


2003-01-01

## Simulation of Dynamic Electrochemical Processes

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### Recommended Citation

W.Breen, J.Cassidy, *Current Topics in Electrochemistry*, vol 9, (2003), 47-91 doi:10.21427/ktkx-by67

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Simulation of Dynamic Electrochemical Processes.

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## Abstract.

This work is designed to introduce electrochemists in a tutorial manner to the basics of modeling of electrochemical systems based primarily on diffusion equations. There is an introduction to analytical and numerical methods with examples taken from typical electrochemical experiments. The Laplace transform is used to derive the Cottrell equation and chronopotentiometry. The response of an electrode to a Gaussian concentration profile is detailed. Laplace's equation is solved for a simple cell to determine the potential distribution. Discrete methods are employed to calculate the current time behavior following a potential step using the explicit finite difference method. Cyclic voltammetry is simulated using the explicit, implicit and hopscotch methods along with the method of orthogonal collocation. In each case the steps used to solve the problem are comprehensively detailed.

## 1. Introduction.

In all physical and chemical experimentation a model is usually required. Electrochemical experimentation, in particular amperometry ( which is primarily described in this chapter) is notorious in the degree of nonideality associated with different processes such as mass transport, adsorption, rate of electron transfer, etc. A celebrated example is the cold fusion sensation where an apparently simple experiment, the reduction of heavy water to form deuterium at a palladium electrode, was found to be quite irreproducible though it was attempted world-wide. That the matter of cold fusion had not been speedily resolved was partly because of the lack of an adequate model. A model is also required for the simplest electrochemical experiment where in order to acquire analytical or physical chemical information, the system should be fully characterised.

Amperometry is concerned with the measurement of current at the working electrode in a certain cell configuration which may vary from a three electrode one compartment conventional cell to within a living cell (which may be examined using microelectrodes) subject to a particular applied potential waveform. In amperometry the primary region of interest is that of the electrode surface where a species in solution either picks up or loses an electron. However at this interface there may be a variety of nonidealities. On a molecular scale for example it is unlikely to be flat, and if polished, some of the grinding material such as alumina may be embedded in the electrode surface. During a particular amperometric experiment a number of nonidealities may appear, corrosion of the electrode, adsorption of electroinactive molecules, oxide formation; many of these nonidealities are disregarded in the simpler models. The current associated with an amperometric experiment may be limited by the electrode kinetics ( how difficult it is to transfer an electron to or from a particular molecule) or the availability of these molecules close to the electrode surface. During an amperometric experiment the 'reagent' is continuously being destroyed through reaction at the electrode and more reagent can reach the electrode through three mass transport mechanisms:

Diffusion

Convection  
Migration.

The equations for these means of mass transport are available, but are quite complicated and so in the first instance, migration ( the movement of a charged species because of a potential field), is experimentally removed through the addition of excess electrolyte and convection is removed by not stirring the solution and curtailing the time scale of the experiment. This leaves us with diffusion, which involves the movement of molecules under a concentration gradient, as a means of mass transport.

The process of diffusion can be characterised using the following partial differential equation. This equation is useful for poking into the future since depending on where we tell it to start, it will predict what way the concentration profiles ( $c(x,t)$ , concentration as a function of distance away from the electrode,  $x$  , and as a function of time,  $t$  ) will change.

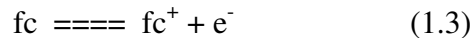
$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2} + \frac{2gD\partial c(x,t)}{(x+R)\partial x} \quad (1.1)$$

where for planar, spherical and cylindrical geometry,  $g$  takes the value 0,1 and 0.5 respectively.  $R$  is the radius of the cylinder or sphere. For the case of diffusion at a planar electrode the equation is simplified to

$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2} \quad (1.2)$$

where  $D$  is the diffusion coefficient .  $D$  may be considered as a factor which allows the units to work out on either side of equation ( 1.2 ) and so has units of  $\text{cm}^2/\text{sec}$ .

It is possible to specify two types of conditions associated with the above equations. Firstly an initial condition. What do the concentration profiles look like before the experiment starts. One of the simpler experiments involves the application of a potential step to an electrode in a solution of ferrocene carboxylic acid ,  $fc$ , in order to oxidise it:



Initially, just before the experiment begins there is a homogeneous solution of ferrocenecarboxylic acid of concentration  $c^*$  ( say 5 mM in aqueous 0.1M KCl). Then we can write:

$$t = 0, \quad x > 0, \quad c(x,0) = c^* \quad (1.4)$$

Should a potential step be applied to the electrode causing all of the  $fc$  at the electrode surface to be oxidised then a depletion or diffusion layer is formed which contains a 'lack' of  $fc$  compared to the original concentration  $c^*$ . This diffusion layer builds out into solution. However, there will be a point out in solution to which the diffusion layer will

not expand to during the time of the experiment. And so it is possible to write a boundary condition that

$$t > 0, x \rightarrow \infty, c(x,t) = c^* \quad (1.5)$$

where  $\delta$  is a thickness much greater than the diffusion layer thickness;  $\delta = \sqrt{6Dt}$

The next boundary condition depends on what is happening at the electrode surface. In this case we know that the fc concentration has been forced to zero since any fc approaching the electrode is completely oxidised i.e.

$$t > 0, x = 0, c(0,t) = 0 \quad (1.6)$$

It can be seen that at the two boundaries there are fixed conditions and that the equation is solved within the range of these conditions. Should there be slow heterogeneous kinetics at the electrode surface then this fact can be incorporated in the boundary condition at the electrode. Finally once the concentration profiles  $c(x,t)$  have been determined by working out the diffusion equation, it is possible to evaluate the current, (which is of interest to the electrochemist) by finding the derivative of the concentration profile and evaluating it at the electrode surface. i.e.

$$i = nFAD \left. \frac{dc}{dx} \right|_{x=0} \quad (1.7)$$

Should this equation be solved for the potential step experiment, an expression for the current as a function of time is obtained as:

$$i = \frac{nFA\sqrt{Dc^*}}{\sqrt{\pi t}} \quad (1.8)$$

The chronoamperometric experiment can be carried out quite successfully at a platinum disk electrode ( diameter = 3mm) in order to determine the electrochemical electrode area once the values of  $c^*$  and  $D$  are known. There are a number of assumptions associated with the above model for a potential step experiment. Double layer charging, adsorption and potential drop through the solution are not considered. In practice, other nonidealities arise in the case of microelectrodes where the diffusion evolves from linear to hemispherical and requires the diffusion equations to be solved in two dimensions and thin layer cells such as those used in spectroelectrochemistry where there are nonuniform current and potential distributions that complicate the process.

The purpose of this chapter is to introduce some typical simulation problems and solve them by a variety of methods as well as indicating to the reader where to locate more advanced models.

## ANALYTICAL METHODS.

The solution of the diffusion equation is fundamental to the simulation of electrochemical models. The solution can be obtained using analytical or numerical techniques. In this section we will briefly examine some of the analytical methods used in solving the diffusion equation.

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

The concentration of the electroactive species will be denoted as  $C(x,t)$ , being a function of both distance away from the electrode,  $x$  and time,  $t$ . The diffusion equation is second order in  $x$  and first order in  $t$ . Therefore two boundary conditions are required with one initial condition for the solution of the equation. The boundary conditions most commonly encountered in electrochemical problems are

$C(0,t)$  which represents the concentration at  $x = 0$ , the electrode surface for all time,  $t$ .

The limit as  $x \rightarrow \infty$  of  $C(x,t)$  represents the concentration in the bulk solution phase for all time,  $t$ .

$C(l,t)$  is a boundary condition used for thin layer cells or for polymer coated electrodes and is the concentration at  $x = l$ .

$\left. \frac{\partial C}{\partial x} \right|_{x=0}$  which represents the rate of change of concentration with distance at the electrode surface. This is essentially the slope of the concentration distance profile at the electrode surface.

The analytical techniques employed for the solution of the diffusion equation can be divided into Steady State Techniques and Time Dependent Techniques. Steady State responses are responses which are independent of time. We will begin our introduction to analytical methods by examining the Steady State Technique as applied to two examples.

### Steady State Techniques.

#### 1. Steady state response at a polymer coated electrode.

The first problem to be examined simulates the Steady State response of an electrode coated with a porous membrane of thickness  $l$ . The electrode is initially in a solution containing no electrochemically active species. The potential is held at a value which would allow the reaction  $A + ne^- \rightarrow B$  to progress under diffusion control. At time greater than zero a pulse of species A flows pass the electrode. This pulse is infinite in duration. The first step in solving this problem is to deduce the boundary conditions and also the initial condition. As there are no kinetics involved in the problem the differential equation for the problem is simply the diffusion equation

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} \quad (1.1)$$

Where  $C_A$  represents the concentration of species A as a function of time and distance,  $C_A(x,t)$ .  $D_A$  is the diffusion coefficient of species A and the rest of the terms have their usual meaning. The boundary conditions for the problem can be obtained by examining the concentrations of species A at the electrode surface and the solution/porous layer boundary. Since the potential is held in the diffusion controlled region such that



the concentration of A at the electrode surface is zero for all times,  $t > 0$ .

$$C_A(0,t) = 0 \quad (1.2)$$

The pulse of material at the layer/solution interface is assumed to be infinite in length. Therefore the concentration of A at the layer/solution interface is  $C^0$  for all times,  $t > 0$ .

$$C_A(l,t) = C^0 \quad (1.3)$$

Intuitively one would expect that the concentration of A within the layer would equilibrate after some time since the concentration of A at the layer/solution interface is constant. (NOTE: this would not be the case if the solution of A was not flowing past the electrode). This time-independent (Steady State) solution  $C_A(x)$  must satisfy equation 1.1 and the boundary conditions. Since the solution is time-independent

$$\frac{\partial C_A(x)}{\partial t} = 0 \quad (1.4)$$

Therefore equation (1.1) reduces to an ordinary differential equation

$$\frac{d^2 C_A}{dx^2} = 0 \quad (1.5)$$

Simple integration of this equation yields an expression for  $C_A$ .

$$C_A(x) = Ex + F \quad (1.6)$$

where E and F are arbitrary constants. Application of the boundary conditions  $C_A(0) = 0$  and  $C_A(l) = C^0$  results in  $F = 0$  and  $E = C^0/l$ .

$$C_A(x) = \frac{C^0 x}{l} \quad (1.7)$$

At this point it is useful to check that the boundary conditions are satisfied by equation (1.7). This solution represents the steady state concentration profile for species A within the porous layer. It can be seen that a plot of  $C_A(x)$  versus  $x$  will yield a straight line of slope  $C^0/l$ .

To calculate the current we employ the following relationship

$$i = -nFAD \left. \frac{\partial C}{\partial x} \right|_{x=0} \quad (1.8)$$

The derivative of  $C_A(x)$  with respect to  $x$  can be found as follows

$$\frac{\partial C}{\partial x} = \frac{\partial}{\partial x} \left( \frac{C^0 x}{l} \right) = \frac{C^0}{l} \quad (1.9)$$

Therefore the resultant current is

$$i = \frac{-nFADC^0}{l} \quad (1.10)$$

Since no time term is present in the result this current will remain constant for all time after equilibrium is achieved. This current is termed the steady state current. This is one of the simplest examples of simulation in electrochemistry.

## 2. Steady State Current Profile for a Spherical Electrode.

The determination of the steady state current for the reaction  $A + ne^- \rightarrow B$  at a spherical electrode, of radius  $r_a$ , is now examined. The potential of the electrode is held at a value such that the reaction is diffusion controlled. Since a steady state solution is required

$$\frac{\partial C}{\partial t} = 0 \quad \text{implies} \quad \frac{\partial^2 C}{\partial x^2} = 0 \quad (2.1)$$

where C represents the concentration of A at a distance x from the electrode. This equation is then transformed from Cartesian co-ordinates to spherical polar co-ordinates. The result of this transformation is

$$\frac{d}{dr} \left( r^2 \frac{dC}{dr} \right) = 0 \quad (2.2)$$

C is now a function of r only, the radial distance from the electrode surface. The boundary conditions for this problem are

$$C(r_a) = 0$$

$$\text{As } r \rightarrow \infty; \quad C(r) \rightarrow C^o \quad (2.3)$$

where  $C(r_a)$  is the concentration of the electroactive species at the surface of the spherical electrode. The integration of equation (2.2) gives

$$C(r) = D + E/r \quad (2.4)$$

Where D and E are arbitrary constants. The boundary conditions on C(r) can now be employed and yield the following values for D and E

$$E = -Dr_a \quad (2.5)$$

$$D = C^o \quad (2.6)$$

Therefore the equation for C(r) is given by

$$C(r) = C^o \left[ 1 - \frac{r_a}{r} \right] \quad (2.7)$$

At this point the equation can be checked to ensure that the boundary conditions are satisfied. The current can be obtained using

$$i = -nFAD \left. \frac{\partial C}{\partial r} \right|_{r=r_a} \quad (2.8)$$

But

$$\frac{\partial C}{\partial r} = C^o \frac{\partial}{\partial r} \left[ 1 - \frac{r_a}{r} \right] = \frac{C^o}{r_a} \quad (2.9)$$

Therefore

$$i = - \frac{nFADC^o}{r_a} \quad (2.10)$$

Again this represents the steady state current which is evident from the lack of a time term in the equation. This equation holds for the steady state current at a microelectrode also as a result of the hemispherical diffusion layer at this type of electrode.

### Time Dependent Problems.

#### 3. The Laplace Transform Technique [1 - 3].

The most widely used technique for the solution of time dependent problems in electrochemistry is the Laplace transform method. As will be seen later other techniques can be employed for certain problems. We shall begin our introduction to the analytical solution of time dependent problems by examining the Laplace transform of some simple functions.



The Laplace transform of a function  $f(t)$  is obtained by multiplying the function by  $e^{-st}$  and integrating the product with respect to  $t$  from 0 to  $\infty$ .

$$\bar{f}(s) = L \{ f(t) \} = \int_0^{\infty} e^{-st} f(t) dt \quad (3.1)$$

However, for some functions the transform does not exist due to the non-existence of the integral. Some simple examples of the application of Laplace transforms are

$$(i) \quad L \{ 1 \} = \int_0^{\infty} e^{-st} dt = \left. \frac{-e^{-st}}{s} \right|_0^{\infty} = \frac{1}{s} \quad (s > 0)$$

$$(ii) \quad L \{ e^{at} \} = \int_0^{\infty} e^{-(s-a)t} dt = \left. \frac{-e^{-(s-a)t}}{s-a} \right|_0^{\infty} = \frac{1}{s-a} \quad (s > a)$$

$$(iii) \quad L \left\{ \frac{\partial C}{\partial x} \right\} \text{ where } c = f(x,t). \quad L \left\{ \frac{\partial C}{\partial x} \right\} = \int_0^{\infty} e^{-st} \frac{\partial C}{\partial x} dt \text{ and since } e^{-st} \neq f(x)$$

$$L \left\{ \frac{\partial C}{\partial x} \right\} = \frac{\partial}{\partial x} \int_0^{\infty} e^{-st} C(x,t) dt = \frac{d}{dx} L \{ C(x,t) \}$$

$$(iv) \quad L \left\{ \frac{\partial^2 C}{\partial x^2} \right\} = \frac{d^2}{dx^2} L \{ C(x,t) \}$$

$$(v) \quad L \left\{ \frac{\partial C}{\partial t} \right\} = \int_0^{\infty} e^{-st} \frac{\partial C}{\partial t} dt$$

integration by parts yields

$$-e^{-st} C(x,t) \Big|_0^{\infty} + s \int_0^{\infty} e^{-st} C(x,t) dt = -C(x,0) + s L \{ C(x,t) \}$$

Providing  $e^{-st} C(x,t)$  approaches zero for sufficiently large  $s$  as  $t \rightarrow \infty$ .

$$(vi) \quad L \{ e^{at} f(t) \} = \int_0^{\infty} e^{-st} e^{at} f(t) dt = \int_0^{\infty} e^{-(s-a)t} f(t) dt = \bar{f}(s-a)$$

$$(vii) \quad L \{ a f(t) + b g(t) \} = \int_0^{\infty} e^{-st} (a f(t) + b g(t)) dt = a \bar{f}(s) + b \bar{g}(s)$$

The function  $f(t)$  can be transformed even if it is only piecewise continuous. Thus

$$(viii) \quad f(t) = \begin{cases} 0 & t < t_1 \\ C^0 & t \geq t_1 \end{cases}$$

$$\begin{aligned} L \{ f(t) \} &= \int_0^{\infty} f(t) e^{-st} dt = \int_0^{t_1} f(t) e^{-st} dt + \int_{t_1}^{\infty} f(t) e^{-st} dt \\ &= \frac{C^0 e^{-st_1}}{s} \end{aligned}$$

Discontinuities such as steps can be dealt with quite readily using Laplace transforms as is evident from the above example. A table of transforms can thus be created. The following table gives some of the more common transforms required for the solution of electrochemical problems. Of course the transforms can be deduced in a similar manner to the examples above.

#### 4. The Cottrell Equation [4].

It is now possible for us to employ the transforms for the solution of an electrochemical problem. The problem chosen to begin with is one of the simplest time dependent electrochemical problems, the deduction of the current-time response on the application of a potential step. It is assumed that at the initial potential no electrochemical reaction is occurring and at the final potential the electrochemical reaction  $A + ne^- \rightarrow B$  occurs under diffusion control. It is also assumed that the solution contains A only at the beginning of the experiment. The equations governing this reaction are the basic diffusion equation (since no kinetics are involved)

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (4.1)$$

The initial condition for the problem is  $C(x,0) = C^0$  since it is assumed that the solution contains A only at the start of the experiment at a concentration  $C^0$ . The boundary conditions are

(i)  $C(0,t) = 0$  since the reaction is under diffusion control, it is assumed that any A at the electrode surface is converted to B rapidly.

(ii) As  $x \rightarrow \infty$ ,  $C(x,t) \rightarrow C^0$  because as we move further from the electrode surface the concentration of A approaches the bulk solution concentration  $C^0$ .

The Laplace transform of this equation is readily obtained using TABLE 1.

$$L \left\{ \frac{\partial C}{\partial t} \right\} = D L \left\{ \frac{\partial^2 C}{\partial x^2} \right\} \quad (4.2)$$

Hence the partial differential equation is reduced to an ordinary differential equation.

$$-C(x,0) + s \bar{C}(x,s) = D \frac{\partial^2 \bar{C}(x,s)}{\partial x^2} \quad (4.3)$$

The boundary conditions are transformed also, giving

$$\bar{C}(0,s) = 0; \quad \lim_{x \rightarrow \infty} \bar{C}(x,s) = \frac{C^0}{s} \quad (4.4)$$

$$C(x,0) = C^0 \quad (4.5)$$

**TABLE 1.**

Laplace Transforms for use in the modelling of electrochemical problems.

FUNCTION	TRANSFORM
$C^0$	
$C(x,t)$	$\bar{C}(x,s) = L\{C(x,t)\}$
	$= \int_0^\infty e^{-st} C(x,t) dt$
$aC(x,t) + bD(x,t)$	$a\bar{C}(x,s) + b\bar{D}(x,s)$
$\frac{\partial C(x,t)}{\partial x}$	$\frac{\partial \bar{C}(x,s)}{\partial x}$
$\frac{\partial^2 C(x,t)}{\partial x^2}$	$\frac{\partial^2 \bar{C}(x,s)}{\partial x^2}$
$\frac{\partial C(x,t)}{\partial t}$	$s\bar{C}(x,s) - C(x,0)$
$\int_0^t C(x,t) dt$	$\frac{\bar{C}(x,s)}{s}$
$(\pi t)^{-\frac{1}{2}}$	$s^{-\frac{1}{2}}$
$e^{-\alpha t}$	$\frac{1}{s + \alpha}$
$\sin(\alpha t)$	$\frac{\alpha}{s^2 + \alpha^2}$
$e^{\alpha t} C(x,t)$	$\bar{C}(x,s - \alpha)$
$\frac{1}{\alpha^2} e^{\alpha t} \operatorname{erf}(\alpha t)^{\frac{1}{2}}$	$\frac{1}{s^{1/2}(s - \alpha)}$
$\frac{1}{(\pi t)^{1/2}} e^{-\frac{\alpha^2}{4t}}$	$\frac{1}{s^{1/2}} e^{-\alpha s^{1/2}}$
$\operatorname{erfc}\left(\frac{\alpha}{2t^{1/2}}\right)$	$\frac{1}{s} e^{-\alpha s^{1/2}}$
$2 \frac{t^{1/2}}{\pi} e^{-\frac{\alpha^2}{4t}} - \alpha \operatorname{erfc}\left(\frac{\alpha}{2t^{1/2}}\right)$	$\frac{1}{s^{3/2}} e^{-\alpha s^{1/2}}$
$t^n C(x,t)$	$(-1)^n \frac{d^n \bar{C}(x,s)}{ds^n}$
$\begin{cases} C(x,t-a) & t > a \\ 0 & t < a \end{cases}$	$e^{-as} \bar{C}(x,s)$
$\int_0^t f(t-u)g(u)du =$	$\bar{f}(s)\bar{g}(s)$
$\int_0^t f(u)g(t-u)du$	

Substituting  $C(x,0) = C^0$  gives

$$D \frac{\partial^2 \bar{C}(x,s)}{\partial x^2} - s \bar{C}(x,s) = -C^0 \quad (4.6)$$

A solution of the resulting Ordinary Differential Equation can be obtained by evaluating the complementary function and the particular integral of the O.D.E.

#### Complementary Function.

$Dm^2 - s = 0$  has the solution  $m = \pm \sqrt{\frac{s}{D}}$ . Any standard textbook on the solution of ordinary differential equations will provide the following solution

$$\bar{C}(x,s) = D e^{\sqrt{\frac{s}{D}}x} + E e^{-\sqrt{\frac{s}{D}}x} \quad (4.7)$$

#### Particular Integral.

The particular integral is obtained following the method of any standard textbook on the solution of ordinary differential equations.

Let  $\bar{C}(x,s) = K$  therefore  $\frac{d\bar{C}}{dx} = 0$ ;  $\frac{d^2\bar{C}}{dx^2} = 0$ . Substituting these values into the ordinary differential equation will lead to the equation  $0 - sK = -C^0$  which gives

$$K = \frac{C^0}{s} \quad (4.8)$$

The solution is obtained by the addition of the particular integral and the complementary function

$$\bar{C}(x,s) = D e^{\sqrt{\frac{s}{D}}x} + E e^{-\sqrt{\frac{s}{D}}x} + \frac{C^0}{s} \quad (4.9)$$

Using the boundary conditions, equations (4.4)

$$\lim_{x \rightarrow \infty} \bar{C}(x,s) = \frac{C^0}{s} = D \cdot \infty + 0 + \frac{C^0}{s}. \text{ Therefore } D = 0. \bar{C}(0,s) = 0 = E + \frac{C^0}{s}. \text{ Therefore}$$

$E = -\frac{C^0}{s}$ . Substitution of these values into equation for  $\bar{C}(x,s)$  yields

$$\bar{C}(x,s) = C^0 \left( \frac{1}{s} - \frac{1}{s} e^{-\sqrt{\frac{s}{D}}x} \right) \quad (4.10)$$

The solution as a function of time is obtained by carrying out an inverse transform on  $\bar{C}(x,s)$ . Employing the table of transforms

$$C(x,t) = C^0 \left( 1 - \operatorname{erfc} \left\{ \frac{x}{2\sqrt{Dt}} \right\} \right) = C^0 \operatorname{erf} \left\{ \frac{x}{2\sqrt{Dt}} \right\} \quad (4.11)$$

The current is obtained using equation (1.8).

$$\frac{\partial C}{\partial x} = \frac{C^0}{\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}}; \quad \left. \frac{\partial C}{\partial x} \right|_{x=0} = \frac{C^0}{\sqrt{\pi Dt}} \quad (4.12)$$

This then yields the current time profile.

$$i = -\frac{nFAD^{1/2}C^o}{\sqrt{\pi t}} \quad (4.13)$$

This is the Cottrell equation and it can readily be seen that plotting  $i$  versus  $1/\sqrt{t}$  will yield a straight line. The charge passed in the experiment can be evaluated by integration of the current time profile with respect to time.

$$Q = \int_0^t -\frac{nFAD^{1/2}C^o}{\sqrt{\pi t}} dt = \frac{2nFAD^{1/2}C^o t^{1/2}}{\sqrt{\pi}} \quad (4.14)$$

Thus a plot of the charge passed against  $\sqrt{t}$  should yield a straight line.

### 5. Constant Current Electrolysis [5].

The next problem to be examined with the aid of the Laplace transform technique is the constant current electrolysis experiment. This involves the application of a constant current to a cell. The potential of the working electrode is therefore allowed to vary to ensure that the current can pass. Only species A is present in solution at the beginning of the experiment and the electrochemical reaction is  $A \rightarrow B + ne^-$ . The equations governing this problem are

$$\frac{\partial C_A(x,t)}{\partial t} = D_A \frac{\partial^2 C_A(x,t)}{\partial x^2} \quad (5.1)$$

where  $C_A(x,t)$  is the concentration of species A in solution at distance  $x$  from the electrode at time  $t$ . The initial condition employed is similar to that employed in the solution of the Cottrell problem  $C_A(x,0) = C^o$ . The semi-infinite boundary condition is employed for the solution of this problem also,  $\lim_{x \rightarrow \infty} C_A(x,t) = C^o$ . As a result of the use of a constant current the boundary condition at the electrode surface is

$$D_A \left. \frac{\partial C_A}{\partial x} \right|_{x=0} = \frac{i(t)}{nFA} \quad (5.2)$$

This boundary condition is simply equation (1.8) with the negative sign removed for an oxidation process. It equates the flux of material at the electrode surface with the applied current. It is important to note that the current term in this equation can be, if necessary, a complex function of time. The Laplace transform of equation (5.1) has been shown in section 4 to be

$$-C_A(x,0) + s \bar{C}_A(x,s) = D_A \frac{\partial^2 \bar{C}_A(x,s)}{\partial x^2} \quad (5.3)$$

Laplace Transform of the boundary conditions yields

$$\lim_{x \rightarrow \infty} \bar{C}_A(x,s) = \frac{C^o}{s} \text{ and } D_A \left. \frac{\partial \bar{C}_A(x,s)}{\partial x} \right|_{x=0} = \frac{\bar{i}(s)}{nFA} \quad (5.4)$$

Substitution of the initial condition, equation (5.3) yields

$$D_A \frac{\partial^2 \bar{C}_A(x,s)}{\partial x^2} = s \bar{C}_A(x,s) - C_A(x,0) \quad (5.5)$$

The solution of this ordinary differential equation is performed in an analogous manner as that used for the solution of the problem in section 4.

$$\bar{C}_A(x,s) = D e^{\sqrt{\frac{s}{D}}x} + E e^{-\sqrt{\frac{s}{D}}x} + \frac{C^o}{s} \quad (5.6)$$

Application of the semi-infinite boundary condition yields the following expression

$$\bar{C}_A(x,s) = E e^{-\sqrt{\frac{s}{D}}x} + \frac{C^o}{s} \quad (5.7)$$

The application of the electrode surface boundary condition involves the calculation of the derivative of equation (5.7) with respect to x.

$$\frac{\partial \bar{C}_A(x,s)}{\partial x} = -\sqrt{\frac{s}{D}} E e^{-\sqrt{\frac{s}{D}}x} \quad (5.8)$$

substituting  $x = 0$  and employing the result in equation (5.2) provides a value for E

$$E = -\frac{\sqrt{D} \bar{i}(s)}{\sqrt{snFAD}} \quad (5.9)$$

This value can now be substituted into equation (5.7) to give

$$\bar{C}_A(x,s) = \frac{C^o}{s} - \frac{\bar{i}(s)}{\sqrt{sDnFA}} e^{-\sqrt{\frac{s}{D}}x} \quad (5.10)$$

This equation is valid for all  $i(t)$ . At this point we assume  $i(t)$  is a constant and proceed with the derivation. If  $i(t)$  is a constant then employing TABLE 1 we see that  $\bar{i}(s) = i/s$  where  $i$  is the constant current employed. Therefore equation (5.10) becomes

$$\bar{C}_A(x,s) = \frac{C^o}{s} - \frac{i}{nFAs^{3/2}\sqrt{D}} e^{-\frac{x}{\sqrt{D}}s^{1/2}} \quad (5.11)$$

The inverse transform of this equation can be obtained through the use of TABLE 1 and the result is

$$C_A(x,t) = C^o - \frac{i}{nFA\sqrt{D_A}} \left\{ \frac{2t^{1/2}}{\pi^{1/2}} e^{-\frac{x^2}{4Dt}} - \frac{x}{\sqrt{D}} \operatorname{erfc} \left[ \frac{x}{2\sqrt{D_A t}} \right] \right\} \quad (5.12)$$

This equation represents the concentration profile for species A. Calculation of the concentration of A at the electrode surface can be achieved by substitution of  $x = 0$ .

$$C_A(0,t) = C^o - \frac{2it^{1/2}}{nFA\sqrt{D_A}\pi} \quad (5.13)$$

Setting  $C_A(0,t) = 0$  and with some manipulation of equation (5.13) we arrive at the Sand Equation.

$$\frac{it^{1/2}}{C^o} = \frac{nFA\sqrt{D_A}\pi}{2} \quad (5.14)$$

Where  $\tau$  is called the transition time and is the time at which  $C_A(0,t)$  drops to zero.

In a similar manner the Corresponding solution for species B can be obtained by solving

$$\frac{\partial C_B(x,t)}{\partial t} = D_B \frac{\partial^2 C_B(x,t)}{\partial x^2} \quad (5.15)$$

subject to the initial condition

$$C_B(x,0) = 0 \quad (5.16)$$

and the boundary condition

$$\lim_{x \rightarrow \infty} C_B(x,t) = 0 \quad (5.17)$$

The other boundary condition is obtained from the following relationship

$$D_A \frac{\partial C_A}{\partial x} \Big|_{x=0} + D_B \frac{\partial C_B}{\partial x} \Big|_{x=0} = 0 \quad (5.18)$$

This equation is as a result of the electrochemical reaction at the electrode surface. It expresses mathematically the fact that as A is consumed electrochemically at the electrode surface as B is produced. Substituting equation (5.2) into equation (5.18) provides us with our second boundary condition

$$- D_B \frac{\partial C_B}{\partial x} \Big|_{x=0} = \frac{i(t)}{nFA} \quad (5.19)$$

In an analogous manner to the derivation of  $C_A(x,t)$  an equation for  $C_B(x,t)$  can be obtained

$$C_B(x,t) = \frac{2it^{1/2}}{nFA\sqrt{\pi D_B}} e^{-\frac{x^2}{4Dt}} - \frac{ix}{nFAD_B} \operatorname{erfc} \left\{ \frac{x}{2\sqrt{Dt}} \right\} \quad (5.20)$$

Evaluation of  $C_B(0,t)$  is achieved by substitution of  $x = 0$

$$C_B(0,t) = \frac{2it^{1/2}}{nFA\sqrt{\pi D_B}} \quad (5.21)$$

The potential time dependence [6] can be evaluated by substitution of  $C_B(0,t)$  and  $C_A(0,t)$  into the Nernst equation

$$E = E^{o'} + \frac{RT}{nF} \operatorname{Ln} \frac{C_A(0,t)}{C_B(0,t)} \quad (5.22)$$

After substitution and some manipulation of the parameters the following equation results

$$E = E^{o'} + \frac{RT}{nF} \operatorname{Ln} \left( \frac{\tau^{1/2}}{t^{1/2}} - \sqrt{\frac{D_B}{D_A}} \right) \quad (5.23)$$

If  $D_B = D_A$  then  $\sqrt{\frac{D_B}{D_A}} = 1$  and the following equation is obtained

$$E = E^{o'} + \frac{RT}{nF} \operatorname{Ln} \left( \frac{\tau^{1/2} - t^{1/2}}{t^{1/2}} \right) \quad (5.24)$$

$E^{o'}$  can be obtained from a plot of E versus  $\operatorname{Ln} \left( \frac{\tau^{1/2} - t^{1/2}}{t^{1/2}} \right)$

### Alternative Methods [1,3].

Several alternative methods may exist for the solution of a particular problem. We shall now solve some problems using some of the alternative methods which are available. Many of the alternative methods involve the separation of variables technique, followed by the solution of two ordinary differential equations, a first order and a second order differential equation. The solution of the second order differential equation is obtained by determining the eigenfunctions and eigenvalues of the equation.

## 6. Thin layer cell.

In this problem we assume that the solution contains only species A at  $t = 0$ . The cell is made up of two glass plates one of which is coated in a thin layer of gold such that it is optically transparent. A thin layer device is fabricated by placing a spacer of thickness  $l$  between both plates. The auxiliary electrode and reference electrodes are external to the device.

To solve this problem we must solve the diffusion equation subject to the following initial and boundary conditions

$$\frac{\partial C_A(x,t)}{\partial t} = D_A \frac{\partial^2 C_A(x,t)}{\partial x^2} \quad (6.1)$$

$$C_A(x,0) = C^0; \quad (6.2)$$

$$C_A(0,t) = 0; \quad \left. \frac{\partial C_A}{\partial x} \right|_{x=l} = 0 \quad (6.3)$$

The latter boundary condition exists because the auxiliary electrode is external to the thin layer and no reaction will occur at the glass insulating wall at  $x = l$ . The first step in the solution of this problem is to transform the partial differential equation (6.1) into two ordinary differential equations. This is accomplished through the use of the separation of variables method. This involves assuming that  $C_A(x,t) = X(x)T(t)$  where  $X(x)$  is some arbitrary function of  $x$  only and  $T(t)$  is some arbitrary function of  $t$  only. Substitution of this relationship into equation (6.1) yields

$$X(x) \frac{\partial T(t)}{\partial t} = D_A T(t) \frac{\partial^2 X(x)}{\partial x^2} \quad (6.4)$$

Manipulation of this equation leads to the following relationship

$$\frac{X''(x)}{X(x)} = \frac{1}{D_A} \frac{T'(t)}{T(t)} = -\alpha \quad (6.5)$$

Where  $\alpha$  is called the separation constant. The choice of a negative value for the separation constant is arbitrary but common.  $X''(x)$  represents the second order derivative of  $X(x)$  with respect to  $x$  and  $T'(t)$  represents the first order derivative of  $T(t)$  with respect to  $t$ . The following ordinary differential equations are obtained from equation (6.5).

$$X''(x) + \alpha X(x) = 0 \quad (6.6)$$

$$T'(t) + \alpha D_A T(t) = 0 \quad (6.7)$$

We shall solve equation (6.6) first. The solution will be obtained by considering different values for  $\alpha$ .

$\alpha = 0$ .

If  $\alpha = 0$  then  $X''(x) = 0$  which implies that  $X(x) = K_1 x + K_2$  where  $K_1$  and  $K_2$  are arbitrary constants. Use of the boundary conditions at this point permits the evaluation of  $K_1$  and  $K_2$ . This gives  $K_1 = 0$  and  $K_2 = 0$ . This solution,  $X(x) = 0$ , is called a Trivial Solution and is not acceptable. Therefore  $\alpha \neq 0$ .

$\alpha < 0$ .

If  $\alpha < 0$  then let  $\alpha = -\lambda^2$  where  $\lambda$  is real and positive. Therefore  $X''(x) - \lambda^2 X(x) = 0$ . Any standard textbook on the solution of second order, ordinary differential equations



will provide the solution,  $X(x) = K_1 \sinh(\lambda x) + K_2 \cosh(\lambda x)$ . Employing the boundary conditions the following solution is obtained.  $X(x) = K_1 \sinh(\lambda x)$  with  $\lambda K_1 \cosh(\lambda l) = 0$ . However  $\cosh(\lambda l) = 0$  has no solution therefore  $K_1 = 0$  since  $\lambda < 0$ . This is the Trivial Solution to the problem and therefore  $\alpha$  is not less than zero.

$\alpha > 0$ .

If  $\alpha > 0$  let  $\alpha = \lambda^2$  where  $\lambda$  is real and positive. Therefore  $X''(x) + \lambda^2 X(x) = 0$ . The solution is  $X(x) = K_1 \sin(\lambda x) + K_2 \cos(\lambda x)$  where  $K_1$  and  $K_2$  are arbitrary constants. Again use of the surface boundary condition gives  $X(x) = K_1 \sin(\lambda x)$ . Application of the boundary condition at  $l$  gives  $\cos(\lambda l) = 0$ .

This equation can be true only if  $\lambda l = \frac{(2m-1)\pi}{2}$  which implies that  $\lambda = \frac{(2m-1)\pi}{2l}$  and that  $\alpha = \frac{(2m-1)^2 \pi^2}{4l^2}$ . The permitted  $m$  values in the equation for  $\lambda$  are  $m = 1, 2, 3, \dots$

because if  $m = 0$  then  $\lambda = 0$  and therefore  $\alpha = 0$  which has been shown not to be acceptable. Therefore the eigenfunctions of the problem are

$$X(x) = K_m \sin\left(\frac{(2m-1)\pi}{2l} x\right) \quad (6.8)$$

with the eigenvalues

$$\lambda = \frac{(2m-1)\pi}{2l} \quad m = 1, 2, 3, \dots (6.9)$$

Equation(6.7) now becomes  $T'(t) + \frac{(2m-1)^2 \pi^2}{4l^2} D_A T(t) = 0$ .

Therefore  $\int_0^\infty \frac{1}{T(t)} dT = \int_0^\infty \frac{-(2m-1)^2 \pi^2}{4l^2} dt$ . This gives the following equation for  $T(t)$

$$T(t) = e^{-\frac{(2m-1)^2 \pi^2 D_A t}{4l^2}} \quad (6.10)$$

Since  $C_A(x,t) = X(x)T(t)$  is a solution so also is any linear combination of  $C_A(x,t)$

$$C_A(x,t) = \sum_{m=1}^{\infty} K_m e^{-\frac{(2m-1)^2 \pi^2 D_A t}{4l^2}} \sin\left(\frac{(2m-1)\pi}{2l} x\right) \quad (6.11)$$

At this point it is useful to check that the boundary conditions are satisfied. The initial condition is employed at this point.

$$C^0 = C_A(x,0) = \sum_{m=1}^{\infty} K_m \sin\left(\frac{(2m-1)\pi}{2l} x\right) \quad (6.12)$$

This equation is a Fourier sine series the coefficients of which are given by the following integral

$$K_m = \frac{2}{l} \int_0^l C^0 \sin\left(\frac{(2m-1)\pi x}{2l}\right) dx \quad (6.13)$$

The solution to this integral can be found to be

$$K_m = \frac{4C^o}{(2m-1)\pi} \quad (6.14)$$

The overall solution to the problem is therefore

$$C_A(x,t) = \sum_{m=1}^{\infty} \frac{4C^o}{(2m-1)\pi} e^{-\frac{(2m-1)^2 \pi^2 D_A t}{4l^2}} \sin\left(\frac{(2m-1)\pi}{2l} x\right) \quad (6.15)$$

At this point the solution to the problem (6.15) can be checked with the boundary values (6.3) and the initial condition (6.2). Checking the agreement of equation (6.15) with the initial condition may require the use of a computer for the determination of the summation.

### Absorbance

This cell can also be used for absorbance measurements. It is possible to determine the absorbance time relationship. Let us assume we are monitoring the absorbance at a wavelength at which the reactant A absorbs. To work out the absorbance of the reactant in the cell we need to know its concentration at all points through the cell. This is given in equation (6.15). For the solution to this problem to be valid we assume that the potential is uniform across the electrode surface. This is a large assumption given the cell geometry. To calculate the absorbance due to species A we first integrate the concentration profile of A with respect to distance  $x$  from 0 to  $l$ . This is then multiplied by the molar absorptivity of A,  $\epsilon_A$  to get the absorbance.

$$\text{Absorbance} = \epsilon_A \int_0^l C_A(x,t) dx \quad (6.16)$$

The solution to this problem is

$$\text{Absorbance} = \sum_{m=1}^{\infty} \frac{4C^o}{(2m-1)\pi} e^{-\frac{(2m-1)^2 \pi^2 D_A t}{4l^2}} \int_0^l \epsilon_A \sin\left(\frac{(2m-1)\pi}{2l} x\right) dx$$

assuming the validity of integrating under the summation sign.

$$\text{Absorbance} = \frac{8C^o l \epsilon_A}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{(2m-1)^2} e^{-\frac{(2m-1)^2 \pi^2 D_A t}{4l^2}} \quad (6.17)$$

It is interesting to note that as  $t \rightarrow \infty$ , Absorbance  $\rightarrow \epsilon_A C_A l$  because

$$\sum_{m=1}^{\infty} \frac{1}{(2m-1)^2} = \frac{\pi^2}{8} \quad (6.18)$$

### Current - time relationship.

The current can be obtained using relationship (1.8). The result is

$$i = -\frac{2nFAD_A C^o}{l} \sum_{m=1}^{\infty} e^{-\frac{(2m-1)^2 \pi^2 D_A t}{4l^2}} \quad (6.19)$$

### Charge - time relationship.

The charge - time relationship can be obtained by integrating the current - time expression with respect to time from 0 to  $t$ .

$$Q(t) = -\frac{2nFAD_A C^o}{1} \sum_{m=1}^{\infty} \int_0^t e^{-\frac{(2m-1)^2 \pi^2 D_A t}{4l^2}} dt \quad (6.20)$$

the result of this integral is

$$Q(t) = \frac{8nFAC^o l}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{(2m-1)^2} \left( e^{-\frac{(2m-1)^2 \pi^2 D_A t}{4l^2}} - 1 \right) \quad (6.21)$$

It is interesting to note that

$$\text{as } t \rightarrow \infty, Q \rightarrow \frac{8nFAC^o l}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{(2m-1)^2} \quad (6.22)$$

Which using relationship (6.18) reduces to

$$\text{as } t \rightarrow \infty, Q \rightarrow nFAC^o l \quad (6.23)$$

This equation is of interest in electrolysis experiments in that the diffusion coefficient does not appear in the relationship. This means that an electrolysis experiment can be employed to determine  $n$ , the number of electrons transferred, without prior knowledge of the diffusion coefficient.

### 7. Complete solution to infinite pulse problem in section 1.

At this stage we derive the complete solution to problem number 1. The governing equations are equations (1.1) - (1.3). The solution to the problem involves shifting the boundary condition at  $l$  to the initial condition. We shall show how this is done here.

Separation of variables as in the last section gives rise to the following equations

$$X''(x) + \alpha X(x) = 0 \quad (7.1)$$

$$T'(t) + \alpha D_A T(t) = 0 \quad (7.2)$$

The steady state concentration profile is found to be (see section 1)

$$C_A(x) = \frac{C^o x}{l} \quad (7.3)$$

The concentration  $C_A(x,t)$  can be expressed as a combination of the steady state concentration term and the transient concentration term  $W_A(x,t)$ .

$$C_A(x,t) = \frac{C^o x}{l} + W_A(x,t) \quad (7.4)$$

Substituting this term into the diffusion equation yields

$$\frac{\partial}{\partial t} \left( \frac{C^o x}{l} \right) + \frac{\partial W}{\partial t} = D \frac{\partial^2}{\partial x^2} \left( \frac{C^o x}{l} \right) + D \frac{\partial^2 W}{\partial x^2} \quad (7.5)$$

Therefore

$$\frac{\partial W}{\partial t} = D \frac{\partial^2 W}{\partial x^2} \quad (7.6)$$

The new boundary conditions can be obtained by substitution of the supplied boundary conditions and the initial condition into equation (7.4). The following initial and boundary conditions are obtained for equation (7.6)

$$W(0,t) = 0; \quad W(l,t) = 0 \quad (7.7)$$

$$W(x,0) = -\frac{C^o x}{l} \quad (7.8)$$

Therefore the original problem has been transformed to a much simpler form with the non-homogenous boundary condition shifted to the initial condition. This problem can be solved following the method of section 6. The eigenfunctions obtained are  $X(x) = \sin\left(\frac{m\pi x}{l}\right)$  with  $m = 1, 2, 3, \dots$  and the eigenvalues obtained are  $\frac{m\pi x}{l}$ . The general solution to this problem is found to be

$$W(x,t) = \sum_{m=1}^{\infty} A_m e^{-\frac{m^2 \pi^2 D t}{l^2}} \sin\left(\frac{m\pi x}{l}\right) \quad (7.9)$$

To evaluate  $A_m$  we note that  $W(x,0)$  has the form of a Fourier series the coefficients of which are deduced from the following integral

$$A_m = \frac{2}{l} \int_0^l \left(\frac{-C^o x}{l}\right) \sin\left(\frac{m\pi x}{l}\right) dx \quad (7.10)$$

Integration by parts provides the solution to the integral and the overall solution to equations (7.6) - (7.8) is found to be

$$W(x,t) = \sum_{m=1}^{\infty} \frac{2C^o (-1)^m}{m\pi} e^{-\frac{m^2 \pi^2 D t}{l^2}} \sin\left(\frac{m\pi x}{l}\right) \quad (7.11)$$

Using equation (7.4) the overall solution to the problem is found.

$$C(x,t) = \frac{C^o x}{l} + \sum_{m=1}^{\infty} \frac{2C^o (-1)^m}{m\pi} e^{-\frac{m^2 \pi^2 D t}{l^2}} \sin\left(\frac{m\pi x}{l}\right) \quad (7.12)$$

It is evident from this equation that the solution has a time independent part and a time dependent part. The current is obtained using equation (1.8).

$$i = -\frac{nFADC^o}{l} \left[ 1 + 2 \sum_{m=1}^{\infty} (-1)^m e^{-\frac{m^2 \pi^2 D t}{l^2}} \right] \quad (7.13)$$

As  $t \rightarrow \infty$ , the exponential component of equation (7.13) will approach zero. Therefore

$$\text{As } t \rightarrow \infty, \quad i \rightarrow -\frac{nFADC^o}{l} \quad (7.14)$$

This is the steady state current obtained in section 1.

### 8. The response of an electrode to a Gaussian Concentration profile of electroactive material [7].

In this section we briefly examine a problem with a time dependent boundary condition. The problem is one which is relevant to electrochemical detection in flow injection analysis. It has been reported that as the distance between the injection port and the detector increases that a perfect plug of material becomes distorted by convection and diffusion to first a Poisson profile and lastly a Gaussian profile [8,9]. We wish to model the response of an polymer coated electrode in contact with a solution which initially contains no analyte, A. At  $t > 0$  a Gaussian profile of A begins to flow past the electrode.

The mean and deviation of the Gaussian profile will be denoted as  $t_p$  and  $\sigma$  respectively.

The problem can be written as follows

$$\frac{\partial C_A(x,t)}{\partial t} = D_A \frac{\partial^2 C_A(x,t)}{\partial x^2} \quad (8.1)$$

$$C_A(x,0) = 0; \quad (8.2)$$

$$C_A(0,t) = 0; \quad C_A(l,t) = C^o e^{-\left\{\frac{1}{2}\left(\frac{t-t_p}{\sigma}\right)^2\right\}} \quad (8.3)$$

where  $l$  is the thickness of the polymer film. The solution of this problem is greatly simplified if the terms are made dimensionless. This is achieved by the following transformations

$$\chi = x/l, \quad \zeta = C_A/C^o, \quad \tau = Dt/l^2 \quad (8.4)$$

The new problem is

$$\frac{\partial \zeta_A(\chi, \tau)}{\partial \tau} = \frac{\partial^2 \zeta_A(\chi, \tau)}{\partial \chi^2} \quad (8.5)$$

subject to

$$\zeta_A(\chi, 0) = 0; \quad (8.6)$$

$$\zeta_A(0, \tau) = 0; \quad (8.7)$$

It is now necessary to move the non-homogeneity from  $\zeta_A(l, \tau)$  to  $\zeta_A(\chi, 0)$ . This is achieved by letting

$$\zeta_A(\chi, \tau) = u(\chi, \tau) + w(\chi, \tau) \quad (8.8)$$

and defining  $w(\chi, \tau)$  as follows

$$w(\chi, \tau) = \chi e^{-\left\{\frac{1}{2}\left(\frac{\tau-t_p}{\sigma}\right)^2\right\}} \quad (8.9)$$

Following the method employed for the transformation of equations (7.3) to (7.8) we arrive at a new problem

$$\frac{\partial u(\chi, \tau)}{\partial \tau} = \frac{\partial^2 u(\chi, \tau)}{\partial \chi^2} + \left(\frac{\tau-t_p}{\sigma^2}\right) \chi e^{-\left\{\frac{1}{2}\left(\frac{\tau-t_p}{\sigma}\right)^2\right\}} \quad (8.10)$$

subject to

$$u(0, \tau) = 0, \quad u(1, \tau) = 0 \quad (8.11)$$

$$u(\chi, 0) = -\chi e^{-\left\{\frac{1}{2}\left(\frac{t_p}{\sigma}\right)^2\right\}} \quad (8.12)$$

We first solve the corresponding homogenous differential equation

$$\frac{\partial u(\chi, \tau)}{\partial \tau} = \frac{\partial^2 u(\chi, \tau)}{\partial \chi^2} \quad (8.13)$$

subject to equations (8.11) by separation of variables in much the same way as that employed in section 6. The eigenfunctions are found to be  $X(\chi) = \sin(m\pi\chi)$ . These are first normalised to give  $X(\chi) = \sqrt{2} \sin(m\pi\chi)$ .  $u(\chi, \tau)$  is now expanded as a series involving the normalised eigenfunctions,

$$u(\chi, \tau) = \sum_{m=1}^{\infty} T_m(\tau) \sin(m\pi\chi) \quad (8.14)$$

The non-homogeneity in equation (8.10) is also expanded in such a series the coefficient of which can be found in the as follows

$$F_m(\tau) = \left( \frac{\tau - t_p}{\sigma^2} \right) e^{-\left\{ \frac{1}{2} \left( \frac{\tau - t_p}{\sigma} \right)^2 \right\}} \sqrt{2} \int_0^1 \chi \sin(m\pi\chi) d\chi \quad (8.15)$$

This has the solution

$$F_m(\tau) = \sqrt{2} \frac{(-1)^{m+1}}{m\pi} \left( \frac{\tau - t_p}{\sigma^2} \right) e^{-\left\{ \frac{1}{2} \left( \frac{\tau - t_p}{\sigma} \right)^2 \right\}} \quad (8.16)$$

In a similar manner the initial condition is expanded in terms of the normalised eigenfunction to give the following coefficient

$$\alpha_m = \sqrt{2} \frac{(-1)^{m+2}}{m\pi} e^{-\left\{ \frac{1}{2} \left( \frac{t_p}{\sigma} \right)^2 \right\}} \quad (8.17)$$

Substitution of the expansions for  $u(\chi, \tau)$  and the non-homogeneity into equation (8.10) gives the following series

$$\sum_{m=1}^{\infty} [T_m'(\tau) + m^2\pi^2 T_m(\tau) - F_m(\tau)] \sin(m\pi\chi) = 0 \quad (8.18)$$

This equation is true for all  $\chi$ ,  $0 \leq \chi \leq 1$ , only if  $T_m'(\tau) + m^2\pi^2 T_m(\tau) - F_m(\tau) = 0$ . The solution to this first order differential equation is  $T_m(\tau) = e^{-m^2\pi^2\tau} \int_0^\tau e^{m^2\pi^2s} F_m(s) ds$ .

However we must also take into account the initial condition this gives

$$T_m(\tau) = \alpha_m e^{-m^2\pi^2\tau} + e^{-m^2\pi^2\tau} \int_0^\tau e^{m^2\pi^2s} F_m(s) ds \quad (8.19)$$

It can be seen from this expression that when  $\tau = 0$  that  $T_m(\tau)$  is equal to the coefficient for the initial condition. Substitution of equation (8.16) into equation (8.19) gives the expression for  $T_m(\tau)$ . Substitution of this expression into equation (8.14) yields the overall solution to equations (8.11 - 8.13).

$$u(\chi, \tau) = 2 \sum_{m=1}^{\infty} \frac{(-1)^{m+2}}{m\pi} e^{-m^2\pi^2\tau} \left[ e^{-\left\{ \frac{1}{2} \left( \frac{t_p}{\sigma} \right)^2 \right\}} - \int_0^\tau \left( \frac{s - t_p}{\sigma^2} \right) e^{m^2\pi^2s} e^{-\left\{ \frac{1}{2} \left( \frac{s - t_p}{\sigma} \right)^2 \right\}} ds \right] \sin(n\pi\chi) \quad (8.20)$$

Substituting this expression into equation (8.8) gives

$$\zeta_A(\chi, \tau) = 2 \sum_{m=1}^{\infty} \frac{(-1)^{m+2}}{m\pi} e^{-m^2\pi^2\tau} \left[ e^{-\left\{ \frac{1}{2} \left( \frac{t_p}{\sigma} \right)^2 \right\}} - \int_0^\tau \left( \frac{s - t_p}{\sigma^2} \right) e^{m^2\pi^2s} e^{-\left\{ \frac{1}{2} \left( \frac{s - t_p}{\sigma} \right)^2 \right\}} ds \right] \sin(n\pi\chi) + \chi e^{-\left\{ \frac{1}{2} \left( \frac{\tau - t_p}{\sigma} \right)^2 \right\}}$$

(8.21)

The solution can be checked at this point for agreement with the boundary conditions. Substitution of  $\tau = 0$  will result in a series which can be evaluated on a computer. The current can be obtained employing equations (8.4) to give equation (1.8) in dimensionless form

$$i = \frac{nFADC^o}{l} \left. \frac{\partial \zeta}{\partial \chi} \right|_{\chi=0} \quad (8.22)$$

Thus the following current time profile is obtained

$$i = \frac{nFADC^o}{l} \left\{ \begin{array}{l} 2 \sum_{m=1}^{\infty} (-1)^m e^{-m^2 \pi^2 \tau} \left[ e^{-\left\{ \frac{1}{2} \left( \frac{t_p}{\sigma} \right)^2 \right\}} - \int_0^{\tau} \left( \frac{s-t_p}{\sigma^2} \right) e^{m^2 \pi^2 s} e^{-\left\{ \frac{1}{2} \left( \frac{s-t_p}{\sigma} \right)^2 \right\}} ds \right] + \\ e^{-\left\{ \frac{1}{2} \left( \frac{\tau-t_p}{\sigma} \right)^2 \right\}} \end{array} \right\} \quad (8.23)$$

A Gaussian profile should approach an infinite plug as the deviation  $\sigma \rightarrow \infty$ . Therefore the current time profile for the Gaussian concentration profile should approach that of the infinite plug as  $\sigma \rightarrow \infty$ . This is in fact the case,

$$\text{as } \sigma \rightarrow \infty, \quad i \rightarrow \frac{nFADC^o}{l} \left\{ 2 \sum_{m=1}^{\infty} (-1)^m e^{-m^2 \pi^2 \tau} + 1 \right\} \quad (8.24)$$

Remembering that  $\tau$  is dimensionless and using the expression for  $\tau$  in equation (8.4) to transform the dimensionless time to real time,  $t$ , we obtain

$$\text{as } \sigma \rightarrow \infty, \quad i \rightarrow \frac{nFADC^o}{l} \left\{ 2 \sum_{m=1}^{\infty} (-1)^m e^{-\frac{m^2 \pi^2 D t}{l^2}} + 1 \right\} \quad (8.25)$$

which of course is the same expression for the current as equation (7.13).

### 9. Evaluation of the potential distribution in a simple electrochemical cell.

The potential distribution in an electrochemical cell is of utmost importance in attempts to reduce ohmic loss and in the plating industry where smooth even deposits are required. In electrochemical cells using a Luggin capillary uncertainties over shielding of the electrode surface have been answered by modelling such cells and examining the potential and current distributions. Two main forms of current distributions can be modelled [10].

#### Primary Current Distribution.

This is the simplest of the current distributions to model and takes no account of the overpotential or kinetics at the electrode surface.

### Secondary Current Distribution.

The secondary current distribution takes into account the kinetics of the electrode reaction. The simplest correction for kinetics is to assume that the current is linear with potential. However some systems have been examined using the complete Butler Volmer equation.

The cell to be modelled in this section consists of two coplanar electrodes a distance  $l$ , away from each other. The electrodes are separated from each other by insulating walls a distance  $l$  apart also.

The governing equation in the modelling of potential distributions is the Laplace equation.

$$\frac{\partial^2 \phi}{\partial x^2} = \frac{\partial^2 \phi}{\partial y^2} \quad (9.1)$$

Being second order in both  $x$  and  $y$  two sets of two boundary conditions will be required for the complete solution of this problem. The following boundary conditions will be employed for this simulation :  $\phi(x,0) = \phi_e$  which is the potential of the working electrode.  $\phi(x,l) = \phi_c$  which represents the potential of the auxiliary electrode.

$\frac{\partial \phi}{\partial x} \Big|_{x=0} = 0$  and  $\frac{\partial \phi}{\partial x} \Big|_{x=l} = 0$  represent the rate of change of potential with distance at the insulating walls of the cell. To simplify the problem we set

$$\phi(x,y) = \phi_c + W(x,y) \quad (9.2)$$

Applying equation (9.1) to (9.2)

$$\frac{\partial^2 W}{\partial x^2} = \frac{\partial^2 W}{\partial y^2} \quad (9.3)$$

substituting equation (9.2) into the boundary conditions gives

$$\frac{\partial W}{\partial x} \Big|_{x=0} = 0 \quad \text{and} \quad \frac{\partial W}{\partial x} \Big|_{x=l} = 0 \quad (9.4)$$

$$W(x,0) = \phi_e - \phi_c \quad (9.5)$$

$$W(x,l) = 0 \quad (9.6)$$

Letting  $W(x,y) = X(x)Y(y)$  and separating the variables yields two second order ordinary differential equations.

$$X''(x) + \lambda X(x) = 0 \quad (9.7)$$

$$Y''(y) - \lambda Y(y) = 0 \quad (9.8)$$

Solving equation (9.7) subject to  $X'(0) = 0$  and  $X'(l) = 0$  yields the following eigenvalues and eigenfunctions following the technique in section 6.

$$\lambda_0 = 0; \quad X_0(x) = 1/2 \quad (9.9)$$

$$\lambda_m = \left( \frac{m\pi}{l} \right)^2; \quad X_m(x) = \cos\left( \frac{m\pi x}{l} \right) \quad m = 1, 2, 3, \dots \quad (9.10)$$

We now employ the eigenvalues in equations (9.9) and (9.10) to evaluate the eigenfunctions,  $Y_m(y)$  of equation (9.8) subject to  $Y(0) = \phi_e$  and  $Y(l) = 0$ .

$$\underline{\lambda_0 = 0.}$$

Therefore  $Y(y) = K_1 y + K_2$ .  $Y(l) = 0$  gives  $K_1 = -K_2/l$ . Therefore



$$Y(y) = K_2(1 - y/l) \quad (9.11)$$

$$\lambda_m = \left( \frac{m\pi}{l} \right)^2$$

$Y''(y) - \left( \frac{m\pi}{l} \right)^2 Y(y) = 0$ . The solution to this problem is

$$Y(y) = K_3 \sinh\left(\frac{m\pi y}{l}\right) + K_4 \cosh\left(\frac{m\pi y}{l}\right) \quad (9.12)$$

Substitution of the boundary condition  $Y(l) = 0$  gives

$$K_3 = -K_4 \frac{\cosh(n\pi)}{\sinh(n\pi)} \quad (9.13)$$

Substitution of (9.13) into (9.12) gives the expression for  $Y(y)$

$$Y(y) = K_4 \left\{ \cosh\left(\frac{m\pi y}{l}\right) - \frac{\cosh(m\pi)}{\sinh(m\pi)} \sinh\left(\frac{m\pi y}{l}\right) \right\} \quad (9.14)$$

The combination of  $X_0(x)$ ,  $Y_0(y)$ ,  $X_m(x)$  and  $Y_m(y)$  will give  $\phi(x,y)$ .

$$W(x,y) = X_0(x)Y_0(y) + X_m(x)Y_m(y) \quad (9.15)$$

Thus the following expression for  $\phi(x,y)$  is obtained

$$W(x,y) = \frac{K_2 \left(1 - \frac{y}{l}\right)}{2} + K_4 \left\{ \cosh\left(\frac{m\pi y}{l}\right) - \frac{\sinh\left(\frac{m\pi y}{l}\right)}{\tanh(n\pi)} \right\} \cos\left(\frac{m\pi x}{l}\right) \quad (9.16)$$

Any linear combination of this solution is also a solution, thus

$$W(x,y) = \frac{K_2 \left(1 - \frac{y}{l}\right)}{2} + \sum_{m=1}^{\infty} K_4 \left\{ \cosh\left(\frac{m\pi y}{l}\right) - \frac{\sinh\left(\frac{m\pi y}{l}\right)}{\tanh(n\pi)} \right\} \cos\left(\frac{m\pi x}{l}\right) \quad (9.17)$$

At this point the boundary condition at  $y = 0$  can be employed

$$W(x,0) = \frac{K_2}{2} + \sum_{m=1}^{\infty} K_4 \cos\left(\frac{m\pi x}{l}\right) \quad (9.18)$$

This is a Fourier Cosine series representation of  $W(x,0)$ , the coefficients of which can be

$$K_2 = \frac{2}{l} \int_0^l (\phi_e - \phi_c) dx = \frac{2(\phi_e - \phi_c)}{l} \Big|_0^l = 2(\phi_e - \phi_c)$$

$$\begin{aligned} \text{determined as follows } K_4 &= \frac{2}{l} \int_0^l (\phi_e - \phi_c) \cos\left(\frac{m\pi x}{l}\right) dx = \frac{2(\phi_e - \phi_c)}{l} \int_0^l \cos\left(\frac{m\pi x}{l}\right) dx \\ &= 0 \end{aligned} \quad (9.19)$$

Substitution of the values for  $K_2$  and  $K_4$  into equation (9.17) gives the overall solution to the problem

$$W(x,y)=(\phi_e - \phi_c)(1 - \frac{y}{l}) \quad (9.20)$$

The potential distribution can be obtained by substitution of this solution into equation (9.2).

$$\phi(x,y) = \phi_e + (\phi_c - \phi_e) \frac{y}{l} \quad (9.21)$$

This is the potential distribution in the cell. The potential at  $y = 0$  is the electrode potential. This falls linearly to a potential of  $\phi_c$  as you approach the auxiliary electrode. The primary current distribution can be obtained using the following expression [10]

$$j_x = \frac{\partial \phi(x,y)}{\partial y} \Big|_{y=0} \quad (9.21)$$

where  $\kappa$  is the conductivity of the solution and  $j_x$  is the current at  $y = 0$ . This gives the following current distribution for the above problem

$$j_x = \frac{\kappa(\phi_c - \phi_e)}{l} \quad (9.22)$$

This represents the primary current distribution. Much more complex geometries have been examined analytically in the literature [10 - 14].

### 10. Evaluation of series solutions.

Many of the solutions obtained analytically involve a series and must be evaluated using a computer programme,. In this section we examine a simple basic program to evaluate solutions (6.15), (6.19) and (6.21). The resulting values for concentration, distance, time, current and charge are printed to screen for noting. The language employed is QUICKBASIC.

```

INPUT "CONCENTRATION OF ANALYTE"; C
INPUT "DIFFUSION COEFFICIENT"; D
INPUT "DURATION OF EXPERIMENT"; T
INPUT "THICKNESS OF CELL"; L
INPUT "AREA OF ELECTRODE"; A
INPUT "NO. OF ITERATIONS"; N
INPUT "NO. OF ELECTRONS IN REACTION"; M
CLS
F = 96487
P = 3.1416
LET COEFF1 = 4 * C / P
LET COEFF2 = 2 * M * F * A * D * C / L
LET COEFF3 = 8 * M * F * A * C * L / (P * P)
FOR TIME = 0 TO T STEP T / 50
FOR X = 0 TO L STEP L / 50
LET CONC = 0
LET CURR = 0
LET CHARG = 0

```

```

FOR COUNT = 1 TO N
LET COEFF4 = 1 / (2 * COUNT - 1)
LET TERM1 = EXP((-2 * COUNT - 1) * (2 * COUNT - 1) * P * P * D * TIME) / (4 *
L * L))
LET TERM2 = SIN((2 * COUNT - 1) * P * X / (2 * L))
LET CONC = CONC + COEFF1 * COEFF4 * TERM1 * TERM2
LET CURR = CURR + COEFF2 * TERM1
LET CHARG = CHARG + COEFF3 * COEFF4 * COEFF4 * (TERM1 - 1)
NEXT COUNT
IF X>0 THEN PRINT "PLEASE, PRESS ANY KEY"
IF X > 0 THEN SLEEP
CLS
PRINT "X = "; X; "          "; "TIME = "; TIME; "          "; "CONC = "; CONC
PRINT "CURRENT = "; CURR; "          "; "CHARGE = "; CHARG
NEXT X
NEXT TIME

```

On running the programme various values necessary for the simulation are required. After inputting these values the programme will proceed with the calculation and provide the first values for the time, distance, current, charge and concentration. When these have been noted, press any key and the next values are displayed. It is quite a simple process to modify this programme so that the data is written to a disc file for examination later. This process facilitates the reading of the files by programmes such as EXCEL for plotting etc. The data obtained can be employed to generate plots of concentration versus distance at different times, current - time and charge - time. The following are some examples of these plots.

This method can of course be extended to the other solutions presented in the previous sections.

### **10. *Limitations of analytical techniques.***

The main advantage of analytical techniques is that an equation results, which informs you of the particular relationship between distance, time and concentration. Although quite a number of problems can be solved analytically, numerical techniques are necessary for the solution of many of the real world type problems. Examples of these problems are many in the literature some of which have been presented earlier in this text. Analytical techniques have been employed for the simulation of quite complex diffusion problems. Some of the original publications on the solution of fundamental electrochemical problems are of value. Publications offering analytical solutions to problems on Cyclic voltammetry [15 - 17], Impedance [18], rotating disc and ring-disc electrode voltammetry [19,20] are available in the literature. They are particularly valuable if partial solutions are required and also show how a problem can be broken down into its constituent boundary and initial conditions. A very brief glance at the literature of electrochemistry provides an indication of the work being done in this area over recent years. The Laplace transform method has been used to develop a model for

the A.C. impedance of a modified electrode in an electrochemical cell [21,22]. Ionic transport through a membrane in the presence of diffusion, convection and migration has also been examined [23]. The Separation of Variables technique can also be applied to problems containing a semi-infinite boundary condition. However, in this case a Fourier integral [3] is employed in place of the Fourier series. Indeed the Cottrell problem is quite readily solved using this technique. Analytical solutions to potential distribution problems are few due to the difficulty of assigning boundary values to the problem in even quite simple geometries. However, modelling of potential distributions around triple band electrodes have been performed using quite diverse analytical techniques such as Conformal Mapping [24,25]. It is hoped that this brief look at some of the mathematical methods available for the solution of electrochemical problems will be of value to you in the future.

## 9. Introduction to finite difference methods.

This section is designed to introduce in a tutorial manner some numerical methods for solving mass transport equations for specific electrochemical systems. Unlike some of the theoretical approaches, numerical methods are considerably more straightforward and require only some knowledge of programming. For a typical mass transport situation, the equation to be solved is:

$$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2} \pm \text{other} \quad (9.1)$$

where the partial derivatives correspond to the diffusion process while the "other" term corresponds to concentration changes with time due to migration, convection or chemical reactions. In equation (9.1)  $c$  is the concentration,  $t$  is time,  $x$  is distance away from the electrode and  $D$  is the diffusion coefficient. However in the first instance, the "other" term will be neglected. The aim is to solve equation (9.1) and to determine an expression for the concentration which is generally as a function of distance away from the electrode and time;  $c(x,t)$ . If an expression for concentration is found then it is possible to determine the current readily. Analytical techniques may be used in a variety of instances to determine explicit expressions for concentration profiles as outlined previously. Generally analytical methods may be applied for simple mechanisms but for more complicated problems, numerical methods are required. The key to these numerical methods involves discretisation of the system. For example in Figure 5 the expected concentration profiles for a species in solution close to an electrode are shown where initially there is a concentration  $c^*$  within the film. Then the cell is switched on or a step potential applied so that the concentration at the electrode surface is forced to zero. Because of this, species from a little further out diffuse in toward the electrode to remove this difference in concentration. This diffusion is characterised by equation (9.1) and should equation (9.1) be solved, the series of concentration profiles  $c(x,t)$ , shown in figure 5 may be found. For these methods, the concentrations are evaluated at specific points in time and positions in distance. Finite difference methods therefore involve the application of a grid with distance and time increments  $h$  and  $k$  respectively. So rather than ending up with the complete profile, a digitised profile at particular distances and times is obtained. This incurs an error which however may be quantitated.

The numerical technique is derived from a Taylor's expansion which states that concentration at a position  $i+h$  may be determined if the concentration at the point  $i$ , and the various derivatives of that concentration at the point  $i$  are known:

$$c_{i+h} = c_i + h c_i' + \frac{h^2}{2!} c_i'' + \frac{h^3}{3!} c_i''' + \dots \quad (9.2)$$

where  $h$  is the distance away from the point  $i$  to the point  $i+h$  and the dashes represent the derivatives. This expression may be applied either for distance (along the  $x$  axis of the grid in Figure 5) or time (along the  $y$  axis of the grid in figure 5) since for a particular distance, the concentration decreases as a function of time. An expression related to equation (9.2) is also possible for a distance in the other direction:

$$c_{i-h} = c_i - h c_i' + h^2 c_i''/2! - h^3 c_i'''/3! + \dots \quad (9.3)$$

These expressions are derived from a theory which says that it is possible to extrapolate a function to a position  $i+h$  if it is known at  $i$  and if its tendency to change (the derivative terms) is also known. A similar expression to equation (9.2) may be written for the time axis as

$$c_{t+k} = c_t + k c_t' + k^2 c_t''/2! + k^3 c_t'''/3! + \dots \quad (9.4)$$

where  $k$  is the time interval. It is possible by algebraically combining equations (9.2 - 9.4) to obtain a digitised form of equation (9.1).

From expression (9.4), one can obtain an approximate expression for  $(dc)/(dt)$  by neglecting the third and remaining terms from the series in equation (9.4)

$$c_t' = (dc)/(dt) \approx (c_{t+k} - c_t)/k \quad (9.5)$$

It can be seen that this is not a true equality. However at least it is an approximate expression for the derivative and the error may be quantified. Furthermore by adding equations (9.2) and (9.3), one can obtain the second derivative since

$$c_{i+h} + c_{i-h} \approx 2c_i + h^2 c_i'' \quad (9.6)$$

and therefore

$$c_i'' = (d^2 c_i)/(dx^2) \approx (c_{i+h} + c_{i-h} - 2c_i)/h^2 \quad (9.7)$$

By a further approximation it is possible to substitute equations (9.5) and (9.7) into equation (9.1) by assuming that the full derivatives are equal to the partial derivatives. In this manner equation (9.1) becomes:

$$(c_{t+k} - c_t)/k = D (c_{i+h} + c_{i-h} - 2c_i)/h^2 \quad (9.8)$$

Since concentration is both a function of time and distance, let us generalise the notation according to figure 6, where  $i,j$  represents the concentration at a position  $i$  and time  $t$  and  $c_{i+1,j}$  represents the concentration at a position  $i+h$  and a time  $t$ . Thus equation (9.8) may be written as:

$$c_{i,j+1} = c_{ij} + D_k(c_{i+1,j} + c_{i-1,j} - 2c_{i,j})/h^2 \quad (9.9)$$

Looking at equation (9.9) and figure 6, it can be seen that information at a particular time  $j$  may be used in order to project into the future in order to get information at a time  $j+1$ . In the diagram the concentration at the full circles are known and the concentrations at the open circle may be evaluated. In order to use this method, it is necessary to have somewhere to start from and this consists of a boundary condition. For example at the electrode surface in Figure 5, we may set a potential so that the concentration of the redox species is always zero, thus it would be possible to extend out from this. A nice aspect of equation (9.9) is that the units 'work out'. Since  $k$  is in seconds and  $h$  is in cm and the diffusion coefficient  $D$  is in  $\text{cm}^2\text{sec}^{-1}$  the parameter  $Dk/h^2 = D_m$  is unitless. Furthermore it is possible to ratio all concentrations to the initial bulk concentration  $c^*$  to obtain dimensionless concentrations  $C = c/c^*$ .

Thus

$$C_{i,j+1} = C_{ij} + D_m(C_{i+1,j} + C_{i-1,j} - 2C_{i,j}) \quad (9.10)$$

Using this technique to probe into the future one point at a time is called the explicit method. It suffers from the problem that the value of  $D_m$  may not be greater than 0.5, otherwise the method is unstable[26].

Since this method is widely used in electrochemistry, and since the concentration profile at the electrode surface is more important than out in bulk solution, a trick has been applied in order to better characterise the profile close to the electrode. By decreasing the distance interval closer to the electrode as shown in Figure 7(b), we would hope to obtain a better indication of the concentration profile rather than in Figure 7(a) where the distance intervals are equal. An estimate of equation (9.9) applied to the situation closer to the electrode namely the derivative evaluated at the point 1 in Figure 7 (b) is[27,28]

$$\left( \frac{C_{1,j+1} - C_{1,j}}{k} \right) = \frac{D}{h} \left( \frac{C_{2,j} - C_{1,j}}{h} - \frac{C_{1,j} - C_{0,j}}{h/2} \right) \quad (9.11)$$

or

$$C_{1,j+1} = C_{1,j} + D_m(C_{2,j} - 3C_{1,j} + 2C_{0,j}) \quad (9.12)$$

where the right hand side of equation (9.11) represents the average of two slopes. We run into a problem at this point. Although equation (9.12) is quoted widely and used frequently in the literature[29], it suffers from the problem that it is unsymmetric[30].

A more detailed expansion of Figure 7(b) is shown in Figure 8. The slope at the point P located at a distance  $h/4$  is  $2(C_1 - C_0)/h$ . The slope at the point R located at a distance  $h$  away from the electrode is  $(C_2 - C_1)/h$  and the slope at the point Q located a distance  $3h/4$  away from the electrode is given by  $2(C_2 - C_0)/(3h)$ . It is possible to get two different estimates of the second derivative. The difference in slopes between R and P (located at  $5h/8$  away from the electrode) is

$$C'' = 4(C_2 - 3C_1 + 2C_0)/(3h^2) \quad (9.13)$$

while the difference between slopes between Q and P located at the point  $C_1$  is also given by equation (9.13)

There is a factor of 4/3 difference between equations (9.12) and (9.13); a fact that has not received a great amount of attention. Britz[26] comments that although equation (9.12) is 'wrong', better results are obtained from it than the technically correct equation (9.13). By leaving out the factor 4/3, implicitly a fudge factor 0.75 is included for which there is no justification. Britz [26] comments that it is better to use equal intervals close to the interface i.e.

$$C_{1,j+1} = C_{1,j} + Dm (C_{2,j} + C_{0,j} - 2C_{1,j}) \quad (9.14)$$

rather than using a  $h/2$  interval close to the electrode.

## 10. Potential Step in an Infinite Solution- Explicit method

Consider a reaction at an electrode in a solution of oxidised species O, of bulk concentration  $c^*$ .



At a certain time ( $t > 0$ ) a potential step is applied so that O is reduced at the electrode and the concentration of O at the electrode is zero i.e. in terms of dimensionless concentrations, i.e.  $C_{0,j}^o = c_{0,j}^o/c^* = 0.0$  where the superscript o represents oxidised species and the subscripts represent a distance  $0 \leq x \leq h$  away from the electrode and a time  $j \times k$  after the potential step is applied. Once the reaction is proceeding, the rate at which O is consumed at the electrode is equal to the rate at which R is produced i.e.

$$\left. \frac{dC^o}{dx} \right|_{x=0} = - \left. \frac{dC^r}{dx} \right|_{x=0} \quad (10.2)$$

Let us use equal spacings to begin with then from figure 7(a), equation (10.2) becomes:

$$(-C_{1,j}^o + C_{0,j}^o)/h = (C_{1,j}^r - C_{0,j}^r)/h \quad (10.3)$$

and since  $C_{0,j}^o = 0.0$ , then

$$C_{0,j}^r = C_{1,j}^r + C_{1,j}^o \quad (10.4)$$

When equation (10.4) is substituted in for equation (9.14) for r, one obtains equation (10.5)

$$C_{1,j+1}^r = C_{1,j}^r + Dm (C_{2,j}^r - C_{1,j}^r + 2C_{1,j}^o) \quad (10.5)$$



Similarly for O one obtains

$$C^o_{1,j+1} = C^o_{1,j} + D_m(C^o_{2,j} + 0.0 - 2 C^o_{1,j}) \quad (10.6)$$

Though the superscripts and subscripts are cumbersome, they help to identify the parameters.

In order to solve the potential step problem a differential equation of the form equation (9.1) needs to be solved for both species. These equations may be approximated using either equation (9.9) for equal spaced panels (figure 7(a)) or equation (9.12) when the spacing of the panel close to the electrode is  $h/2$  (figure 7(b)).

Let us set the number of iterations within the timescale of the experiment to some constant value  $L$ . Based on this, if the timescale of the experiment is  $t_c$  then  $k = t_c/L$ . For this particular method  $D_m$  may not take values greater than 0.5, so it is set to 0.45 then

$$h = (Dt_c/D_m L)^{1/2} \quad (10.7)$$

Based on an approximation that the diffusion layer thickness does not reach a distance  $6(Dt_c)^{1/2}$  out in solution, we may set up the distance  $x$  if there are  $JMAX$  points in the  $x$  direction. i.e.

$$(JMAX) h = 6 (Dt_c)^{1/2} \quad (10.8)$$

On substituting equation (10.7) into (10.8), one finds that  $JMAX = 6(D_m L)^{1/2}$

Following this we can use an expression for the current as[31]

$$i = -nFAD \left. \frac{dC}{dx} \right|_{x=0} \quad (10.9)$$

which becomes if the distance divisions are all the same,

$$i = -nFAD c^* (C^o_{1,t} - C^o_{0,t})/h \quad (10.10)$$

If one defines a dimensionless parameter  $Z$  as

$$Z = i (t_c)^{1/2} / (n F A (D)^{1/2} c^*) \quad (10.11)$$

and ratioing equation (10.11) compared to the expected dimensionless Cottrell result ,  $Z_c = (L/\pi k)^{1/2}$  one obtains

$$Z/Z_c = \frac{i(t_c k \pi)^{1/2}}{\quad} \quad (10.12)$$

$$(LD)^{1/2} nFAc^*$$

Program one is the FORTRAN listing for the solution of the problem. The initial concentrations are defined in the DO loop labelled 10. The diffusion equation is described in the DO loop labelled 30 . It is possible to change the program to deal with the situation where the spacing close to the electrode is  $h/2$  by changing the lines:

$$FONEW(1) = FOOLD(1) + DM*(-2.D0*FOOLD(1)+FOOLD(2))$$

$$FRNEW(1) = FROLD(1) + DM*(FOOLD(1)-FROLD(1)+FROLD(2))$$

$$W=DSQRT(FLOAT(L)*DM)*FONEW(1)$$

to

$$FONEW(1) = FOOLD(1) + DM*(-3.D0*FOOLD(1)+FOOLD(2))$$

$$FRNEW(1) = FROLD(1) + DM*(2*FOOLD(1)-FROLD(1)+FROLD(2))$$

$$W=2.D0*DSQRT(FLOAT(L)*DM)*FONEW(1)$$

Similar changes may be made for programs two and three. Figure 9 shows the output of this program for two different values of L. It can be seen that the output  $Z/Z_c$  settles to a value of one more quickly when the value of L is large.

## 11. Cyclic Voltammetry Using the Explicit Method .

The next situation considered is that of Sweep Voltammetry which involves the application of a slowly varying linear waveform starting at a potential where no electrochemistry occurs. The potential is swept past the formal potential of the couple. Once again we will consider the reduction of the species O, equation (10.1).

A potential profile as shown in Figure 10 is applied to the electrode and the aim is to examine the current potential characteristics. The current initially increases as the potential is swept toward  $E^0$  and afterward the current decays to zero since all the O is reduced. A similar situation occurs on the reverse sweep for the oxidation of R where a 'mirror image' peak occurs for its oxidation. It can be seen that the bulk solution cyclic voltammogram has a slightly asymmetric shape. The two equations to be solved are

$$\frac{\partial C^o}{\partial t} = D \frac{\partial^2 C^o}{\partial x^2} \quad (11.1)$$

$$\frac{\partial C^r}{\partial t} = D \frac{\partial^2 C^r}{\partial x^2} \quad (11.2)$$

The system is assumed to be at equilibrium and therefore follows the Nernst equation and so the surface concentrations are given by

$$C^o_{0,j}/C^r_{0,j} = \exp(nF(V-V^0)/(RT)) \quad (11.3)$$

where  $V^0$  is the formal potential of the couple and V is the applied potential. This potential may be made dimensionless by defining  $E = V/0.0256 = FV/(RT)$  at  $T = 298K$ . The scan rate  $v$  determines the time of the experiment  $t_c$  since  $t_c = (V_f - V_i)/v$  where  $V_f$  is the final potential and  $V_i$  is the initial potential of the sweep.

The other boundary conditions for the situation shown in figure 6 are  
At the electrode surface

$$\left. \frac{dC^o}{dx} \right|_{x=0} = - \left. \frac{dC^r}{dx} \right|_{x=0} \quad (11.4)$$

or

$$(C^o_{1,j} - C^o_{0,j})/h = - (C^r_{1,j} - C^r_{0,j})/h \quad (11.5)$$

and

$$C^o_{0,j}/C^r_{0,j} = \exp(nEm) \quad (11.6)$$

where  $Em$  is the potential increment i.e.  $(E_f - E_i)/L$  and  $n$  is the number of steps of time up to a particular time where  $L$  is the total number of time divisions and  $E^o$ , the formal potential, is taken to be zero. Equation (11.5) may be substituted into equation (11.6) to give an expression for the concentration at the electrode surface

$$C^r_{0,j} = \frac{C^r_{1,j} + C^o_{1,j}}{(1 + \exp(nEm))} \quad (11.7)$$

Furthermore there is a point out in solution labelled  $N$  to which the diffusion layer does not extend within the timescale of the experiment i.e.

$$C^o_{N,j} = 1 \text{ and } C^r_{N,j} = 0 \quad (11.8)$$

An expression for the current is as follows[29]

$$i = \frac{nFAc^*D}{h} \left[ \frac{C^o_{0,j} - \exp(nE_m)C^r_{0,j}}{1 + \exp(nE_m)} \right] \quad (11.9)$$

This will be ratioed to the dimensionless current function from Nicholson and Shain[17].  $\sqrt{\pi}\chi$  (at) where

$$\sqrt{\pi}\chi$$
 (at) =  $i/(nFAc^*\sqrt{aD})$  (11.10)

where  $a = nFv/(RT)$ . This dimensionless function takes the value 0.4463 as a maximum which occurs 28.5 mV after the formal potential. Equation (11.9) may be converted into the dimensionless form :

$$\sqrt{\pi} \chi(at) = \frac{\sqrt{D}}{\sqrt{ah}} \left[ \frac{C_{0,j}^o - \exp(nE_m) C_{0,j}^r}{1 + \exp(nE_m)} \right] \quad (11.11)$$

and since  $h = (Dt_c/(D_m L))^{1/2}$  and  $t_c = (E_i - E_f)/v$  then

$$\sqrt{\pi} \chi(at) = \frac{\sqrt{D_m L}}{\sqrt{(E_i - E_f)}} \left[ \frac{C_{0,j}^o - \exp(nE_m) C_{0,j}^r}{1 + \exp(nE_m)} \right] \quad (11.12)$$

Program two is a listing of the explicit cyclic voltammetry system in FORTRAN with an integral box spacing.

Table 2.

Peak current and peak potential values as a function of input values of L and Dm for the explicit method using Program two.

(a) denotes h/2 spacing at the electrode surface without the factor 4/3.

(b) denotes h/2 spacing at the electrode surface with the factor 4/3

(c) denotes h spacing at the electrode.

Condition	Dm	L	Ep	$\sqrt{\pi} \chi(at)$
(a)	0.01	5000	-0.03024	0.44351
(a)	0.1	5000	-0.02964	0.43833
(a)	0.04	5000	-0.02950	0.44124
(a)	0.45	1000	-0.0336	0.41001
(a)	0.45	5000	-0.0308	0.42959
(a)	0.04	6000	-0.02920	0.44168
(b)	0.04	5000	-0.03120	0.42606
(b)	0.1	5000	-0.03084	0.42868
(b)	0.01	5000	-0.03228	0.41494
(c)	0.45	500	-0.036	0.3936
(c)	0.1	500	-0.0384	0.3772
(c)	0.04	500	-0.0444	0.35116
(c)	0.45	6000	-0.0306	0.43101
(c)	0.45	3000	-0.0314	0.42371
(c)	0.10	5000	-0.0318	0.42288
(c)	0.04	5000	-0.03324	0.41339
(c)	0.45	1000	-0.0336	0.40811

Table 2 shows a set of results for the output of the explicit program obtained from program two for cyclic voltammetry for different values of Dm and L. It can be seen that there is reasonable agreement with the literature values. The program was run under different conditions for the box closest to the electrode. When the interval is h/2, the equations are solved with the factor 4/3 (case b) and without the factor 4/3 (case a). The best values are obtained with the half box spacing close to the electrode without the factor 4/3. However the results seem to converge to the true value with increasing values of L. Figure 11 shows the cyclic voltammogram for Dm = 0.45 and L = 6000. Using equation (9.13) ( case b in table 2), the results can be seen to be better, but with a value of Dm = 0.45 , the program does not work. The problem with the results from the case (a) in Table 2 is that there is no justification for leaving out the factor 4/3 even though the results are better[26]

## 12. Cyclic Voltammetry Using the Implicit Method

From above, the following has been shown

$$C_{i,j+1} = C_{i,j} + D_m (C_{i+1,j} - 2C_{i,j} + C_{i-1,j}) \quad (9.10)$$

as may be seen in figure 6. The reverse of the above is also valid;

$$C_{i,j+1} + D_m(C_{i+1,j+1} - 2C_{i,j+1} + C_{i-1,j+1}) = -C_{i,j} \quad (12.1)$$

At the point A in Figure 12 the term  $dC/dt$  may be approximated as

$$\frac{dC}{dt} = \frac{C_{i,j+1} - C_{i,j}}{k} \quad (12.2)$$

Also at the point A the  $C''$  term may be an average of equations (9.10) and (12.1) i.e.

$$\frac{C_{i,j+1} - C_{i,j}}{k} = \frac{D}{2} \left[ \frac{C_{i+1,j+1} + C_{i-1,j+1} - 2C_{i,j+1}}{h^2} + \frac{C_{i+1,j} + C_{i-1,j} - 2C_{i,j}}{h^2} \right] \quad (12.3)$$

which becomes

$$(2+2Dm)C_{i,j+1} - D_m C_{i+1,j+1} - D_m C_{i-1,j+1} = \frac{D}{2} (C_{i+1,j} + C_{i-1,j} - 2C_{i,j}) \quad (12.4)$$

Everything on the right hand side is known and it is possible to set up a series of algebraic equations to determine concentration on the left hand side. In the case of the explicit method we were progressing forward in time for each distance point, whereas in this case we progress by determining the concentrations at all the distances simultaneously at each time increment. The resulting series of equations may be shown in matrix form as

$$\begin{pmatrix} (2+2Dm) & -Dm & 0 & 0 & 0 \\ -Dm & (2+2Dm) & -Dm & 0 & 0 \\ 0 & \dots & \dots & \dots & 0 \\ 0 & 0 & -Dm & (2+2Dm) & -Dm \\ 0 & 0 & 0 & -Dm & (2+2Dm) \end{pmatrix} \begin{pmatrix} C_{1,j+1} \\ C_{2,j+1} \\ \dots \\ C_{N-1,j+1} \\ C_{N,j+1} \end{pmatrix} = \begin{pmatrix} (2-2Dm) & Dm & 0 & 0 & 0 \\ Dm & (2-2Dm) & Dm & 0 & 0 \\ 0 & \dots & \dots & \dots & 0 \\ 0 & 0 & Dm & (2-2Dm) & Dm \\ 0 & 0 & 0 & Dm & (2-2Dm) \end{pmatrix} \begin{pmatrix} C_{1,j} \\ C_{2,j} \\ \dots \\ C_{N-1,j} \\ C_{N,j} \end{pmatrix} \begin{pmatrix} k_1 \\ k_2 \\ \dots \\ k_{N-1} \\ k_N \end{pmatrix} \quad (12.5)$$

It should be noted that in addition to these N points there are also two boundary points at the electrode surface and also at in bulk solution. Since these boundary conditions are known at all times then the right hand side has to be modified as follows

$$\begin{pmatrix} (2+2Dm) & -Dm & 0 & 0 & 0 \\ -Dm & (2+2Dm) & -Dm & 0 & 0 \\ 0 & \dots & \dots & \dots & 0 \\ 0 & 0 & -Dm & (2+2Dm) & -Dm \\ 0 & 0 & 0 & -Dm & (2+2Dm) \end{pmatrix} \begin{pmatrix} C_{1,j+1} \\ C_{2,j+1} \\ \dots \\ C_{N-1,j+1} \\ C_{N,j+1} \end{pmatrix} = \begin{pmatrix} k_1 + D_m(C_{0,j} + C_{0,j+1}) \\ k_2 \\ \dots \\ k_{N-1} \\ k_N + D_m(C_{N+1,j} + C_{N+1,j+1}) \end{pmatrix} \quad (12.6)$$

In this manner the boundary conditions are included. The above set of equations are tridiagonal and may be solved by using the Thomas Algorithm[26].

Booman and Pence used an implicit methods for kinetic complications for bulk solution reactions[32] and Heinze at al.[33] used the Crank Nicolson method for cyclic voltammetry and Lasia[34] employed it for examining dimerisation. A review of the Crank Nicolson methods has appeared[35]

Table 3.

Peak current and peak potential values as a function of input values of L and Dm for the implicit method in Program three; the implicit finite difference method. The program uses an interval of h at the electrode.

Dm	L	Ep	$\sqrt{\pi} \chi(\text{at})$
0.45	500	-0.0324	0.4174
1.00	500	-0.0312	0.4267
1.45	500	-0.0300	0.4299
2.00	500	-0.030	0.4323
2.50	500	-0.030	0.4338
3.00	500	-0.030	0.4348
0.45	6000	-0.0297	0.4377
0.04	6000	-0.0326	0.4183

Program three is a listing of the FORTRAN version of the solution to this problem. Table 3 shows the output of program three. This program takes considerably longer to run than the explicit method. The output for the full box interval at the electrode surface is marginally better than in the case of the explicit method. However when the half

spacing at the electrode is introduced, there is a discrepancy in the output. The current is a factor of two greater than expected, which happens whether the factor 4/3 is included or not. However the advantage of the implicit method is that larger values of  $D_m$  ( $> 0.5$ ) can be used.

### 13. Cyclic Voltammetry Using the Hopscotch Algorithm.

This method is also based on the equation mentioned above

$$C_{i,j+1} = C_{i,j} + D_m (C_{i+1,j} - 2C_{i,j} + C_{i-1,j}) \quad (9.10)$$

which yields when rearranged

$$C_{i,j+1} = (C_{i,j} + D_m (C_{i+1,j+1} + C_{i-1,j+1})) / (1 + 2D_m) \quad (13.1)$$

Furthermore since

$$C_{i,j+2} - C_{i,j+1} = C_{i,j+1} - C_{i,j} \quad (13.2)$$

then equation (13.1) becomes

$$C_{i,j+2} = 2(C_{i,j} + D_m (C_{i+1,j+1} - C_{i-1,j+1})) / (1 + 2D_m) - C_{i,j} \quad (13.3)$$

Equations (13.1) and (13.3) may be seen to be extrapolating further in time in order to obtain the concentration in the future at a particular position.

From equation (13.3) we can obtain algebraically

$$C_{i,j+2} = C_{i,j} + 2D_m (C_{i+1,j+1} - 2C_{i,j} + C_{i-1,j+1}) / (1 + 2D_m) \quad (13.4)$$

We are interested in the node close to the electrode node 2, where node 1 is at the electrode surface as shown in Figure 13.

The procedure is as follows as described in the paper by Shoup and Szabo[36] Initially  $j=0$ .

- (1) For nodes where  $(i+j)$  is odd  $C_{i,j}$  is overwritten from equation (13.3) and for the node 2 ( $i=2$ ) when  $(j+2)$  is odd store  $C_{2,j+1}$  in a parameter  $S_{2,j+1}$ .
- (2) When  $(j+2)$  is even the calculate  $C_{2,j+1}$  using equation (13.1) and store it in  $S_{2,j+1}$ .
- (3) For the rest of the nodes then with  $(i+j)$  even, overwrite  $C_{i,j}$  with  $C_{i,j+2}$  calculated from equation (13.4).
- (4) Then increment  $j$  by 1 and go back to the start.

Program four shows a listing of the solution of cyclic voltammetric problem for a species in bulk solution as described previously. By using the series of steps outlined above the



evolution of how the concentration at each point is calculated is shown in Figure 13. Initially  $j=0$  and the concentrations in the filled circles are known concentrations. Applying step (1) to  $i = 3$ ,  $C_{3,1}$  is found. Applying step (2),  $C_{2,1}$  is then found and applying step (3) for  $i+j$  even i.e for  $i = 2$  and  $i = 4$ ,  $C_{i,j+2}$  is found from equation (13.3). It can be seen that the points are calculated in a hopscotch manner.

Table 4.

Peak current and peak potential outputs as a function of the input values of  $Dm$  and  $L$  using the hopscotch program ; program four. The asterisk denotes slight oscillation about the current values.

$Dm$	$L$	$E_p$	$\sqrt{\pi} \chi(at)$
0.45	6000	-0.0298	0.43773
1.00	6000	-0.02920	0.44051
1.45	6000	-0.02920	0.44151
2.00	6000	-0.02900	0.44223
0.04	6000	-0.03270	0.418827
0.1	6000	-0.03140	0.42833
0.45	1000	-0.03120	0.42573
0.45	7000	-0.02966	0.43836
1.00	7000	-0.02923	0.44096
3.00	1000	-0.02760	0.43846
4.00	2000	-0.02880	0.44151
4.00	3000	-0.02860	0.44225*
6.00	2000	-0.02880	0.44252*

Table 4 shows some typical results using Program four. It can be seen that a range of values of  $Dm$  can be used with the hopscotch algorithm but at higher values there is a slight oscillation of the current ( $Dm= 4,6$  when  $L = 3000$ ). The outputs can be seen to be closer to the true values than those obtained using the other two methods described above. The hopscotch method has been used for chronoamperometry[36], and to characterise the diffusion process at microelectrodes[37,38].

#### 14. Orthogonal Collocation

The method involves solving the diffusion equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \pm f(c) \quad (14.1)$$

where  $f(c)$  represents some kinetic complications in the process

An approximate solution is chosen as

$$\Phi = \sum_{i=1}^N \alpha_i(t) \phi_i(x) \quad (14.2)$$

in such a way as to make the residual of equation equal to zero[39] i.e.

$$R = \frac{\partial \Phi}{\partial t} - D \frac{\partial^2 \Phi}{\partial x^2} \pm f(\Phi) = 0 \quad (14.3)$$

In fact what is done is to make the weighted residual equal to zero

$$\int_w w_j R(\phi) dx = R|_{x=x_j} \quad (14.4)$$

The choice of the weighting function determines the method[40]. In the method of collocation the weighting function is chosen to be a displaced dirac function

$$w_j = \delta(x-x_j) \quad (14.5)$$

which means that

$$\int_w w_j R(\phi) dx = 0 \quad (14.6)$$

and so the residual is zero at specified points  $x_j$ [39]. The choice of these points can make the calculations both convenient and accurate. In orthogonal collocation the points which are chosen are roots of orthogonal polynomials. Sets of orthogonal polynomials which satisfy the boundary conditions are chosen and their roots represent the collocation points. Following the notation of Whiting and Carr[41], the general evolution of the problem is as follows:

Once the system of polynomials have been chosen they essentially clamp the problem down so that solution is only found at particular positions within the polymer layer defined by the roots of these polynomials. For example, using shifted Jacobi polynomials if  $\alpha$  is 0.0 and  $\beta$  is 0.0 then for 6 points the concentrations are determined at the dimensionless positions 0.03376, 0.16939, 0.38069, 0.619309, 0.83060, 0.96623 away from the electrode. The solution is in the general form

$$C(x_i, t) = \sum_{j=1}^{N+2} b_j(t) (x_i)^{j-1}; i = 1, 2, 3, 4, \dots, N + 2 \quad (14.7)$$

where there are  $N+2$  collocation points. Notice that the function  $C(x_i, t)$  has been split into two independent parts, one in time and the other in distance. Thus since the positions in distance have been fixed, the problem is simplified to a time dependent problem only.

First and second derivatives of equation (14.7) may be found:

$$dC(x, t) \quad N+2 \quad d(x)^{j-1}$$

$$\frac{dC(x,t)}{dx} \Big|_{x=x_i} = \sum_{j=1}^{N+2} \frac{d^2(x)^{j-1}}{dx^2} \Big|_{x=x_i} b_j(t) \quad (14.8)$$

$$\frac{d^2C(x,t)}{dx^2} \Big|_{x=x_i} = \sum_{j=1}^{N+2} \frac{d^2(x)^{j-1}}{dx^2} \Big|_{x=x_i} b_j(t) \quad (14.9)$$

These equations may be evaluated at all the  $N+2$  collocation points. The above expressions may be expressed in a simpler matrix notation where the - superscript represents a one dimensional matrix and = superscript represents a two dimensional matrix.

$$\overline{C(t)} = \overline{Q} \overline{b(t)} \quad (14.10)$$

where  $Q_{i,j} = x_i^{j-1}$

and

$$\frac{d\overline{C(t)}}{dx} = \overline{C} \overline{b(t)}; \frac{d^2\overline{C(t)}}{dx^2} = \overline{D} \overline{b(t)} \quad (14.11)$$

where

$$C_{i,j} = \frac{dx^{j-1}}{dx} \Big|_{x=x_i}; D_{i,j} = \frac{d^2x^{j-1}}{dx^2} \Big|_{x=x_i} \quad (14.12)$$

from above

$$\overline{b(t)} = \overline{Q}^{-1} \overline{C(t)} \quad (14.13)$$

and thus these can be substituted into (14.8) and (14.9) to get

$$\frac{d\overline{C(t)}}{dx} = \overline{C} \overline{Q}^{-1} \overline{C(t)} = \overline{A} \overline{C(t)} \quad (14.14)$$

$$\frac{d^2\overline{C(t)}}{dx^2} = \overline{D} \overline{Q}^{-1} \overline{C(t)} = \overline{B} \overline{C(t)} \quad (14.15)$$

Once the matrices A and B are computed they are invariant for a given number of collocation points. The final expression to be solved is composed of a series of ordinary differential equations of the form

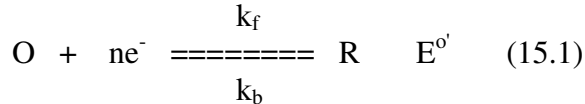
$$\left. \frac{dC(t)}{dt} \right|_{x=x_i} = \beta \overline{BC(t)} + \overline{f(C(t))} \quad (14.16)$$

where  $\beta$  is a dimensionless parameter which is a function of the diffusion coefficient D. This set of ordinary differential equations may be solved by any standard technique[42,43].

Collocation methods have been widely used in electrochemistry[44,45] and the method was first applied to electrochemistry by Whiting and Carr[41]. Eddows[46] solved a rotating disk problem using both finite difference and collocation and stated that the collocation method is more efficient and that its efficiency may be optimised by using a change of space variable. However Magno[47] compared collocation to finite difference for an ECir mechanism and with a large value of k, the orthogonal collocation method was the least valid because of the computation time and the choice of a parameter  $\beta$  which is related to the diffusion layer thickness. Techniques for  $\beta$  optimisation subsequently appeared[48-50].

## 15. Cyclic Voltammetry Using Orthogonal Collocation.

Consider the reduction of the species O as before but in this case the electrode kinetics are slow.



The following diffusion equations are to be solved for each half of the couple:

$$\frac{\partial c^o}{\partial t} = D \frac{\partial^2 c^o}{\partial x^2} \quad (15.2)$$

$$\frac{\partial c^r}{\partial t} = D \frac{\partial^2 c^r}{\partial x^2} \quad (15.3)$$

The initial conditions are

$$t = 0; \quad c^o(x,0) = c^* \text{ and } c^r(x,0) = 0.0 \quad (15.4)$$

i.e. that initially there is a solution of O present .

The boundary condition is that at a distance L outside the diffusion layer the concentrations do not change

$$t > 0 ; \quad c^o(L,t) = c^* \text{ and } c^r(L,t) = 0.0 \quad (15.5)$$

and at the electrode:

$$D \frac{dc^o}{dx} \Big|_{x=0} = k_f c^o(o,t) - k_b c^r(o,t) \quad (15.6)$$

where

$$k_f = k^o \exp\{-\alpha nF(E-E^o)/(RT)\} \quad (15.7)$$

and

$$k_b = k^o \exp\{(1-\alpha)nF(E-E^o)/(RT)\} \quad (15.8)$$

and also

$$D \frac{dc^o}{dx} \Big|_{x=0} = -D \frac{dc^r}{dx} \Big|_{x=0} \quad (15.9)$$

For the purposes of using orthogonal collocation it is convenient to make each of the parameters dimensionless as follows:

$$X = x/L; \quad C = c/c^* ; \quad T = at; \quad K = kL/D ; \quad \beta = D/(aL^2) \quad (15.10)$$

When these dimensionless parameters are substituted into equations ( 15.2 ) and (15.3) then they become

$$\frac{\partial C^o}{\partial T} = \beta \frac{\partial^2 C^o}{\partial X^2} \quad (15.11)$$

$$\frac{\partial C^r}{\partial T} = \beta \frac{\partial^2 C^r}{\partial X^2} \quad (15.12)$$

The boundary conditions become:

$$C^r(1,t) = 0 \text{ and } C^o(1,t) = 1 \quad (15.13)$$

and

$$\frac{dC^o}{dx} \Big|_{x=0} = Kf C^o(0,t) - KbC^r(0,t) \quad (15.14)$$

and the other two boundary conditions are as follows:

$$\frac{dC^r}{dX} \Big|_{X=0} = - \frac{dC^o}{dX} \Big|_{X=0} \quad (15.15)$$

The following substitutions may be made:

$$\frac{dC^o}{dX} \Big|_{X=0} = \sum_{j=1}^{N+2} A_{i,j} C^o(X_j, T) \quad \text{and} \quad \frac{d^2 C^o}{dX^2} \Big|_{X=0} = \sum_{j=1}^{N+2} B_{i,j} C^o(X_j, T) \quad (15.16)$$

Substituting these discretised equations into equation (15.5), one obtains:

$$\sum_{j=1}^{N+2} A_{1,j} C^o(X_j, T) = - \sum_{j=1}^{N+2} A_{1,j} C^r(X_j, T) \quad (15.17)$$

which becomes on expansion and substituting the outer boundary conditions and rearranging:

$$A_{1,1} C^o(0, T) + A_{1,N+2} C^o(X_{N+2}, T) + \sum_{j=2}^{N+1} A_{1,j} C^o(X_j, T) + A_{1,1} C^r(0, T) + \sum_{j=2}^{N+1} A_{1,j} C^r(X_j, T) = 0 \quad (15.18)$$

From the boundary condition (15.14):

$$\sum_{j=1}^{N+2} A_{1,j} C^o(X_j, T) = K_f C^o(0, T) - K_b C^r(0, T) \quad (15.19)$$

one obtains after expansion and rearrangement:

$$C^o(0, T) = - \left\{ A_{1,N+2} C^o(X_{N+2}, T) + \sum_{j=2}^{N+1} A_{1,j} C^o(X_j, T) \right\} / (A_{1,1} - K_f) \quad (15.20)$$

which may be substituted into (15.18) to get

$$C^r(0, T) =$$

$$\{A_{1,N+2}CN2 + \sum_{j=2}^{N+1} A_{1,j} CN2 C^0(X_j, T) - \sum_{j=2}^{N+1} A_{1,j} C^r(X_j, T)\} / CN1 \quad (15.21)$$

where

$$CN1 = A_{1,1} - A_{1,1} Kb / (A_{1,1} - Kf) \quad (15.22)$$

and

$$CN2 = A_{1,1} / (A_{1,1} - Kf) - 1 \quad (15.23)$$

Using this and equation (15.20) we can get an expression for  $C^0(0, T)$

$$C^0(0, T) = - \{ A_{1,N+2} + Kb(A_{1,N+2}CN2 + \sum_{j=2}^{N+1} A_{1,j} CN2 C^0(0, T) - \sum_{j=2}^{N+1} A_{1,j} C^r(X_j, T)) / CN1 + \sum_{j=2}^{N+1} A_{1,j} C^0(X_j, T) \} / (A_{1,1} - Kf) \quad (15.24)$$

This may be substituted into

$$\begin{aligned} \frac{dC^0}{dT} &= \sum_{j=1}^{N+2} B_{i,j} C^0(X_j, T) \\ &= \{ B_{i,1} C^0(0, T) + B_{i,N+2} + \sum_{j=2}^{N+1} B_{i,j} C^0(X_j, T) \} \end{aligned} \quad (15.25)$$

to yield a set of ordinary differential equations which may be solved by conventional means.

Finally the current may be evaluated as follows:

$$i = nFAD \frac{dc}{dx} \Big|_{x=0} \quad (15.26)$$

$$= \frac{nFAc^*}{L} \sum_{j=1}^{N+2} A_{1,j} C^0(X_j, T) \quad (15.27)$$

The structure of the collocation program (program five) is as follows. The subroutine JCOBI calculates the roots and derivatives of the polynomial. The subroutine DFOPR calculated the parameters  $A_{i,j}$  and  $B_{i,j}$  associated with these roots. The subroutine FUN supplies the information on the differential equations. F is the vector on the right hand side of equation (15.25). The subroutine OUT is the output subroutine. The latter two subroutines are supplied for DFOPR from the IMSL library, which solves a system of

first order differential equations with given initial conditions.  $\beta$  optimisation is included in this program and the theory behind this is detailed elsewhere[39,49,50].



Table 5.

A table of the peak current position and dimensionless current values along with peak to peak separation as a function of different values of the dimensionless heterogeneous rate constant . The number of collocation points was N, Estart = 0.3V, Eswit = -0.3V,  $E^o = 0.0$ , Concentration =  $10^{-6} \text{mol.cm}^{-3}$ , scan rate =  $10^{-3} \text{V/s}$ , T = 298K,  $D = 10^{-5} \text{cm}^2/\text{s}$  and  $\alpha = 0.5$ .

$E^*$  is the literature peak to peak separation[51]

$\phi$	N	$E_p/V$	$\Delta E/mV$	$\Delta E^*/mV$	$\sqrt{\pi} \chi(at)$	20	12	-0.02911	58.81
	61	0.44477							
5	12	-0.03131	62.81	65	0.44037				
4	18	-0.03191	64.01	66	0.4389				
1	18	-0.04191	82.41	84	0.42082				
0.75	18	-0.04611	90.01	92	0.41432				
0.5	18	-0.05391	104.2	105	0.38332				
0.35	18	-0.06311	121.0	121	0.39316				
0.25	18	-0.07391	140.8	141	0.38332				
0.10	18	-0.11271	214.2	212	0.36264				

Table 5 gives the output of program five where the dimensionless heterogeneous rate constant  $\phi$  is varied where

$$\phi = k^o / (D a)^{1/2} \quad (15.28)$$

where  $k^o$  is the standard heterogeneous rate constant and  $a = nFv/(RT)$  where  $v$  is the scan rate. It can be seen that the peak to peak separation compares well with the literature values[51]. Figure 14 shows some typical outputs for certain values of  $\phi$  under the conditions listed in the figure legend.

Orthogonal Collocation has been used for the simulation of diffusion at rotating ring disk electrodes[52] and cyclic voltammetry for CE and EC mechanisms[53]. Furthermore it has been employed for characterising at diffusion at microelectrodes[54] and microelectrode arrays[55,56].

## 16. More Advanced Numerical Methods Applied to Electrochemistry.

Peaceman and Rachford[57] developed an Alternate Direction Implicit method (ADI) which retains a tridiagonal matrix and allows two dimensional equations to be solved. Such a method has been used in microelectrode studies[58].

In an effort to reduce computation time and to make methods mentioned above more amenable to microprocessors, methods were devised using unequal distance intervals so that there is more emphasis on the points closer to the electrode. Joslin and Pletcher[59] were the first to employ such ideas for electrochemistry. Functions such as[59]

$$y = (1 - \exp(-ax))/a \quad (16.1)$$

and[26]

$$y = ax/(ax+1) \quad (16.2)$$

have been employed where  $a$  is a constant and  $y$  is the transformed distance. Feldberg[60] developed a refinement which allows the points in the expanding panels to shift progressively toward the inner boundary closer to the electrode. This has been used by Seeber and Stefani[61] and expanding panel methods have been used widely in electrochemistry[62-64]. Several authors[65-67] have introduced a quasi explicit algorithm based on the DuFort Frenkel approach which have been characterised by simulating the potential step technique. The numerical integration algorithm[68] and more recent versions of implicit methods[69] have been used for cyclic voltammetry. Numerical methods have been also used for spectroelectrochemistry[70] and chronoamperometry and adsorption[71].

## 17. Conclusion

In general the choice of the method, be it analytical or numerical, depends on the computational ability of the chemist. Methods based on understanding the model rather than computational efficiency are frequently more useful and lately packages for the automatic solution of specific electrochemical problems have appeared. DIGISIM [72] uses the Rudolph algorithm to simulate cyclic voltammograms for following first and second order homogeneous reactions for a wide range of electrode geometries. CONDESIM 100 [73] allows the simulation of cyclic voltammetry, chronoamperometry and chronopotentiometry for a variety of electrochemical systems. With the simulations outlined above, as well as with the packages, care must be taken not to neglect any nonidealities of the model such as those mentioned in the introduction. For example, it is not a trivial experiment to obtain a peak to peak separation of 57 mV for the cyclic voltammetry of a reversible system. Potential drop in the cell is only one of the many experimental difficulties. These difficulties are compounded when semiconducting electrodes are employed ( such as doped tin oxide) or tortuous cell configurations are used, as in the case of reflectance infrared spectroelectrochemistry. However, once a reasonable model has been developed for the system, both for the electroactive species as well as the electrode configuration, the methods outlined above for simulating the system can be used.

## Acknowledgements

JC would like to acknowledge funding from FOCAS

## Table 2.

Peak current and peak potential values as a function of input values of  $L$  and  $D_m$  for the explicit method using Program two.

(a) denotes  $h/2$  spacing at the electrode surface without the factor  $4/3$ .

(b) denotes  $h/2$  spacing at the electrode surface with the factor  $4/3$

(c) denotes  $h$  spacing at the electrode.

Condition	$D_m$	$L$	$E_p$	$\sqrt{\pi} \chi(at)$
(a)	0.01	5000	-0.03024	0.44351

(a)	0.1	5000	-0.02964	0.43833
(a)	0.04	5000	-0.02950	0.44124
(a)	0.45	1000	-0.0336	0.41001
(a)	0.45	5000	-0.0308	0.42959
(a)	0.04	6000	-0.02920	0.44168
(b)	0.04	5000	-0.03120	0.42606
(b)	0.1	5000	-0.03084	0.42868
(b)	0.01	5000	-0.03228	0.41494
(c)	0.45	500	-0.036	0.3936
(c)	0.1	500	-0.0384	0.3772
(c)	0.04	500	-0.0444	0.35116
(c)	0.45	6000	-0.0306	0.43101
(c)	0.45	3000	-0.0314	0.42371
(c)	0.10	5000	-0.0318	0.42288
(c)	0.04	5000	-0.03324	0.41339
(c)	0.45	1000	-0.0336	0.40811

Table 3.

Peak current and peak potential values as a function of input values of L and Dm for the implicit method in Program three; the implicit finite difference method. The program uses an interval of h at the electrode.

Dm	L	Ep	$\sqrt{\pi} \chi(at)$
0.45	500	-0.0324	0.4174
1.00	500	-0.0312	0.4267
1.45	500	-0.0300	0.4299
2.00	500	-0.030	0.4323
2.50	500	-0.030	0.4338
3.00	500	-0.030	0.4348
0.45	6000	-0.0297	0.4377
0.04	6000	-0.0326	0.4183

Table 4.

Peak current and peak potential outputs as a function of the input values of Dm and L using the hopscotch program ; program four. The asterisk denotes slight oscillation about the current values.

Dm	L	Ep	$\sqrt{\pi} \chi(at)$
0.45	6000	-0.0298	0.43773
1.00	6000	-0.02920	0.44051
1.45	6000	-0.02920	0.44151
2.00	6000	-0.02900	0.44223
0.04	6000	-0.03270	0.418827
0.1	6000	-0.03140	0.42833
0.45	1000	-0.03120	0.42573

0.45	7000	-0.02966	0.43836
1.00	7000	-0.02923	0.44096
3.00	1000	-0.02760	0.43846
4.00	2000	-0.02880	0.44151
4.00	3000	-0.02860	0.44225*
6.00	2000	-0.02880	0.44252*

Table 5.

A table of the peak current position and dimensionless current values along with peak to peak separation as a function of different values of the dimensionless heterogeneous rate constant . The number of collocation points was N, Estart = 0.3V, Eswit = -0.3V,  $E^0 = 0.0$ , Concentration =  $10^{-6} \text{mol.cm}^{-3}$ , scan rate =  $10^{-3} \text{V/s}$ , T = 298K,  $D = 10^{-5} \text{cm}^2/\text{s}$  and  $\alpha = 0.5$ .

E\* is the literature peak to peak separation[51]

$\phi$	N	Ep/V	$\Delta E/\text{mV}$	$\Delta E^*/\text{mV}$	$\sqrt{\pi} \chi(\text{at})$	20	12	-0.02911
58.81	61	0.44477						
5	12	-0.03131	62.81	65	0.44037			
4	18	-0.03191	64.01	66	0.4389			
1	18	-0.04191	82.41	84	0.42082			
0.75	18	-0.04611	90.01	92	0.41432			
0.5	18	-0.05391	104.2	105	0.38332			
0.35	18	-0.06311	121.0	121	0.39316			
0.25	18	-0.07391	140.8	141	0.38332			
0.10	18	-0.11271	214.2	212	0.36264			



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