qquad \left(\frac{\delta c_C}{\delta x}\right)_{x=0} = 0 \tag{167}$$

$$\left.\frac{dc_A}{dt}\right|_{z_i} = \frac{1}{x_s^2}\,[B_{i,N+2}+\sum_{j=2}^{N+1} B_{i,j}c_A(z_j,t)] \tag{168}$$

$$\left.\frac{dc_B}{dt}\right|_{z_i} = \frac{1}{x_s^2}\left\{-\frac{B_{i,1}}{A_{1,1}}[A_{1,N+2}+\sum_{j=2}^{N+1} A_{1,j}[c_A(z_j,t)+c_B(z_j,t)]] + \sum_{j=2}^{N+1} B_{i,j}c_B(z_j,t)\right\} - \beta[c_B(z_i,t)-Kc_C(z_i,t)] \tag{169}$$

$$\left.\frac{dc_C}{dt}\right|_{z_i} = \frac{1}{x_s^2}\left\{-\frac{B_{i,1}}{A_{1,1}}\sum_{j=2}^{N+1}A_{1,j}c_C(z_j,t) + \sum_{j=2}^{N+1}B_{i,j}c_C(z_j,t)\right\}$$

$$+ \beta[c_B(z_i,t) - Kc_C(z_i,t)] \qquad (170)$$

(c) Reversible Electron Transfer - Dimerization

$$A \underset{+ne^-}{\overset{-ne^-}{\rightleftharpoons}} B \qquad 2B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C \qquad (171)$$

$$t = \frac{TD}{L^2} \quad x = \frac{X}{L} \quad z = \frac{x}{x_s} \quad K = \frac{k_b}{k_f[A°]} \quad k = [A°]k_f + k_b$$

$$\beta = \left(\frac{k}{1+K}\right)\left(\frac{L^2}{D}\right) \qquad (172)$$

$$c_A = \frac{[A]}{[A°]} \quad c_B = \frac{[B]}{[A°]} \quad c_C = \frac{[C]}{[A°]} \quad D = D_A = D_B = D_C \qquad (173)$$

$$c_A(0,t) = c_B(1,t) = c_C(1,t) = c_B(x,0) = c_C(x,0) = 0 \qquad (174)$$

$$c_A(1,t) = c_A(x,0) = c_{A°} \qquad (175)$$

$$\left(\frac{\delta c_A}{\delta t}\right)_{x_1=0} = -\left(\frac{\delta c_B}{\delta x}\right)_{x_1=0} \quad \left(\frac{\delta c_C}{\delta x}\right)_{x=0} = 0 \qquad (176)$$

$$\left.\frac{dc_A}{dt}\right|_{z_i} = \frac{1}{x_s^2}[B_{i,N+2} + \sum_{j=2}^{N+1}B_{i,j}c_A(z_j,t)] \qquad (177)$$

$$\left.\frac{dc_B}{dt}\right|_{z_i} = \frac{1}{x_s^2}\left\{-\frac{B_{i,1}}{A_{1,1}}\left[A_{1,N+2} + \sum_{j=2}^{N+1}[c_A(z_j,t)+c_B(z_j,t)]\right]\right.$$

$$\left. + \sum_{j=2}^{N+1}B_{i,j}c_B(z_j,t)\right\} - \beta[c_B^2(z_i,t) - Kc_C(z_i,t)] \qquad (178)$$

$$\left.\frac{dc_C}{dt}\right|_{z_i} = \frac{1}{x_s^2}[-\frac{B_{i,1}}{A_{1,1}}\sum_{j=2}^{N+1}A_{1,j}c_C(z_j,t) + \sum_{j=2}^{N+1}B_{i,j}c_C(z_j,t)]$$

$$+ \beta[\tfrac{1}{2}c_B^2(z_i,t) - Kc_C(z_i,t)] \qquad (179)$$

(d) Reversible Charge Transfer - Disproportionation

$$A \underset{+ne^-}{\overset{+ne^-}{\rightleftharpoons}} B \qquad A + B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C \tag{180}$$

$$t = \frac{TD}{L^2} \quad x = \frac{X}{L} \quad z = \frac{x}{x_s} \quad K = \frac{k_b}{c_{A^\circ} k_f} \quad k = [A^\circ]k_f + k_b \quad \beta = \left(\frac{k}{1+K}\right)\left(\frac{L^2}{D}\right) \tag{181}$$

$$c_A = \frac{[A]}{[A^\circ]} \quad c_B = \frac{[B]}{[A^\circ]} \quad c_C = \frac{[C]}{[A^\circ]} \tag{182}$$

$$c_A(0,t) = c_B(1,t) = c_C(1,t) = c_B(1,0) = c_C(1,0) = 0 \tag{183}$$

$$c_A(1,t) = c_A(z,0) = [A^\circ] \tag{184}$$

$$\left(\frac{\delta c_A}{\delta x}\right)_{x_1=0} = -\left(\frac{\delta c_B}{\delta x}\right)_{x_1=0} \qquad \left(\frac{\delta c_C}{\delta x}\right)_{x_1=0} = 0 \tag{185}$$

$$\left.\frac{dc_A}{dt}\right|_{z_i} = \frac{1}{x_s^2}\,[B_{i,N+2} + \sum_{j=2}^{N+1} B_{i,j} c_A(z_j,t)] - \beta[c_A(z_i,t)c_B(z_i,t)$$

$$-Kc_C(z_i,t)] \tag{186}$$

$$\left.\frac{dc_B}{dt}\right|_{z_i} = \frac{1}{x_s^2}\left\{-\frac{B_{i,1}}{A_{1,1}}\left[A_{1,N+2} + \sum_{j=2}^{N+1} A_{1,j}[c_A(z_j,t)+c_B(z_j,t)]\right]\right.$$

$$\left. + \sum_{j=2}^{N+1} B_{i,j} c_B(z_j,t)\right\} - \beta[c_A(z_i,t)c_B(z_i,t)-Kc_C(z_i,t)] \tag{187}$$

$$\left.\frac{dc_C}{dt}\right|_{z_i} = \frac{1}{x_s^2}\,[-\frac{B_{i,1}}{A_{1,1}} \sum_{j=2}^{N+1} A_{1,j} c_C(z_j,t) + \sum_{j=2}^{N+1} B_{i,j} c_C(z_j,t)]$$

$$+ \beta[c_A(z_i,t)c_B(z_i,t)-Kc_C(z_i,t)] \tag{188}$$

(e) Reversible Charge Transfer - Catalytic Reaction

(The FORTRAN listings for this example are given in the Appendix.)

$$A \underset{+ne^-}{\overset{-ne^-}{\rightleftharpoons}} B \underset{[M]}{\overset{k}{\rightleftharpoons}} A + C \tag{189}$$

$$t = \frac{kT}{\beta} \quad x = \frac{X}{L} \quad z = \frac{x}{x_s} \quad\quad = \frac{kL^2}{D} \quad D = D_A = D_B = D_C \tag{190}$$

$$c_A = \frac{[A]}{[A^\circ]} \quad c_B = \frac{[B]}{[A^\circ]} \quad c_C = \frac{[C]}{[A^\circ]} \tag{191}$$

$$c_A(0,t) = c_B(1,t) = c_B(z,0) = 0 \tag{192}$$

$$c_A(1,t) = c_A(z,0) = c_B(0,t) = c_A(z_i,t) + c_B(z_i,t) = 1 \tag{193}$$

$$\left(\frac{\delta c_A}{\delta z}\right)_{z_1=0} = -\left(\frac{\delta c_B}{\delta z}\right)_{z_1=0} \tag{194}$$

$$\left.\frac{dc_A}{dt}\right|_{z_i} = \frac{1}{{x_s}^2}\,[B_{i,N+2} + \sum_{j=2}^{N+1} B_{i,j}c_A(z_j,t)] + \beta c_B(z_i,t) \tag{195}$$

$$\left.\frac{dc_B}{dt}\right|_{z_i} = \frac{1}{{x_s}^2}\,[B_{i,1} + \sum_{j=2}^{N+1} B_{ij}c_B(z_j,t)] - \beta c_B(z_i,t) \tag{196}$$

The Jacobians for these two equations are given by:

$$J_{ij} = \frac{\delta\left(\frac{dc_A}{dt}\right)_{z_i}}{\delta z_j} = \frac{1}{{x_s}^2}\,B_{ij} + \beta\delta_{ij} \tag{197}$$

$$J_{ij} = \frac{\delta\left(\frac{dc_B}{dt}\right)_{z_i}}{\delta z_j} = \frac{1}{{x_s}^2}\,B_{ij} - \beta\delta_{ij} \tag{198}$$

where δ_{ij} is the Kronecker delta (=1 if $i = j$; = 0 if $i \neq j$).

Example 4: Spherical Diffusion - Chronoamperometric Single Pulse

(a) Reversible Charge Transfer

$$A \underset{+ne^-}{\overset{-ne^-}{\rightleftharpoons}} B \tag{199}$$

The equations for the system are:

$$\frac{\delta[A]}{\delta T} = D_A \frac{\delta^2[A]}{\delta R^2} + \frac{2}{R}\frac{\delta[A]}{\delta R} \tag{200}$$

$$[A]_{R_0,T} = 0 \tag{201}$$

$$[A]_{\infty,T} = [A]_{R\geq R_0,0} = [A°] \tag{202}$$

$$\left.\frac{\delta[A]}{\delta R}\right|_{R=R_0} = -\left.\frac{\delta[B]}{\delta R}\right|_{R=R_0} \tag{203}$$

where R is the radial distance from the center of the spherical electrode, and R_0 is the radius of the electrode. We choose the following convenient variable transformations:

$$t = \frac{TD}{(L-R_0)^2} \quad r = \frac{R-R_0}{L-R_0} \quad D = D_A \quad c_A = \frac{[A]}{[A°]} \tag{204}$$

Effecting these transformations on equation (200) we obtain

$$\frac{\delta c_A}{\delta t} = \frac{\delta^2 c_A}{\delta r^2} + \frac{2(L-R_0)^2}{r(L-R_0)^2+R_0(L-R_0)}\frac{\delta c_A}{\delta r} \tag{205}$$

or, after simplifying,

$$\frac{\delta c_A}{\delta t} = \frac{\delta^2 c_A}{\delta r^2} + \frac{2}{r+\beta^*}\frac{\delta c_A}{\delta r} \tag{206}$$

where

$$\beta^* = \frac{R_0}{(L-R_0)} \tag{207}$$

Also, we have

$$c_A(0,t) = 0 \tag{208}$$

$$c_A(1,t) = 1 \tag{209}$$

$$\left.\frac{\delta c_A}{\delta r}\right|_{r_1} = - \left.\frac{\delta c_B}{\delta r}\right|_{r_1} \tag{210}$$

The second term containing r and the first partial derivative of the concentration present no problem in orthogonal collocation since we have the discretization for all partial derivatives:

$$\left.\frac{dc_A}{dt}\right|_{r_i} = \sum_{j=1}^{N+2} B_{ij}c_A(r_j,t) + \frac{2}{r_i+\beta^*} \sum_{j=1}^{N+2} A_{ij}c_A(r_j,t) \tag{211}$$

The r is simply replaced by the r_i at each collocation point, where the r_i are the roots of the approximating polynomial (i.e. the x_i or collocation points in the planar cases). We then proceed as before to solve the set of simultaneous differential equations. We reduce the order by 2 by inserting the boundary conditions.

$$\begin{aligned}\left.\frac{dc_A}{dt}\right|_{r_i} &= B_{i,1}c_A(0,t) + B_{i,N+2}c_A(1,t) + \sum_{j=2}^{N+1} B_{ij}c_A(r_j,t) \\ &\quad + \frac{2}{r_i+\beta^*} [A_{i,1}c_A(0,t) + A_{i,N+2}c_A(1,t) + \sum_{j=2}^{N+1} A_{ij}c_A(r_j,t)\end{aligned} \tag{212}$$

Substituting the known values for $c_A(0,t)$ and $c_A(1,t)$, we have

$$\left.\frac{dc_A}{dt}\right|_{r_i} = B_{i,N+2} + \sum_{j=2}^{N+1} B_{ij}c_A(r_j,t) + \frac{2}{r_i+\beta^*} [A_{i,N+2} + \sum_{j=2}^{N+1} A_{ij}c_A(r_j,t) \tag{213}$$

At this point, it is worth considering the effect of choosing orthogonal polynomials other than the Legendre ($\gamma = \delta = 0$ in equation (75)) polynomials. Although beyond the scope of this chapter, it may be shown that a more suitable symmetry for spherical diffusion involving the differential equations used here is one in which we choose $\gamma = 1$ and $\delta = 1/2$.

The collocation points and the A_{ij} and B_{ij} thus are different from the planar diffusion cases. The new values are given by the JCOBI and DFOPR subroutines simply by changing the value for γ(AL) and δ (BE) in the main program.

Although the Legendre polynomials give excellent simulations even in this case, the new choice of γ and δ is even better. For example, integration of the equations and subsequent calculation of the current from

$$I = \frac{nFAD[A^\circ]}{(L-R_0)}\left(\frac{\delta c_A}{\delta r}\right)_{r=R_0} = \frac{nFAD[A^\circ]}{(L-R_0)}\left[A_{1,N+2} + \sum_{j=2}^{N+1} A_{ij} c_A(r_j,t)\right] \tag{214}$$

leads to the following results for $\beta^* = 1 \times 10^{-4}$ in equation (213), and time point $t = 0.03715$:

	$\frac{I_{exact}}{I_{simulated}}$
$\gamma = \delta = 0$ (Legendre)	0.997372
$\gamma = 1$; $\delta = 1/2$	0.999958

Six internal collocation points were used in the integration. The additional accuracy can become important in dealing with very rapidly changing profiles.

Spherical symmetry may also be treated by recognizing that in such a case, the differential equation is also valid for all radial directions, i.e. the equation is valid for R^2 as well as R. One may make the variable transformation

$$u = r^2 \tag{215}$$

in equation (200).

We notice that

$$\frac{dc_A}{dr} = \frac{dc_A}{du}\,\frac{du}{dr} = 2\sqrt{u}\,\frac{dc_A}{du} \tag{216}$$

and

$$\frac{d^2c_A}{dr^2} = \frac{d}{dr}\left(\frac{dc_A}{dr}\right) = \frac{d}{dr}\,(2\sqrt{u}\,\frac{dc_A}{du}) = 2\,\frac{dc_A}{du} + 4u\,\frac{d^2c_A}{du^2}) \tag{217}$$

At the collocation points, equation (211) becomes

$$\left.\frac{dc_A}{dt}\right|_{u_i} = 2\,\frac{dc_A}{du} + 4u\,\frac{d^2c_A}{du^2} + \frac{4u^{1/2}}{u^{1/2+\beta*}}\,\frac{dc_A}{du} \tag{218}$$

with

$$c_A(0,t) = 0 \tag{219}$$

$$c_A(1,t) = c_A(u,0) = 1 \tag{220}$$

$$\left.\frac{\delta c_A}{\delta u}\right|_{u=0} = -\left.\frac{\delta c_B}{\delta u}\right|_{u=0} \tag{221}$$

Discretization of equation (218) with insertion of the boundary conditions yields

$$\begin{aligned}\left.\frac{dc_A}{dt}\right|_{u_i} &= 2\,[A_{1,N+2} + \sum_{j=2}^{N+1} A_{ij}c_A(u_j,t)] + 4u_i\,[B_{i,N+2} + \sum_{j=2}^{N+1} B_{ij}c_A(u_j,t)] \\ &+ \frac{4u_i^{1/2}}{u_i^{1/2+\beta*}}\,[A_{i,N+2} + \sum_{j=2}^{N+1} A_{ij}c_A(u_j,t)] = \frac{6u_i^{1/2}}{u_i^{1/2+\beta*}}\,[A_{i,N+2} \\ &+ \sum_{j=2}^{N+1} A_{ij}c_A(u_j,t)] + 4u_i\,[B_{i,N+2} + \sum_{j=2}^{N+1} B_{ij}c_A(u_j,t)]\end{aligned} \tag{222}$$

The u_i are simply the squares of the values of the collocation points. This set of equations may then be integrated by the standard methods to obtain the concentration profiles. This set of equations is probably more accurate than those previously described, but a detailed comparison has not been made. The polynomials used here again should be those where $\gamma = 1$ and $\delta = 1/2$.

Example 5: Chronopotentiometry - Planar Electrodes

(a) Simple Reversible Charge Transfer

$$A \overset{ne^-}{\rightleftharpoons} B \qquad (223)$$

The diffusion equations and boundary conditions describing this experiment are

$$\frac{\delta[A]}{\delta T} = D_A \frac{\delta^2[A]}{\delta X^2} \qquad (224)$$

$$\frac{\delta[B]}{\delta T} = D_B \frac{\delta^2[B]}{\delta X^2} \qquad (225)$$

$$[A]_{x,0} = [A]_{\infty,t} = [A°] \qquad (226)$$

$$[B]_{x,0} = [B]_{\infty,t} = 0 \qquad (227)$$

$$D = D_A = D_B \qquad (228)$$

$$D_A\left(\frac{\delta[A]}{\delta X}\right)_{X=0} = -D_B\left(\frac{\delta[B]}{\delta X}\right)_{X=0} \qquad (229)$$

$$i = nFA'D_A\left(\frac{\delta[A]}{\delta X}\right)_{X=0} \qquad (230$$

$$E = E° - \frac{RT'}{nF} \ln \frac{[B]_{X=0}}{[A]_{X=0}} \qquad (231$$

Insertion of the usual dimensionless variables for concentration and distance, and the new time variable $t = T/\tau$, τ the transition time, yields:

$$\frac{[A^\circ]\delta c_A}{\tau\ \delta t} = \frac{d[A^\circ]\delta^2 c_A}{L^2 \delta x^2} \tag{232}$$

$$\frac{[A^\circ]\delta c_B}{\tau\ \delta t} = \frac{D[A^\circ]\delta^2 c_B}{L^2 \delta x^2} \tag{233}$$

and after simplifying and letting $\beta = \frac{D\tau}{Z^2}$

$$\frac{\delta c_A}{\delta t} = \beta \frac{\delta^2 c_A}{\delta x^2} \tag{234}$$

$$\frac{\delta c_B}{\delta t} = \beta \frac{\delta^2 c_B}{\delta x^2} \tag{235}$$

The boundary conditions (226-228) are treated similarly and become:

$$c_A(x,0) = 1 \qquad c_A(1,t) = 1 \tag{236}$$

$$c_B(x,0) = 0 \qquad c_B(1,t) = 0 \tag{237}$$

$$\left(\frac{\delta c_A}{\delta x}\right)_{x=0} = -\left(\frac{\delta c_B}{\delta x}\right)_{x_1=0} \tag{238}$$

Discretization of equations (234) and (235) yields

$$\left.\frac{dc_A}{dt}\right|_{x_i} = \beta \sum_{j=1}^{N+2} B_{i,j} c_A(x_j,t) \tag{239}$$

$$\left.\frac{dc_B}{dt}\right|_{x_i} = \beta \sum_{j=1}^{N+2} B_{i,j} c_B(x_j,t) \tag{240}$$

Expanding (239) and (240) partially, we have

$$\left.\frac{dc_A}{dt}\right|_{x_i} = \beta[B_{i,1}c_A(0,t)+B_{i,N+2}c_A(1,t)+\sum_{j=2}^{N+1} B_{i,j}c_A(x_j,t)] \tag{241}$$

$$\left.\frac{dc_B}{dt}\right|_{x_i} = \beta[B_{i,1}c_B(0,t)+B_{i,N+2}c_B(1,t)+\sum_{j=2}^{N+1} B_{i,j}c_B(x_j,t)] \tag{242}$$

Insertion of the boundary conditions (236) and (237) yields

$$\left.\frac{dc_A}{dt}\right|_{x_i} = \beta[B_{i,1}c_A(0,t) + B_{i,N+2} + \sum_{j=1}^{N+2} B_{i,j}c_A(x_j,t)] \tag{243}$$

$$\left.\frac{dc_B}{dt}\right|_{x_i} = \beta[B_{i,1}c_B(0,t) + \sum_{j=1}^{N+2} B_{i,j}c_B(x_j,t)] \tag{244}$$

We need an expression for $c_A(0,t)$ and $c_B(0,t)$ explicitly. From (92) applied to the boundary flux condition (238), we have

$$\left.\frac{dc_A}{dx}\right|_{x_1=0} = \sum_{j=1}^{N+2} A_{1,j}'c_A(x_j,t) \tag{245}$$

$$\left.\frac{dc_B}{dx}\right|_{x_1=0} = \sum_{j=1}^{N+2} A_{1,j}'c_B(x_j,t) \tag{246}$$

Now, equation (230) is also made dimensionless as follows. Since:

$$\left(\frac{\delta[A]}{\delta X}\right)_{X=0} = \frac{[A^\circ]}{L}\left(\frac{dc_A}{dx}\right)_{x_1=0} \quad \text{, we have} \tag{247}$$

$$i = \frac{nFA'D[A^\circ]}{L}\left(\frac{dc_A}{dx}\right)_{x_1=0} = \frac{nFA[A^\circ]D^{1/2}\beta^{1/2}}{\tau^{1/2}} \tag{248}$$

Combining this expression with (245) and (246), we have

$$c_A(0,t) = Q - \sum_{j=2}^{N+1} a_jc_A(x_j,t) \tag{249}$$

$$c_B(0,t) = R - \sum_{j=2}^{N+1} a_jc_B(x_j,t) \tag{250}$$

where

$$\Omega = \frac{1}{A_{1,1}}\left[\frac{i\tau^{\frac{1}{2}}}{nFA[A^{\circ}]D^{\frac{1}{2}}\beta^{\frac{1}{2}}} - A_{1,N+2}\right] \quad , \tag{251}$$

$$R = \frac{1}{A_{1,1}}\left[\frac{i\tau^{\frac{1}{2}}}{nFA[A^{\circ}]D^{\frac{1}{2}}\beta^{\frac{1}{2}}}\right] , \text{ and} \tag{252}$$

$$a_j = \frac{A_{1,j}}{A_{1,1}} \quad , \tag{253}$$

Substitution of (249) and (250) back into (243) and (244), we have

$$\frac{dc_A}{dt} = S_i + \beta \sum_{j=2}^{N+1} b_{i,j}c_A(x_j,t) \quad , \text{ and} \tag{254}$$

$$\frac{dc_B}{dt} = T_i + \beta \sum_{j=2}^{N+1} b_{i,j}c_B(x_j,t) \quad , \text{ where} \tag{255}$$

$$S_i = \beta[B_{i,1}Q + B_{i,N+2}] \quad , \tag{256}$$

$$T_j = \beta\ B_{i,1}R \quad , \text{ and} \tag{257}$$

$$b_{i,j} = -B_{i,1}a_j + B_{i,j} \tag{258}$$

Simultaneous solution of the 2N differential equations by the integration subroutines described previously give accurate and fast approximations to the concentration profiles of A and B as a function of time.

The desired response, potential as a function of time, is given then by equation (231) in the form

$$E = E^{\circ} = \frac{RT'}{nF}\ln\left(\frac{c_B(0,t)}{c_A(0,t)}\right) \quad , \tag{259}$$

with $c_B(0,t)$ and $c_A(0,t)$ being supplied at each time integration step by equations (254) and (255).

(b) EC_{rev} Mechanism

The extension of the mathematics to include kinetic reactions is immediate. Consider (under the same experimental conditions) the EC_{rev} mechanism:

$$A \overset{ne^-}{\rightleftharpoons} B \qquad B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \tag{260}$$

with

$$K = \frac{k_{-1}}{k_1}, \quad \text{and} \tag{261}$$

$$\lambda = (k_1 + k_{-1})\tau \tag{262}$$

The diffusion-kinetic equations and boundary conditions describing the system are:

$$\frac{\delta[A]}{\delta T} = D_A \frac{\delta^2[A]}{\delta X^2} \tag{263}$$

$$\frac{\delta[B]}{\delta T} = D_B \frac{\delta^2[B]}{\delta X^2} - k_1[B] + k_{-1}[C] \tag{264}$$

$$\frac{\delta[C]}{\delta T} = D_C \frac{\delta^2[C]}{\delta X^2} + k_1[B] = k_{-1}[C] \tag{265}$$

$$[A]_{X,0} = [A]_{\infty,T} = [A^*] \tag{266}$$

$$[B]_{X,0} = [B]_{\infty,T} = 0 \tag{267}$$

$$[C]_{X,0} = [C]_{\infty,T} = 0 \tag{268}$$

$$D_A\left(\frac{\delta[A]}{\delta X}\right)_{X=0} = -D_B\left(\frac{\delta[B]}{\delta X}\right)_{X=0} \tag{269}$$

$$D_C\left(\frac{\delta[C]}{\delta X}\right)_{X=0} = 0 \tag{270}$$

Introducing the dimensionless parameters for concentration, time, and distance, the following simplified equations are readily obtained:

$$\frac{\delta c_A}{\delta t} = \beta\frac{\delta^2 c_A}{\delta x^2} \tag{271}$$

$$\frac{\delta c_B}{\delta t} = \beta\frac{\delta^2 c_B}{\delta x^2} - \lambda(1+K)^{-1}(c_B-Kc_C) \tag{272}$$

$$\frac{\delta c_C}{\delta t} = \beta\frac{\delta^2 c_C}{\delta x^2} + \lambda(1+K)^{-1}(c_B-Kc_C) \tag{273}$$

$$c_A(x,0) = c_A(1,t) = 1 \tag{274}$$

$$c_B(x,0) = c_B(1,t) = 0 \tag{275}$$

$$c_C(x,0) = c_C(1,t) = 0 \tag{276}$$

$$\left(\frac{\delta c_A}{\delta x}\right)_{x_1=0} = -\left(\frac{\delta c_B}{\delta x}\right)_{x_1=0} \tag{277}$$

$$\left(\frac{\delta c_C}{\delta x}\right)_{x_1=0} = 0 \tag{278}$$

Equations (271-273) are discretized (93) to yield, after partial expansion and substitution of boundary conditions (274-276),

$$\left.\frac{dc_A(t)}{dt}\right|_{x_i} = \beta[B_{i,1}c_A(0,t) + B_{i,N+2} + \sum_{j=2}^{N+1} B_{ij}c_A(x_j,t)] \quad . \tag{279}$$

$$\left.\frac{dc_B(t)}{dt}\right|_{x_i} = \beta[B_{i,1}c_B(0,t) + \sum_{j=2}^{N+1} B_{i,j}c_B(x_j,t)] -$$

$$\lambda(1+K)^{-1}[c_B(x_i,t) = Kc_C(x_i,t)] \tag{280}$$

$$\left.\frac{dc_C(t)}{dt}\right|_{x_i} = \beta[B_{i,1}c_C(0,t) + \sum_{j=2}^{N+1} B_{i,j}c_C(x_j,t)] +$$

$$\lambda(1+K)^{-1}[c_B(x_i,t) - Kc_C(x_i,t)] \tag{281}$$

The flux relation (277) is identical to the simple reversible charge transfer case, and is discretized in precisely the same manner to yield equations (249) and (250). The flux relation for species C is equation (278), and is discretized as follows:

$$\left(\frac{\delta c_C}{\delta x}\right)_{x=0} = 0 = \sum_{j=1}^{N+2} A_{1,j}c_C(x_j,t)$$

$$= A_{1,1}c_C(0,t)+A_{1,N+2}c_C(1,t)+\sum_{j=2}^{N+1} A_{1,j}c_C(x_j,t)$$

$$= A_{1,1}c_C(0,t) + \sum_{j=2}^{N+1} A_{1,j}c_C(x_j,t) \tag{282}$$

or

$$c_C(0,t) = \sum_{j=2}^{N+1} a_j c_C(x_j,t) \tag{283}$$

where a_j was defined by (253).

Substitution of (249), (250) and (283) into (279), (280), and (281) gives

$$\left.\frac{dc_A}{dt}\right|_{x_i} = S_i + \beta \sum_{j=2}^{N+1} b_{i,j}c_A(x_j,t) \tag{284}$$

$$\left.\frac{dc_B}{dt}\right|_{x_i} = T_i + \beta \sum_{j=2}^{N+1} b_{i,j}c_B(x_j,t) - \lambda(1+K)^{-1}[c_B(x_i,t)-Kc_C(x_i,t)] \tag{285}$$

$$\left.\frac{dc_C}{dt}\right|_{x_i} = \beta \sum_{j=2}^{N+1} b_{i,j}c_C(x_j,t) + \lambda(1+K)^{-1}[c_B(x_i,t)-Kc_C(x_i,t)] \tag{286}$$

As before, simultaneous solution of equations (284) - (286) provides the time dependent concentration profiles. The chronopotentiometric response for this mechanism is still given by equation (259) with the term in parentheses being supplied by equations (249) and (250). The concentration terms in (249) and (250) however, are now calculated numerically from equations (284) - (286).

The elements of the Jacobian matrix are simply the derivatives of equations (254-255) or (284-286) with respect to each x_j. The matrix elements of the Jacobian for the simple reversible electron transfer mechanism then are given by:

$$J_{i,j} = \frac{\delta}{\delta x_j}\left(\frac{dc_A(t)}{dt}\right)\Bigg|_{x_i} \qquad \text{for species A} \tag{287}$$

and

$$J_{i,j} = \frac{\delta}{\delta x_j}\left(\frac{dc_B(t)}{dt}\right)\Bigg|_{x_i} \qquad \text{for species B} \tag{288}$$

These are given explicitly by:

$$J_{i,j} = \frac{\delta}{\delta x_j}\left(S_i + \sum_{j=2}^{N+1} b_{i,j}c_A(x_j,t)\right) \tag{289}$$

for species A, and

$$J_{i,j} = \frac{\delta}{\delta x_j}\left(T_i + \sum_{j=2}^{N+1} b_{i,j}c_B(x_j,t)\right) \tag{290}$$

for species B, or finally,

$$J_{i,j} = b_{i,j} = \frac{-B_{i,1}A_{1,j}}{A_{i,1}} + B_{i,j} \tag{291}$$

for both species.

Similarily, the matrix elements of the Jacobian for the EC_{rev} mechanism are given by:

$$J_{i,j} = \text{equation (291)} \qquad \text{(292)}$$

for species A, and

$$J_{i,j} = \frac{-B_{i,1}A_{1,j}}{A_{1,1}} + B_{i,j} - \lambda K(1+K)^{-1}c_B(x_i,t)\delta_{ij} \qquad \text{(293)}$$

for species B, where δ_{ij} is the Kronecker delta, and

$$J_{i,j} = \frac{-B_{i,1}A_{1,j}}{A_{1,1}} + B_{i,j} - \lambda K(1+K)^{-1}c_C(x_i,t)\delta_{ij} \qquad \text{(294}$$

for species C.

Listed below are the discretized equations for several other commonly occurring electrochemical mechanisms. As above, it is assumed that the diffusion is to a planar electrode in quiet solution, and species A is the only electroactive species present initially.

(c) Catalytic Mechanism

$$A \overset{ne^-}{\rightleftharpoons} B \xrightarrow{k} A + C \qquad \text{(295)}$$

$$\left.\frac{dc_A}{dt}\right|_{x_i} = S_i + \beta \sum_{j=2}^{N+1} b_{i,j}c_B(x_j,t) = k\tau c_B(x_j,t) \qquad \text{(296)}$$

$$\left.\frac{dc_B}{dt}\right|_{x_i} = T_i + \beta \sum_{j=2}^{N+1} b_{i,j}c_B(x_j,t) - k\tau c_B(x_j,t) \qquad \text{(297)}$$

For the E-t profile, equation (231) is used along with equations (249) and (250), the unknown concentration terms being furnished by the simultaneous solution of the 2N equations (296) and (297).

(d) Dimerization

$$A \overset{ne^-}{\rightleftharpoons} B \qquad \text{(298}$$

$$2B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \tag{299}$$

We let

$$\lambda = ([A^\circ]k_1 + k_{-1})\tau, \text{ and} \tag{300}$$

$$K = \frac{k_{-1}}{[A^\circ]k_1} \tag{301}$$

Then

$$\left.\frac{dc_A}{dt}\right|_{x_i} = S_i + \beta \sum_{j=2}^{N+1} b_{i,j}c_A(x_j,t) \tag{302}$$

$$\left.\frac{dc_B}{dt}\right|_{x_i} = T_i + \beta \sum_{j=2}^{N+1} b_{i,j}c_B(x_j,t) - \lambda(1+K)^{-1}(c_B(x_i,t)^2 - Kc_C(x_i,t)) \tag{303}$$

$$\left.\frac{dc_C}{dt}\right|_{x_i} = \sum_{j=2}^{N+1} b_{i,j}c_C(x_j,t) + \lambda(1+K)^{-1}(c_B(x_i,t)^2 - Kc_C(x_i,t)) \tag{304}$$

Once more, equations (231), (249), and (250) are used for the E-t profiles. Note that in this case, 3N equations must be solved because $c_B(0,t)$ depends on the concentration of the C species.

(e) Second Order Reaction

$$A \overset{ne^-}{\rightleftharpoons} B \qquad B + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \tag{305}$$

λ and K are defined as in equations (300) and (301).

$$\left.\frac{dc_A}{dt}\right|_{x_i} = S_i + \beta \sum_{j=2}^{N+1} b_{i,j}c_A(x_j,t) - \lambda(1+K)^{-1}(c_A(x_i,t)c_B(x_i,t) -$$
$$Kc_C(x_i,t)) \tag{306}$$

$$\left.\frac{dc_B}{dt}\right|_{x_i} = T_i + \beta \sum_{j=2}^{N+1} b_{i,j} c_B(x_j,t) + \lambda(1+K)^{-1}(c_A(x_i,t)c_B(x_i,t) -$$

$$Kc_C(x_i,t)) \qquad (307)$$

$$\left.\frac{dc_C}{dt}\right|_{x_i} = \beta \sum_{j=2}^{N+1} b_{i,j} c_C(x_j,t) + \lambda(1+K)^{-1}(c_A(x_i,t)c_B(x_i,t)-Kc_C(x_i,t)) \qquad (308)$$

F. Cyclic Voltammetry - Planar Diffusion

Rieker and Speiser [7] have derived the discretized equations necessary to simulate cyclic voltammetric responses by orthogonal collocation. They are presented in this section. The only difference in the mathematical treatment for this case and chronoamperometry is the statement of the surface concentrations of each species, which of course must be modified to reflect the new potential program. It should be noted that the computer time expended in these cases is approximately the same as Feldberg's finite difference approach.

(a) Discretization of Cyclic Voltammetric Experiments [7]

1. Simple electron transfer $A \underset{+ne^-}{\overset{ne^-}{\rightleftharpoons}} B$

From the original boundary conditions and differential equations, we have the following dimensionless equations:

$$\frac{\delta c_A}{\delta t} = \beta \frac{\delta^2 c_A}{\delta x^2} \qquad (309$$

$$\frac{\delta c_B}{\delta t} = \beta \frac{\delta^2 c_B}{\delta x^2} \qquad (310$$

$$c_A(x,0) = 1,\ c_B(x,0) = 0 \qquad (311$$

$$c_A(1,t) = 1,\ c_B(1,t) = 0 \qquad (312$$

$$\frac{\delta c_A}{\delta x}_{x=0} = -\frac{\delta c_B}{\delta x}_{x=0} \tag{313}$$

$$\frac{c_A(0,t)}{c_B(0,t)} = \theta_{A/B}\, S_\lambda(t) \tag{314}$$

with $\theta_{A/B} = \exp[nF/RT\ (E^\circ_{A/B} - E_{start})]$ (315)

$$S_\lambda(t) = \begin{cases} \exp(-nFvt/RT) = \exp(-at) & t \le t_\lambda \quad (316) \\ \exp(at-2at_\lambda) & t_\tau \le t \le 2t_\lambda \quad (317) \end{cases}$$

t_λ = potential sweep switching time

$a = nFv/RT$ (318)

$v = \frac{dE}{dt}$, the scan rate (319)

$E^\circ_{A/B}$ = the formal potential of the A/B couple

E_{start} = the starting potential of the scan

$\beta = D/aL^2$ (320)

The differential equations (309) and (310) are discretized by the approximation (93) at the collocation points x_i.

$$\left.\frac{dc_A}{dt}\right|_{x_i} = \beta \sum_{j=1}^{N+2} B_{i,j} c_A(x_j,t) \tag{321}$$

$$\left.\frac{dc_B}{dt}\right|_{x_i} = \beta \sum_{j=1}^{N+2} B_{i,j} c_B(x_j,t) \tag{322}$$

Expanding out the two boundary terms at $x = 0$ and $x = 1$, i.e. $x_i = x_0$ and $x_i = x_{N+2}$, we have

$$\left.\frac{dc_A}{dt}\right|_{x_i} = \beta[B_{i,1}c_A(0,t)+B_{i,N+2}c_A(1,t) + \sum_{j=2}^{N+1} B_{i,j}c_A(x_j,t) \tag{323}$$

$$\left.\frac{dc_B}{dt}\right|_{x_i} = \beta[B_{i,1}c_B(0,t)+B_{i,N+2}c_B(1,t)+\sum_{j=2}^{N+1} B_{i,j}c_B(x_j,t) \qquad (324)$$

Substituting the boundary conditions .3 and .4 yield

$$\left.\frac{dc_A}{dt}\right|_{x_i} = \beta[B_{i,1}c_A(0,t)+B_{i,N+2}+\sum_{j=2}^{N+1} B_{i,j}c_A(x_j,t)] \qquad (325)$$

$$\left.\frac{dc_B}{dt}\right|_{x_i} = \beta[B_{i,1}c_B(0,t)+\sum_{j=2}^{N+1} B_{i,j}c_B(x_j,t)] \qquad (326)$$

An explicit value for $c_A(0,t)$ and $c_B(0,t)$ may be derived exactly as was done for previous equations by using the boundary condition (313). The intermediate result

$$A_{1,1}c_A(0,t)+A_{1,N+2}+\sum_{j=2}^{N+1} A_{1,j}c_A(x_j,t) = -[A_{1,1}c_B(0,t)$$

$$\sum_{j=2}^{N+1} A_{1,j}c_B(x_j,t)] \qquad (327)$$

is now modified to include the time dependence of potential and to eliminate one of the unknowns $c_A(0,t)$ or $c_B(0,t)$ by the insertion of the boundary condition (314).

The result is

$$c_A(0,t) = -\frac{\theta_{A/B}S_\lambda(t)}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}\left\{A_{1,N+2}+\sum_{j=2}^{N+1} A_{1,j}[c_A(x_j,t)+c_B(x_j,t)]\right\} \quad (328$$

and

$$c_B(0,t) = -\frac{1}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}\left\{A_{1,N+2}+\sum_{j=2}^{N+1} A_{1,j}[c_A(x_j,t)+c_B(x_j,t)]\right\} \quad (329$$

Insertion of these explicit values of $c_A(0,t)$ and $c_B(0,t)$ into (325) and (326) yield the final set of N differential equations to be solved simultaneously for the N values of $c_A(x_j,t)$ and $c_B(x_j,t)$ (at the collocation points):

$$\left.\frac{dc_A}{dt}\right|_{x_i} = \beta\left\{-\frac{B_{i,1}\theta_{A/B}S_\lambda(t)}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}\left[A_{1,N+2}+\sum_{j=2}^{N+1}A_{1,j}[c_A(x_j,t)+c_B(x_j,t)]\right]\right.$$
$$\left.+\,B_{i,N+2}+\sum_{j=2}^{N+1}B_{i,j}c_A(x_j,t)\right\} \qquad (330)$$

$$\left.\frac{dc_B}{dt}\right|_{x_i} = \beta\left\{-\frac{B_{i,1}}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}\left[A_{1,N+2}+\sum_{j=2}^{N+1}A_{1,j}[c_A(x_j,t)+c_B(x_j,t)]\right]\right.$$
$$\left.+\sum_{j=2}^{N+1}B_{i,j}c_B(x_j,t)\right\} \qquad (331)$$

The concentration profiles are fully developed from the solution of these equations.

The current is given by

$$i = nFA'D\left.\frac{\delta c_A}{\delta X}\right|_{X=0} = nFA'\sqrt{D\beta a}\,[A°]\left.\frac{dc_A}{dx}\right|_{x_1=0} \qquad (332)$$

where A' is the electrode area.

The discretization of $\left.\frac{dc_A}{dx}\right|_{x_1=0}$ follows from

$$\left.\frac{dc_A}{dx}\right|_{x_1=0} = \sum_{j=1}^{N+2}A_{1,j}c_A(x_j,t) \qquad (333)$$

Expansion of (333), insertion of the boundary conditions (312) and (314) with insertion of the result back into (332) yields

$$i = \frac{nFA'\sqrt{D\beta a}\,[A°]}{1+\theta_{A/B}S_\lambda(t)}\left[A_{1,N+2}+\sum_{j=2}^{N+1}A_{1,j}c_A(x_j,t)-\theta_{A/B}S_\lambda(t)\sum_{j=2}^{N+1}A_{1,j}c_B(x_j,t)\right] \qquad (33$$

Since we know the $c_A(x_j,t)$ and $c_B(x_j,t)$ from the solution of (330) and (331), the current as a function of time is immediately found. Since the real time T = at is related to the potential by

$$E = E_{Start} + vT \qquad T_\lambda \geq T \geq 0 \qquad 0 \leq T \leq T_\lambda \qquad (335)$$

$$E = E_{Start} + v(2T_\lambda - T) \qquad T_\lambda \leq T \leq 2T_\lambda \tag{336}$$

or dimensionless time by

$$E = E_{Start} + vat \qquad 0 \leq t \leq t_\lambda \tag{337}$$

$$E = E_{Start} + va(2t_\lambda - t) \qquad t_\lambda \leq t \leq 2t_\lambda \tag{338}$$

The spectroelectrochemical absorbance response $\bar{A}$ is given for each species A and B for cyclic voltammetry by the quadratures

$$\bar{A}_A = \gamma \sum_{i=1}^{N+2} V_i c_{A_i} \tag{339}$$

$$\bar{A}_B = \gamma \sum_{i=1}^{N+2} V_i c_{B_i} \tag{340}$$

where the V_i are given by the weight vector formula solved. In the programs, the $\bar{A}$ are given at any time t simply by using the $c_A(x_i,t)$ or $c_B(x_i,t)$ in (339) or (340) respectively, that correspond to that time t.

2. Reversible electron transfer followed by irreversible first order chemical reaction:

$$A \underset{+ne^-}{\overset{-ne^-}{\rightleftharpoons}} B \xrightarrow{k} C \qquad (EC_{IRR})$$

The dimensionless partial differential equation for species B is now

$$\frac{\delta c_B}{\delta t} = \beta \frac{\delta^2 c_B}{\delta x^2} - \alpha c_B \tag{341}$$

where

$$\alpha = k/a \tag{342}$$

By inspection of the equations for the reversible charge transfer median it is seen that only the equations describing the B species need to be changed to fit the EC_{IRR} case. The changes yield these new equations for B:

$$\left.\frac{dc_B}{dt}\right|_{x_i} = \beta[B_{i,1}c_B(0,t)+B_{i,N+2}c_B(1,t)+\sum_{j=2}^{N+1} B_{i,j}\, c_B(x_j,t)]-\alpha c_B(x_j,t) \qquad (343)$$

$$\left.\frac{dc_B}{dt}\right|_{x_i} = \beta\left\{-\frac{B_{i,1}}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}\left[A_{1,N+2}+\sum_{j=2}^{N+1}A_{1,j}[c_A(x_j,t)+c_B(x_j,t)]\right]\right.$$
$$\left.+\sum_{j=2}^{N+1}B_{i,j}c_B(x_j,t)\right\} - \alpha c_B(x_i,t) \qquad (344)$$

The current is exactly the same in the forward direction as in the previous case since the kinetic term does not affect the flux of species A to the electrode. The spectroelectrochemical absorbance is also identical for species A, but is changed for species B.

$$\begin{array}{lll}
3. & A \underset{+n_1e^-}{\overset{-n_1e^-}{\rightleftharpoons}} B & E^\circ_{A/B} \\
 & B \longrightarrow H^+ + C & k_1 \text{ (first or pseudo first order)} \\
 & H^+ + A \longrightarrow HA^+ & k_2 \text{ (second order)} \\
 & HA^+ \underset{+n_2e^-}{\overset{-n_2e^-}{\rightleftharpoons}} D & E^\circ_{HA^+/D} \\
 & D \longrightarrow 2H^+ + C & k_3 \text{ (first or pseudo first order)}
\end{array} \qquad (345)$$

The results are given below for this complicated mechanism. The reader is referred to the original literature [7] for the details of the derivation.

$$\left.\frac{dc_A}{dt}\right|_{x_i} = \beta\left\{- \frac{B_{i,1}\theta_{A/B}S_\lambda(t)}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}\left[A_{1,N+2}+\sum_{j=2}^{N+1} A_{i,j}[c_A(x_j,t)+c_B(x_j,t)]\right]\right.$$

$$\left. + B_{i,N+2}+\sum_{j=2}^{N+1} B_{i,j}c_A(x_j,t)\right\} - \alpha_2 c_A(x_i,t)c_{H^+}(x_i,t) \tag{346}$$

$$\left.\frac{dc_B}{dt}\right|_{x_i} = \beta\left\{- \frac{B_{i,1}}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}\left[A_{1,N+2}+\sum_{j=1}^{N+1} A_{i,j}[c_A(x_j,t)+c_B(x_j,t)]\right]\right.$$

$$\left. + \sum_{j=1}^{N+1} B_{i,j}c_B(x_j,t)\right\} - \alpha_1 c_B(x_i,t) \tag{347}$$

$$\left.\frac{dc_C}{dt}\right|_{x_i} = \beta[- \frac{B_{i,1}}{A_{1,1}}\sum_{j=2}^{N+1} A_{1,j}c_C(x_j,t)+\sum_{j=2}^{N+1} B_{i,j}c_C(x_j,t)]$$

$$+ \alpha_1 c_B(x_i,t)+\alpha_3 c_D(x_i,t) \tag{348}$$

$$\left.\frac{dc_{H^+}}{dt}\right|_{x_i} = \beta[- \frac{B_{i,1}}{A_{1,1}}\sum_{j=2}^{N+1} A_{1,j}c_{H^+}(x_j,t)+\sum_{j=2}^{N+1} B_{i,j}c_{H^+}(x_j,t)]$$

$$+ \alpha_1 c_B(x_i,t)+2\alpha_3 c_D(x_i,t)-\alpha_2 c_A(x_i,t)c_{H^+}(x_i,t) \tag{349}$$

$$\left.\frac{dc_{HA^+}}{dt}\right|_{x_i} = \beta\left\{- \frac{B_{i,1}\theta_{HA^+/D}S_\lambda(t)}{A_{1,1}[1+\theta_{HA^+/D}S_\lambda(t)]}\sum_{j=2}^{N+1} A_{1,j}[c_{HA^+}(x_j,t)+c_D(x_j,t)]\right.$$

$$\left. + \sum_{j=2}^{N+1} B_{i,j}c_{HA^+}(x_j,t)\right\} + \alpha_2 c_A(x_i,t)c_{H^+}(x_i,t) \tag{350}$$

$$\left.\frac{dc_D}{dt}\right|_{x_i} = \beta\left\{- \frac{B_{i,1}}{A_{1,1}[1+\theta_{HA^+/D}S_\lambda(t)]}\sum_{j=2}^{N+1} A_{1,j}[c_{HA^+}(x_j,t)+c_D(x_j,t)]\right.$$

$$\left. + \sum_{j=2}^{N+1} B_{i,j}c_D(x_j,t)\right\} - \alpha_3 c_D(x_i,t) \tag{351}$$

In the above equations,

$$\alpha_1 = k_{1/a} \tag{352}$$

$$\alpha_2 = k_2[A^\circ]/a \tag{353}$$

$$\alpha_3 = k_{3/a} \tag{354}$$

$$\theta_{HA^+/D} = \exp\ [nF/RT(E^\circ_{HA^+/D} - E_{Start}')] \tag{355}$$

The current is given by

$$i = FA\ D\beta a\ [A^\circ]\ [n_1 \frac{dc_A}{dx}\bigg|_{x_1=0} + n_2 \frac{dc_{HA^+}}{dx}\bigg|_{x_1=0}] \tag{356}$$

or

$$\begin{aligned} i = FA\ D\beta a[A^\circ]\Bigg\{ & \frac{n_1}{1+\theta_{A/B}S_\lambda(t)}\ [A_{1,N+2} + \sum_{j=2}^{N+1} A_{1,j}c_A(x_j,t) \\ & - \theta_{A/B}S_\lambda(t) \sum_{j=2}^{N+1} A_{1,j}c_B(x_j,t)] + \frac{n_2}{1+\theta_{HA^+/D}S_\lambda(t)}\ [\sum_{j=2}^{N+1} A_{1,j}c_{HA^+}(x_j,t) \\ & - \theta_{HA^+/D}S_\lambda(t) \sum_{j=2}^{N+1} A_{1,j}c_D(x_j,t)]\Bigg\} \end{aligned} \tag{357}$$

(b) Optimization of the Dimensionless Parameter β

The dimensionless parameter β that is introduced into the collocation equations must be chosen such that (a) it is not so low as to distort the simulations, and (b) it is not so high as to cause oscillation at a collocation point. Since the parameter β is a function of the dimensionless rate constant, simply choosing a fixed value will not give the best results for all possible values of rate constants. Speiser [18] has recognized this fact and has developed an analysis of the problem based on stability criterion for the particular integration method used. An optimal value of β then is calculated in the program itself.

A numerical integration is "stable" if the difference between the true and approximate solution decreases, while the condition

$$\frac{\delta f(x,y)}{\delta dy} < 0 \qquad (358)$$

where

$$f(x,y) = \frac{dy}{dx} \qquad (359)$$

holds.

If we are referring to a system of N ordinary differential equations, then y, f(x,y), and $\frac{f(x,y)}{dy}$ represent column vectors with N components. For example, in the EC_{IRR} mechanism, the components of the vector

$$\frac{\delta\left(\frac{dc(x_i,t)}{dt}\right)}{\delta c(x,t)} \qquad (360)$$

are the partial differentials of equation (330) and (344) and are

$$\frac{\delta\left(\frac{dc(x_i,t)}{dt}\right)}{\delta c(x_i,t)} = \begin{cases} -\frac{B_{i,1}\theta_{A/B}S_\lambda(t)}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}\cdot A_{1,i}+B_{i,i} & i = 2, \ldots N+1 \qquad (361) \\ -\frac{B_{i,1}}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}\cdot A_{1,i}+B_{i,i}+\alpha & i=2, \ldots N+1 \qquad (362) \end{cases}$$

It is noted that for the values of the $A_{i,j}$ and $B_{i,j}$ found in program DFOPR (see Appendix), the expressions (362) and (363) are always negative, and hence always stable.

For the Hammings predictor-corrector method, such as that found in IBM's SSP library, Speiser points out that a particular stability criterion for our problems is

$$h < \frac{0.65}{\dfrac{\delta\left(\dfrac{dc(x,t)}{dt}\right)}{\delta c(x_j,t)}} \tag{363}$$

where h is the integration interval step.

(361) and (362) may then be combined with (363) to develop values for β for which the integration of the differential equation using the Hammings predictor corrector method is stable.

The results are

$$\beta < \begin{cases} \dfrac{0.65}{h\left|-\dfrac{B_{i,1}\theta_{A/B}S_\lambda(t)}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}A_{1,i}+B_{i,i}\right|}, \quad i=2,\ldots N+1 & (364) \\[2em] \dfrac{0.65-h\alpha}{h\left|-\dfrac{B_{i,1}}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}A_{1,i}+B_{i,i}\right|}, \quad i=2,\ldots N+1 & (365) \end{cases}$$

The results for the complicated mechanism (345) are found similarly, and are found to be:

$$\beta < \begin{cases} \dfrac{0.65 - h\alpha_2 c_{H^+}(x_i,t)}{h\left|-\dfrac{B_{i,1}\theta_{A/B}S_\lambda(t)}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}A_{1,i}+B_{i,i}\right|}, \quad i=2,\ldots N+1 \\[2em] \dfrac{0.65 - h\alpha_1}{h\left|-\dfrac{B_{i,1}}{A_{1,1}[1+\theta_{A/B}S_\lambda(t)]}A_{1,i}+B_{i,i}\right|}, \quad i=2,\ldots N+1 \\[2em] \dfrac{0.65}{h\left|-\dfrac{B_{i,1}}{A_{1,1}}A_{1,i}+B_{i,i}\right|}, \quad i=2,\ldots N+1 \\[2em] \dfrac{0.65-h\alpha_3}{h\left|-\dfrac{B_{i,1}}{A_{1,1}[1+\theta_{HA^+/D}S_\lambda(t)]}A_{1,i}+B_{i,i}\right|}, \quad i=2,\ldots N+1 \end{cases}$$

$$\left\lfloor \begin{array}{ll} \dfrac{0.65}{h\left|-\dfrac{B_{i,1}\theta_{HA^+/D}S_\lambda(t)}{A_{1,1}[1+\theta_{HA^+/D}S_\lambda(t)]}A_{1,i}+B_{i,i}\right|} & , \ i=2, \ldots N+1 \\ \\ \dfrac{0.65-h\alpha_2 c_A(x_i,t)}{h\left|-\dfrac{B_{i,1}}{A_{1,1}}A_{1,i}+B_{i,i}\right|} & , \ i=2, \ldots N+1 \end{array}\right. \qquad (366)$$

Thus using the inequalities defined in (365) and (365), and in (366) one may optimize β such that the integrations approach the highest possible accuracy without going into oscillation. Speiser notes that negative values of β cannot be used since the current is proportional to $\beta^{1/2}$, so negative values of β must be eliminated for a given set of kinetic parameters by decreasing h until β becomes positive.

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APPENDIX

Subroutine JCOBI: Calculates roots and derivatives of a polynomial.

*Usage: CALL JCOBI (ND, N, N0, N1, ALFA, BETA, DIF1, DIF2, DIF3, ROOT)

Input parameters:

Integer ND: The dimension of vectors DIF1, DIF2, DIF3, and ROOT. These vectors should be dimensioned in a DIMENSION statement in the calling program. ND should be at least as large as the total number of interpolation points.

Integer N: The degree of the Jacobi polynomial (i.e. the number of interior interpolation points).

Integer N0: Control index. If N1=1, x=0 is used as a collocation point; if N0=0, x=0 is not used.

Integer N1: Control index. If N1=1, x=1 is used as a collocation point; if N1=0, x=1 is not used. Normally, both N0 and N1 are set to 1.

Real ALFA, BETA: Determines the symmetry of polynomial chosen. (See equation (75)). The Legendre polynomials described herein have ALFA=BETA=0 for linear diffusion problems.

Output parameters:

Real Array Root: One dimensional vector containing on exit of the subroutine the N+N0+N1 roots or zeros of the chosen polynomial.

Real Array DIF1, DIF2, and DIF3: Three one dimensional arrays containing on exit from JCOBI the first, second, and third derivatives of the polynomials at the roots of the polynomial.

*Please note that in order to retain Villaden's original program, ALFA and BETA are used here for γ and δ in the text (equation (75)).

```
      SUBROUTINE JCOBI(ND,N,NO,N1,AL,BE,DIF1,DIF2,DIF3,ROOT)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION DIF1(ND),DIF2(ND),DIF3(ND),ROOT(ND)
      AB=AL+BE
      AD=BE-AL
      AP=BE*AL
      DIF1(1)=(AD/(AB+2)+1)/2
      DIF2(1)=0.
      IF(N.LT.2)GO TO 15
      DO 10 I=2,N
      Z1=I-1
      Z=AB+2*Z1
      DIF1(I)=(AB*AD/Z/(Z+2)+1)/2
      IF(I.NE.2)GO TO 11
      DIF2(I)=(AB+AP+Z1)/Z/Z/(Z+1)
      GO TO 10
   11 Z=Z*Z
      Y=Z1*(AB+Z1)
      Y=Y*(AP+Y)
      DIF2(I)=Y/Z/(Z-1)
   10 CONTINUE
   15 X=0.
      DO 20 I=1,N
   25 XD=0.
      XN=1.
      XD1=0.
      XN1=0.
      DO 30 J=1,N
      XP=(DIF1(J)-X)*XN-DIF2(J)*XD
      XP1=(DIF1(J)-X)*XN1-DIF2(J)*XD1-XN
      N1=1
      XD=XN
      XD1=XN1
      XN=XP
   30 XN1=XP1
      ZC=1.
      Z=XN/XN1
      IF(I.EQ.1)GO TO 21
      DO 22 J=2,I
   22 ZC=ZC-Z/(X-ROOT(J-1))
   21 Z=Z/ZC
      X=X-Z
      IF(DABS(Z).GT.1.D-09)GO TO 25
      ROOT(I)=X
      X=X+.0001
   20 CONTINUE
      NT=N+NO+N1
      IF(NO.EQ.0)GO TO 35
      DO 31 I=1,N
      J=N+1-I
   31 ROOT(J+1)=ROOT(J)
      ROOT(1)=0
   35 IF(N1.EQ.1)ROOT(NT)=1.
      DO 40 I=1,NT
      X=ROOT(I)
      DIF1(I)=1.
      DIF2(I)=0.
      DIF3(I)=0.
      DO 40 J=1,NT
      IF(J.EQ.I)GO TO 40
      Y=X-ROOT(J)
      DIF3(I)=Y*DIF3(I)+3*DIF2(I)
      DIF2(I)=Y*DIF2(I)+2*DIF1(I)
      DIF1(I)=Y*DIF1(I)
   40 CONTINUE
      RETURN
      END
```

Subroutine DFOPR: Calculates the A_{ij}, B_{ij}, and Q_i interpolation and quadrature weights.

Usage: CALL DFOPR (ND, N, N0, N1, I ID, DIF1, DIF2, DIF3, ROOT)

Input parameters:

Integer ND,
N, N0, N1: Same as in JCOBI

Integer I: Index of the root at which A_{ij}, B_{ij}, or Q_i is being evaluated.

Integer ID: Control index. ID=1 causes calculation of A_{ij}; ID=2 is for the B_{ij}; ID=3 is for the Q_i.

Real Array
ROOT, DIF1,
DIF2, DIF3: The vectors calculated in JCOBI.

Output parameters:

Real Array
VEC: The vector containing the A_{ij}, B_{ij}, or Q_i at the given root upon exit.

```
      SUBROUTINE DFOPR(ND,N,NO,N1,I,ID,DIF1,DIF2,DIF3,ROOT,VECT)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION DIF1(ND),DIF2(ND),DIF3(ND),ROOT(ND),VECT(ND)
      NT=N+NO+N1
      IF(ID.EQ.3)GO TO 10
      DO 20 J=1,NT
      IF(J.NE.I)GO TO 21
      IF(ID.NE.1)GO TO 5
      VECT(I)=DIF2(I)/DIF1(I)/2
      GO TO 20
    5 VECT(I)=DIF3(I)/DIF1(I)/3
      GO TO 20
   21 Y=ROOT(I)-ROOT(J)
      VECT(J)=DIF1(I)/DIF1(J)/Y
      IF(ID EQ.2)VECT(J)=VECT(J)*(DIF2(I)/DIF1(I)-2/Y)
   20 CONTINUE
      GO TO 50
   10 Y=0.
      DO 25 J=1,NT
      X=ROOT(J)
      AX=X*(1-X)
      IF(NO EQ.0)AX=AX/X/X
      IF(N1.EQ.0)AX=AX/(1-X)/(1-X)
      VECT(J)=AX/DIF1(J)**2
   25 Y=Y+VECT(J)
      DO 60 J=1,NT
   60 VECT(J)=VECT(J)/Y
   50 RETURN
      END
```

Subroutine STIFF3: Performs the integration of single or coupled systems of stiff differential equations by the ISI3 method.

Usage: CALL STIFF3 (N, ND, NPRINT, FUN, DFUN, OUT, X0, X1, H0, EPS, W, Y, YOLD, YOLD1, IP, YA, YK1, YK2, YK3, DF, DFOLD, F, FOLD)

IP is an internally used integer vector and should be dimensioned as such in the calling program with dimension ND. The following are real vectors of dimension ND and should also be dimensioned in the calling program as such: W, Y, YOLD, YOLD1, YA, YK1, YK2, YK3, F, FOLD. All but W and Y are internally used only. DF and DFOLD are internally used arrays of dimension (NDXND) and should be designated as such also.

FUN, DFUN, and OUT are external subroutines called from STIFF3 and should appear in an EXTERNAL statement in the calling program.

Input parameters:

Integer N: Number of equations to be integrated.

Integer ND: As in JCOBI - main program array dimension.

Integer NPRINT: Printing interval. The solution is printed at every NPRINT step. The solution is always printed at X1.

Real X0, X1: The limits of time over which the differential equations are integrated.

Real H0: Suggested initial half-steplength for integration. On exit, H0 contains suggested value for half-steplength for continued integration beyond X1.

Real Vector W and real EPS: These parameters determine subsequent steplengths for integrations. They are part of the automatic step size selection part of the program. Suggested values are given in the examples. Further information is given in the original literature.

Real Vector Y: Vector of concentration solutions at the collocation points. Initially, these are specified as the boundary conditions (t=0) for each species.

STIFF3 also uses three internal subroutines, SIRK3, LU and BACK. The listings for these are included.

```
      SUBROUTINE SIRK3(N,ND,FUN,IPIV,F,Y,YK1,YK2,YK3,DF,H)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION F(ND),Y(ND),YK1(ND),YK2(ND),YK3(ND),IPIV(ND),DF(ND,ND)
      DIMENSION R(4)
      DATA A,R/.43586652150845899D0,1.0376094961318590O, .834930483852637
     170D0,-.6302020887244523D0,-.2423378912600452/
      DO 5 I=1,N
      DO 6 J=1,N
      DF(I,J)=-H*A*DF(I,J)
      IF(DABS(DF(I,J)).LT.1.D-12)DF(I,J)=0.
    6 CONTINUE
    5 DF(I,I)=DF(I,I)+1.
      CALL LU(ND,N,IPIV,DF)
      CALL BACK(ND,N,IPIV,DF,F)
      DO 8 I=1,N
      YK1(I)=H*F(I)
    8 YK2(I)=Y(I)+.75D0*YK1(I)
      CALL FUN(YK2,F)
      CALL BACK(ND,N,IPIV,DF,F)
      DO 9 I=1,N
      YK2(I)=H*F(I)
      Y(I)=Y(I)+R(1)*YK1(I)+R(2)*YK2(I)
    9 YK2(I)=R(3)*YK1(I)+R(4)*YK2(I)
      CALL BACK(ND,N,IPIV,DF,YK2)
      DO 10 I=1,N
   10 Y(I)=Y(I)+YK2(I)
      RETURN
      END
      SUBROUTINE STIFF3(N,ND,NPRINT,FUN,DFUN,OUT,XO,X1,HO, EPS,W,Y,YOLD,
     1YOLD1,IP,YA,YK1,YK2,YK3,DF,DFOLD,F,FOLD)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION IP(ND),Y(ND),YOLD(ND),YOLD1(ND),YA(ND),YK1(ND),YK2(ND)
      DIMENSION YK3(ND),W(ND),F(ND),FOLD(ND),DF(ND,ND),DFOLD(ND,ND)
      ICON=O
      NOUT=O
      X=XO
      H=HO
      IF(XO + 2.*H .LT.X1)GO TO 1
 2    H=(X1-X)/2
      ICON=1

 1    IF (ICON .EQ. O .AND. X+4*H .GT. X1)H=(X1-X)/4
      CALL FUN(Y,F)
      CALL DFUN(Y,DF)
      IHA=-1
      DO 30 I=1,N
      YOLD(I)=Y(I)
      FOLD(I)=F(I)
      DO 30 J=1,N
 30   DFOLD(I,J)=DF(I,J)
 37   CALL SIRK3(N,ND,FUN,IP,F,Y,YK1,YK2,YK3,DF,2*H)
      DO 35 I=1,N
      YA(I)=Y(I)
      Y(I)=YOLD(I)
      F(I)=FOLD(I)
      DO 35 J=1,N
 35   DF(I,J)=DFOLD(I,J)
 38   IHA=IHA+1
      CALL SIRK3(N,ND,FUN,IP,F,Y,YK1,YK2,YK3,DF,H)
      CALL FUN(Y,F)
      CALL DFUN(Y,DF)
      DO 40 I=1,N
 40   YOLD1(I)=Y(I)
      CALL SIRK3(N,ND,FUN,IP,F,Y,YK1,YK2,YK3,DF,H)
      E=O.
      DO 41 I=1,N
      ES=W(I)*DABS(YA(I)-Y(I))/(1.+DABS(Y(I)))
      IF(ES .GT. E)E=ES
 41   CONTINUE
      Q=E/EPS
      QA=(4.*Q)**.25
      IF(Q .LE. 1.) GO TO 48
      DO 45 I=1,N
      YA(I)=YOLD1(I)
      F(I)=FOLD(I)
      Y(I)=YOLD(I)
      DO 45 J=1,N
 45   DF(I,J)=DFOLD(I,J)
      H=H/2
      ICON=O
      GO TO 38
 48   DO 49 I=1,N
 49   Y(I)=Y(I)+(Y(I)-YA(I))/7.DO
      X=X+2*H
      QA=1./(QA+1.D-10)
      IF(QA .GT. 3.)QA=3.
      H=QA*H
      NOUT=NOUT+1
      IF((NOUT/NPRINT)*NPRINT .EQ. NOUT .OR. ICON .EQ. 1)CALL OUT(X,Y ,I
     1HA,QA)
      IF(ICON .EQ. 1) GO TO 187
      HO:
      IF(x+2.*H .LT. X1) GO TO 1
      GO TO 2
 187  RETURN
      END
      SUBROUTINE LU(ND,N,IPIV,A)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION IPIV(ND),A(ND,ND)
      IPIV(N)=N
      N1=N-1
      DO 10 I=1,N1
      X=A(I,I)
      IF(X.LT.O.)X=-X
      IPIV(I)=I
      I1=I+1
      DO 11 J=I1,N
      Y=A(J,I)
      IF(Y.LT.O.)Y=-Y
      IF(Y.LE.X)GO TO 11
      X=Y
      IPIV(I)
   11 CONTINUE
      IF(IPIV(I).EQ.I)GO TO 14
      K=IPIV(I)
      DO 12 J=I,N
      X=A(I,J)
      A(I,J)=A(K,J)
   12 A(K,J)=X
   14 DO 10 J=I1,N
      X=-A(J,I)/A(I,I)
      A(J,I)=X
      DO 10 K=I1,N
   10 A(J,K)=A(J,K)+X*A(I,K)
      RETURN
      END
      SUBROUTINE BACK(ND,N,IPIV,A,V)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION IPIV(ND),A(ND,ND),V(ND)
      N1=N-1
      DO 10 I=1,N1
      I1=I+1
      K=IPIV(I)
      IF(K.EQ.I)GO TO 11
      X=V(I)
      V(I)=V(K)
      V(K)=X
   11 DO 10 J=I1,N
   10 V(J)=V(J)+A(J,I)*V(I)
      V(N)=V(N)/A(N,N)
      DO 15 II=2,N
      I=N+1-II
      I1=I+1
      DO 16 J=I1,N
   16 V(I)=V(I)-A(I,J)*V(J)
   15 V(I)=V(I)/A(I,I)
      RETURN
      END
C
C
```

Subroutine FUN (Y,F): User supplied subprogram for defining the differential equations. F is the vector of the right hand side of the differential equations. (See examples.)

Subroutine DFUN (Y, DF): User supplied subroutine for evaluation of the Jacobian of the differential equations. DF is the Jacobian matrix with elements DF (I,J)=F(i)/Y(J). (See examples.)

Subroutine OUT (X, Y, IH, Q): User supplied subprogram for output.
X: Current value of time.
Y: Current value of concentration vector at each collocation point.
IH: Number of bisections (unsuccessful integrations) in the current integration step.
Q: Steplength acceleration factor.

STIFF3 also uses three internal subroutines: SIRK3, LU, and BACK. No extra programming allowances need be made for their use.

The first set of listings following are MAIN, FUN, OUT, and DFUN for the catalytic mechanism including spectrochemical absorbances as described in Section E, example 3e. The second set of listings are for spherical symmetry simple electron transfer including the current calculation as described in Section E, example 4a.

```
C
C
C
C
C ** PROGRAM TO SIMULATE THE STANDARD CATALYTIC MECHANISM
C ** THE CONCENTRATION PROFILES, CURRENT, AND
C ** SPECTROELECTROCHEMICAL ABSORBANCES ARE GIVEN ON OUTPUT.
C
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION DIF1(30),DIF2(30),DIF3(20),VECT(30),F(30),FOLD(30)
      DIMENSION YOLD1(30),YA(30),YK1(30),YK2(30),YK3(30)
      DIMENSION DF(30,30),DFOLD(30,30),W(30),Y(30),YOLD(30)
      DIMENSION YY(30),YYY(30)
      COMMON AAA(30,30),BBB(30,30),ROOT(30),WK(30) ,MANUAL
      EXTERNAL FUN,OUT,DFUN
C ** SET NUMBER OF SPLINES
      DO 1000 MANUAL=1,10
C ** GIVE ORDER OF POLYNOMIAL DESIRED
      N=6
C ** STIPULATE WHETHER 0 AND 1 ARE TO BE USED AS INTERPOLATION POINTS
      NO=1
      N1=1
C ** ENTER ALPHA AND BETA DETERMINING POLYNOMIAL TYPE
C ** (WE USE LEGENDRE HERE)
      AL=0.
      BE=0.
C ** ENTER PROGRAM DIMENSION
      ND=30
C ** CALCULATE ROOTS OF SPECIFIED POLYNOMIAL(COLLOCATION POINTS)
      CALL JCOBI(ND,N,NO,N1,AL,BE,DIF1,DIF2,DIF3,ROOT)
      WRITE(6,2)(ROOT(I),I=1,8)
2     FORMAT(4F15.12)
C ** CALCULATE A MATRIX DESCRETIZATION COEFFICIENTS
      DO 4 I=1,8
      CALL DFOPR(ND,N,NO,N1,I,1,DIF1,DIF2,DIF3,ROOT,VECT)
      DO 4 J=1,8
4     AAA(I,J)=VECT(J)
C ** CALCULATE B MATRIX DESCRETIZATION COEFFICIENTS
      DO 5 I=1,8
      CALL DFOPR(ND,N,NO,N1,I,2,DIF1,DIF2,DIF3,ROOT,VECT)
      DO 5 J=1,8
5     BBB(I,J)=VECT(J)
C ** CALCULATE QUADRATURE INTEGRATION WEIGHT COEFFICIENTS
      DO 791 I=1,8
      CALL DFOPR(ND,N,NO,N1,I,3,DIF1,DIF2,DIF3,ROOT,VECT)
      WK(I)=VECT(I)
791   CONTINUE
C ** ENTER TIME  LIMITS BETWEEN WHICH INTEGRATION IS TO BE PERFORMED
      XO=0.DO
      X1=20.DO
C ** ENTER INTEGRATION ERROR TOLERANCE
      EPS=1.D-06
C ** ENTER INITIAL CONDITIONS FOR ALL SPECIES
      DO 300 I=1,6
      Y(I)=1.DO
      Y(I+6)=0.DO
C ** SET WEIGHT FACTORS FOR ANSWERS
      W(I+6)=1.DO

300   W(I)=1.DO
C ** SET INITIAL VALUE FOR INTEGRATION INTERVAL STEP
      HO=1.D-06
C ** BEGIN INTEGRATION
      CALL STIFF3(12,30,10,FUN,DFUN,OUT,XO,X1,HO,EPS,W,Y,YOLD, YOLD1,IP,
     1YA,YK1,YK2,YK3,DF,DFOLD,F,FOLD)
1000  CONTINUE
      STOP
      END
```

```
       SUBROUTINE FUN(Y,F)
       IMPLICIT REAL*8(A-H,O-Z)
       DIMENSION Y(16),F(16)
       COMMON AA(30,30),BB(30,30),ROO(30),WK(30) ,MANUAL
       TR=MANUAL
C ** SET UP SPLINE POINT MUL IPLIER
       VAR=(1.DO/((.1DO*TR)**2))
C ** STATE THE DESCRETIZED DIFFERENTIAL EQUATIONS

      DO 350 I=1,6
      TDDER1=O.
      TDDER2=O.
      DO 351 J=1,6
      TDDER1=TDDER1+VAR*(BB(I+1,J+1)*Y(J))
      TDDER2=TDDER2+VAR*(BB(I+1,J+1)*Y(J+6))
351   CONTINUE
      F(I)=TDDER1+VAR*BB(I+1,8)+Y(I+6)
      F(I+6)=TDDER2+VAR*BB(I+1,1)-Y(I+6)
350   CONTINUE
      RETURN
      END
C
C
```

```
      SUBROUTINE OUT(X,Y,IH,Q)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION YY(30),YYY(30)
      COMMON AA(30,30),BB(30,30),ROO(30),WK(30) ,MANUAL
      DIMENSION Y(30)
      WRITE(6,130)X,(Y(I),I=1,6),(Y(I+6),I=1,6)
 130  FORMAT(' TIME =',E20.15,/,4X,'0.00000000000 ', 3(F16.11,1X),/,1X,3
     1(F16.11,1X),3X,'1.00000000000',//,4X,'1.00000000000',3(F16.11,1X),
     2/,1X,3(F16.11,1X),3X,'0.00000000000')
C ** CALCULATE THE ABSORBANCES FROM THE NOW KNOWN CONCENTRATION
C ** AT THE COLLOCATION POINTS (Y), AND THE INTEGRATION
C ** COEFFICIENTS (WK).
      GAUSSA=0.D0
      GAUSSB=0.D0
      YY(1)=0.D0
      YY(8)=1.D0
      YYY(1)=1.D0
      YYY(8)=0.D0
      DO 792 I=1,6
      YY(I+1)=Y(I)
      YYY(I+1)=Y(I+6)
 792  CONTINUE
      DO 793 I=1,8
      GAUSSA=GAUSSA+WK(I)*YY(I)
      GAUSSB=GAUSSB+WK(I)*YYY(I)
 793  CONTINUE
      GAUSSA=GAUSSA*1.D-6*.1D0*MANUAL*1.D-3**.5
      GAUSSB=GAUSSB*1.D-6*.1D0*MANUAL*1.D-3**.5
      WRITE(6,794)GAUSSA,GAUSSB
 794  FORMAT(' ABSORBANCE A =',E20.15,'   ABSORBANCE B =',E20.15,//)
      RETURN
      END
      SUBROUTINE DFUN(Y,DF)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION DF(30,30)
      COMMON AA(30,30),BB(30,30),ROO(30),WK(30) ,MANUAL
      TR=MANUAL
      VAR=1.D0/((.1D0*TR)**2)
      DO 90 I=1,6
      DO 90 J=1,6
      DF(I,J)=VAR*BB(I+1,J+1)

      DF(I+6,J+6)=VAR*BB(I+1,J+1)
   90 CONTINUE
      DO 365 M=1,6
      DF(M+6,M+6)=DF(M+6,M+6)-1.D0
  365 CONTINUE
      RETURN
      END
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION DIF1(30),DIF2(30),DIF3(30),VECT(30),F(30),FOLD(30)
      DIMENSION YOLD1(30),YA(30),YK1(30),YK2(30),YK3(30)
      DIMENSION DF(30,30),DFOLD(30,30),W(30),Y(30),YOLD(30)
      COMMON AAA(30,30),BBB(30,30),ROOT(30)
      EXTERNAL FUN,OUT,DFUN
      N=6
      NO=1
      N1=1
      AL = 1.
      BE=1.5
      ND=30
      CALL JCOBI(ND,N,NO,N1,AL,BE,DIF1,DIF2,DIF3,ROOT)
      WRITE(6,2)(ROOT(I),I=1,8)
2     FORMAT(4F15.12)
      DO 4 I=1,8
      CALL DFOPR(ND,N,NO,N1,I,1,DIF1,DIF2,DIF3,ROOT,VECT)
      DO 4 J=1,8
4     AAA(I,J)=VECT(J)
      DO 5 I=1,8
      CALL DFOPR(ND,N,NO,N1,I,2,DIF1,DIF2,DIF3,ROOT,VECT)
      DO 5 J=1,8
5     BBB(I,J)=VECT(J)
1     FORMAT(1X,8(F9.3,1X))
      X0=0.D0
      X1=20.D0
      EPS=.1D-6
      DO 300 I=1,6
      Y(I)=1.D0
300   W(I)=1.D0
      HO=1.D-6
      CALL STIFF3(6,30,5,FUN,DFUN,OUT,X0,X1,HO,EPS,W,Y,YOLD, YOLD1,IP,Y
     1A,YK1,YK2,YK3,DF,DFOLD,F,FOLD)
      STOP
      END
      SUBROUTINE FUN(Y,F)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION Y(12),F(12)
      COMMON AA(30,30),BB(30,30),ROO(30)
      DO 350 I=1,6
      TDDER1=0.
      TDDER2=0.
      DO 351 J=1,6
      TDDER1=TDDER1+BB(I+1,J+1)*Y(J)+2.D0/(ROO(I+1)*1.D2)*AA(I+1,J+1)
     1*Y(J)
351   CONTINUE
      F(I)=TDDER1+BB(I+1,8)+2.D0/(ROO(I+1)*1.D2)*AA(I+1,8)
350   CONTINUE
      RETURN
      END
      SUBROUTINE OUT(X,Y,IH,Q)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON AA(30,30),BB(30,30),ROO(30)
      DIMENSION Y(30)
      WRITE(6,130)X,(Y(I),I=1,6)
130   FORMAT(' T=',F15.11,/,6X,'0.00000000000',1X,F16.11
     1,1X,2(F16.11,1X),/,3X,3(F16.11,1X),3X,'1.00000000000')
      TD=0.D0
      DO 33 J=1,6
      TD=TD+AA(1,J+1)*Y(J)
33    CONTINUE
      CUR=96486.D0*1.D-5*(AA(1,8)+TD)
      WRITE(6,131)CUR
131   FORMAT(1X,'CURRENT=',F16.11,///)
      RETURN
      END
      SUBROUTINE DFUN(Y,DF)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON AA(30,30),BB(30,30),ROO(30)
      DIMENSION DF(30,30)
      DO 360 I=1,6
      DO 360 J=1,6
      DF(I,J)=BB(I+1,J+1)+2.D0/(ROO(I+1)*1.D2)*AA(I+1,J+1)
360   CONTINUE
      RETURN
      END
```

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