Simulation of Charge Transfer at Ultramicrointerfaces

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Doctorate of Philosophy, Edinburgh University, 1991
To Adam Cairns-Smith,

who deserved recognition more than any of us.
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Abstract

This work details the simulation of charge transfer at ultramicrointerfaces. A novel algorithm is presented for the simulation of electrochemical techniques applied to both ultramicrodisc and ultramicropipette electrodes.

Numerical Method

The simulations employ the Crank-Nicolson finite differences or the Alternating Direction Implicit (ADI) method extended to include expansion of the space grid in two dimensions, a n-point current calculation and implicit determination of boundary conditions. The effects are determined of; point separation, choice of grid expansion equation, boundary conditions and relative number of points on electrode and in solution. Also, diffusion geometry, time increment, and the stability of the algorithm are considered in detail. The various methods currently available to model electrochemical response at ultramicrointerfaces are discussed, together with their limitations and a suggested protocol for their use.

Computing

All programs are written in FORTRAN and all calculations performed in double precision. Source codes were compiled and run on the Edinburgh Multi-Access System (EMAS).

Electrochemical techniques

Techniques simulated include cyclic voltammetry and chronoamperometry at macro, ultramicrodisc and ultramicropipette electrodes, including asymmetric sweep voltammetry at ultramicropipette electrodes. Results are presented for both reversible
and quasi-reversible charge transfer. Effects of sweep rate, electrode radius, charge transfer coefficient and rate of charge transfer are studied. Disc and pipette electrochemical responses are compared over a range of experimental parameters.

The simulation method presented is fast, accurate and stable over a wide range of experimental parameters and is easily adapted to different electrode geometries and experimental techniques.
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Chapter 1

Introduction

The unique properties of ultramicropipette electrodes were first realised in 1986[1]. The Interface presented at the tip of an ultramicropipette is one between Two Immiscible Electrolyte Solutions (ITIES). Previous work on ion transfer at an ITIES had been in the macro scale only [2–14]. The versatility and analytical selectivity presented by a liquid-liquid interface combined with the practical and rapid mass-transport advantages of an ultramicroelectrode lead to the obvious combination of the two; an ultramicrointerface between two immiscible electrolyte solutions supported at the tip of an ultramicropipette [1].

1.1 Applications of the liquid-liquid interface

The liquid-liquid interface has been the subject of much study, detailed comprehensively in a recent review [15]. Of particular interest is the modelling of ion transfer across biological interfaces such as lipid bilayers [16–18] and the possible use of liquid-liquid micro electrodes for drug detection, particularly those which have their sites of action in the brain [19,20] A specific advantage of the liquid-liquid interface is the discrimination of protonated neurotransmitters over common brain metabolites and physiological species such as ascorbate. Ascor-
bate replenishes the oxidised forms of the neurotransmitters after detection at the solid electrodes, giving a deceptively high charge transfer current due to feedback. Ascorbate in relatively large concentrations in the brain presents a particularly large obstacle to the detection of such messenger molecules that occur in extremely small, nanomolar concentrations in the sub\textit{stantia nigra}.

Selectivity is essential as the interferents are present in overwhelmingly large concentrations preventing an assay by conventional redox methods. Conventional, solid ultramicroelectrodes coated with perfluorosulphonated polymers \[21-30\] confer some selectivity and give a rapid response but fail to discriminate between different types of choline. Specificity towards dopamine, norepinephrine, epinephrine and 5-hydroxytryptamine is particularly desired \[31-37\]. The preferential ion-transfer of neurotransmitters may be achieved through a difference of charge transfer energies, \(\Delta G_t\) \[4\], the Gibbs free energy of transfer.

The neurotransmitters mentioned above are particularly hydrophilic, so, although selectivity over metabolites and other interferents may be easily attained using a liquid-liquid interface, detection within an available potential window is not always straightforward. The potential window may be extended through use of particularly hydrophobic, organic-phase, supporting electrolytes \[38-42\] or a judicious choice of electrolyte solutions (page 121, reference \[15\]). The free energy of transfer may be shifted to within the potential window through facilitated ion-transfer using organic receptor molecules \[43-59\].

As a prerequisite to the practical problem of detection of neurotransmitters, the diffusion to and from, and charge transfer across a liquid-liquid ultramicrointerface interface must first be understood. An attempt to develop this understanding through a series of models forms a basis for the remainder of this work. Before we begin the treatment in depth, let us briefly consider the numerous additional advantages conferred by the geometry of an ultramicroelectrode.
1.2 Applications of ultramicroelectrodes

An ultramicrointerface may be described as an interface with a maximum dimension of 20\( \mu \)m. The geometry is usually circular, for example, an ultramicropipette or an ultramicrohole in an extremely thin insulating substrate. The small size of the electrode and therefore the extremely small currents passed, make the design ideal for a chemical sensor and, additionally, circumvent problems associated with larger electrodes. Ultramicroelectrodes as sensors, due to their size and use of a very low current do not destroy the sample being monitored, they are essentially non-invasive. There is a rapid time response due to the enhanced mass transport allowing time independent currents to be measured. Steady state behaviour occurs in most applications.

For ion transfer across a large scale liquid-liquid interface, experimental determination of the kinetics by convolution voltammetry\([60,61]\) and A.C. voltammetry\([62,7,63]\) is hindered by a large iR drop. This occurs mainly in the organic phase and cannot be adequately compensated for. Supporting electrolyte of high concentration, \((10^{-3} - 10^{-1} M)\) to minimise the iR drop does not alleviate the problem as the transferring ion may exhibit strong ion-pairing with a counter ion in the base electrolyte.

Nevertheless, though lacking in accuracy, experiments of this kind have yielded rate constants of the orders \(10^{-1} - 10^{-2} \text{ cms}^{-1}\). With enhanced mass transport of the ion to the ultramicroelectrode surface, high rates of interfacial charge transfer may be measured accurately and unproductive catalytic reactions may be reduced, (such as ascorbate redox reactions with dopamine, above) as reaction products diffuse rapidly away from the electroactive area. Fast measurements are also aided by the low capacitance to faradaic current ratio at ultramicroelectrodes. The double layer charging current is proportional to electrode area, small electrodes enabling faradaic currents to be measured at very short times. The low value of iR
Chapter 1. Introduction

drop at a liquid-liquid ultramicrointerface also permits the investigation of charge transfer reactions in low polarity media.

Ultramicroelectrodes may be most gainfully employed as amperometric ion sensors. The advantages over similar potentiometric electrodes are numerous: selectivity is obtained from control of interfacial potential, ion transfer current is proportional to concentration, over a wide range from nanomolar to molar and measurement does not rely on the establishment of an equilibrium or stability of a reference electrode. This thesis will concentrate on amperometric electrochemical techniques, namely potential step chronoamperometry, cyclic voltammetry and stripping voltammetry.

1.3 An analogy between metal and liquid interfaces

The mass transport into an ultramicropipette or through an ultramicrohole is equivalent to that at a solid ultramicrodisc electrode of equivalent dimensions.

The analogy depends on an agreement between the kinetics of charge-transfer across a metal-electrolyte interface and ion-transfer across an ITIES, both possessing identical but arbitrary geometries.

The mechanism of ion-transfer between two phases $A$ and $B$ may be represented by three equations [15].

\[
X_A^\infty = X_A^\sigma \quad (1.1)
\]

\[
X_A^\sigma = X_B^\sigma \quad (1.2)
\]

\[
X_B^\sigma = X_B^\infty \quad (1.3)
\]
where $X^\infty$ is the species in the bulk solution and $X^\circ$ the species at the interface. The above equations describe a common three stage process illustrated in figure 1–1; transportation of reactants to the interface, charge transfer, then transport of products away from the interface. The processes corresponding to equations (1.1) and (1.3) may be expressed using Fick's laws of diffusion in the same manner as diffusion to and from a metal-electrolyte interface. These processes are detailed further in Section 1.4.

An analogy with charge-transfer kinetics at a metal electrolyte interface may be derived for equation (1.2), the ion-transfer reaction across the interface. Consider an ion-transfer reaction at a polarised interface where there is no specific adsorption and there is only one current carrying ion, adsorption and diffusion potentials do not feature and the distribution potential determines the behaviour of the system:
1.3.1 The Nernstian (reversible) system

The solutions for a metal-electrolyte and a liquid-liquid interface may be developed in a similar manner. Defining chemical potential as

$$\mu_X = \mu_X^\Theta + RT \ln a_X$$  \hspace{1cm} (1.4)

where $\mu_X^\Theta$ is the standard chemical potential, and expressing the electrochemical potential of species $X$ with charge $z$ in phase $A$ as

$$\tilde{\mu}_X^A = \mu_X^A + zF\phi^A$$  \hspace{1cm} (1.5)

For the metal-electrolyte interface the charge transfer reaction may be described by

$$O + e^- \rightleftharpoons R$$  \hspace{1cm} (1.6)

equating electrochemical potentials gives

$$\Delta G^\Theta = -nFE^0 = \sum \tilde{\mu}_{X,i}$$  \hspace{1cm} (1.7)

where $i$ corresponds to the solution or metal phase. Substitution of equations (1.4) and (1.5) into the above gives

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_O}{a_R}$$  \hspace{1cm} (1.8)

The electrode potential, $E$, is defined as the potential difference between the metal and the electrolyte solution.

$$E = \phi^m - \phi^s$$  \hspace{1cm} (1.9)

Similarly, for a liquid-liquid interface the ion transfer reaction may be described by equation (1.2)

$$X^\sigma_A = X^\sigma_B$$  \hspace{1cm} (1.10)
equating electrochemical potentials gives
\[ \Delta_A^B \mathcal{G} = -zF \Delta_A^B \phi_X = \sum \bar{\mu}_{X,i} \] (1.11)

substitution of equations (1.4) and (1.5) into the above gives
\[ \Delta_A^B \phi = \Delta_A^B \phi_X + \frac{RT}{zF} \ln \frac{a_A^X}{a_B^X} \] (1.12)

where the Galvani potential difference, defined as the potential difference between the two phases, is expressed as
\[ \Delta_A^B \phi = \phi^B - \phi^A \] (1.13)

1.3.2 The kinetically controlled (quasi-reversible) system

The charge-transfer current is dependent on the rate of forward and backward reactions and species concentration in each phase
\[ \frac{i}{zFA} = k_f C_{A,X}^o - k_b C_{B,X}^o \] (1.14)

Girault and Schiffrin [15] applied Eyring activated state theory to obtain a solution for the interfacial charge transfer. They considered ion transfer as a charge transfer process and the interface as a mixed solvent region. Thus the variation of standard chemical potential is monotonic and the Galvani potential profile has a continuous distribution between phases. The flux of an ion X is given as
\[ j_{X}^{A \rightarrow B} = \frac{i}{zFA} \]
\[ = \frac{LkT}{h} \exp \left( \frac{-\Delta G_f^*}{RT} \right) \exp \left( \frac{-\alpha_n}{RT} \Delta_G^{A \rightarrow B, t,x} \right) \exp \left( \frac{-\alpha_n}{RT} zF \Delta_A^B \phi \right) C_{A,X}^o - \]
\[ \frac{LkT}{h} \exp \left( \frac{-\Delta G_b^*}{RT} \right) \exp \left( \frac{1 - \alpha_n}{RT} \Delta_G^{A \rightarrow B, t,x} \right) \exp \left( \frac{1 - \alpha_n}{RT} zF \Delta_A^B \phi \right) C_{B,X}^o \] (1.15)

We may define coefficients
\[ Z_f = \frac{LkT}{h} \exp \left( \frac{-\Delta G_f^*}{RT} \right) \] (1.16)
and

\[ Z_b = \frac{LkT}{\hbar} \exp \left( \frac{-\Delta G_b^*}{RT} \right) \]  

(1.17)

giving from equation (1.14) above,

\[ k_f = Z_f \exp \left( \frac{-\alpha_n}{RT} \Delta G_{t,X}^{A-B} \right) \exp \left( \frac{-\alpha_e}{RT} zF \Delta A^B \phi \right) \]  

(1.18)

and

\[ k_b = Z_b \exp \left( \frac{1 - \alpha_n}{RT} \Delta G_{t,X}^{A-B} \right) \exp \left( \frac{1 - \alpha_e}{RT} zF \Delta A^B \phi \right) \]  

(1.19)

Applied potential difference is related to Galvani potential difference by a reference potential, \( E_{\text{ref}} \)

\[ E = \Delta A^B \phi + E_{\text{ref}} \]  

(1.20)

or

\[ \Delta A^B \phi = E - E_{\text{ref}} \]  

(1.21)

Defining potential independent rate constants \( k_f^o \) and \( k_b^o \) as follows

\[ k_f^o = Z_f \exp \left( \frac{-\alpha_n}{RT} \Delta G_{t,X}^{A-B} \right) \exp \left( \frac{-\alpha_e}{RT} zF E_{\text{ref}} \right) \]  

(1.22)

and

\[ k_b^o = Z_b \exp \left( \frac{1 - \alpha_n}{RT} \Delta G_{t,X}^{A-B} \right) \exp \left( \frac{1 - \alpha_e}{RT} zF E_{\text{ref}} \right) \]  

(1.23)

the flux in response to an applied potential may be expressed as

\[ \frac{i}{zFA} = k_f^o \exp \left( \frac{-\alpha_e}{RT} zF E^o \right) C_{A,X}^\sigma - k_b^o \exp \left( \frac{1 - \alpha_e}{RT} zF E^o \right) C_{B,X}^\sigma \]  

(1.24)

At the formal potential \( E^o \), equivalent to the standard Galvani potential plus the reference potential, interfacial concentrations are equivalent to bulk values and no net current flows. Equation (1.24) may then be re-expressed as

\[ k_f^o \exp \left( \frac{-\alpha_e}{RT} zF E^o \right) C_{A,X}^\sigma = k_b^o \exp \left( \frac{1 - \alpha_e}{RT} zF E^o \right) C_{B,X}^\sigma = k^o \]  

(1.25)
$k^0$ is the standard rate constant for the reaction. Substitution of $k^0$ into equation (1.24) yields the Butler-Volmer equation.

$$\frac{i}{zFA} = k^0 \exp \left( \frac{-\alpha_z zF(E - E^0)}{RT} \right) - k^0 \exp \left( \frac{1 - \alpha_z zF(E - E^0)}{RT} \right) \quad (1.26)$$

The analogy given above yields a form of the Butler-Volmer equation derived for an ITIES. Thus we have an expression that covers both electron transfer over a metal-electrolyte interface and ion transfer over an ITIES. For the Butler-Volmer equation to hold there must be negligible mass transfer effects. That is, interface concentrations must not differ appreciably from the bulk radius. Assuming an enhanced rate of mass transport to liquid-liquid ultramicroelectrodes due to radial diffusion (see section 1.5) there will be no mass transfer effects. As shown later, the rapid dominance of radial diffusion terms also results in steady-state conditions for ion transfer across an ITIES.

### 1.4 Interfacial charge transfer and diffusional mass transport

Now that we may apply metal-electrode methodology to the liquid-liquid interface let us consider the charge transfer processes at such an interface. Charge transfer may be broadly separated into Ion transfer and Electron transfer (figure 1-1). For a full treatment one must consider:

- Mass transport of reactants and products; the diffusion regimes to and from the interface (1 & 3 in figure 1-1).
- Charge transfer rate; reversibility of reaction and charge transfer coefficient, $\alpha$ (2 in figure 1-1).
- Chemical reactions preceeding or following electron transfer (CE or EC mechanisms).
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The current resulting from the movement of charge over a polarisable interface may be expressed as a flux

$$i = zF A J_e$$  \hspace{1cm} (1.27)

where $z$ is the charge number of the ion involved or the number of electrons transferred and $A$ the interfacial area. The equivalence between ion and electron transfer [15] applies.

$$J_e \equiv J_O \equiv J_R \equiv J_A \equiv J_B$$  \hspace{1cm} (1.28)

where $J$ are the fluxes of the species detailed in figure 1.1. Mass transfer may be by:

- Migration - electrical, influenced by potential difference.
- Diffusion - chemical, influenced by concentration difference.
- Convection - hydrodynamic, dependent on thermal effects.

For a mass transfer controlled reaction, mass transfer is controlled by the Nernst-Planck equation. Taking as an example, species A, undergoing one-dimensional mass transfer along the $x$ axis.

$$J_A(x) = -D_A \frac{\partial c_A(x)}{\partial x} - \frac{z_A F}{RT} D_A c_A \frac{\partial \phi(x)}{\partial x} + c_A v(x)$$  \hspace{1cm} (1.29)

where $J_A(x)$ is the flux of species $A$ at a distance $x$ from the interface (mol sec$^{-1}$ cm$^{-2}$). $D_A$ is the diffusion coefficient (cm$^2$s$^{-1}$),$v(x)$ is the hydrodynamic velocity and $z_A$ and $C_A$ are the charge and concentration of species $A$. The Nernst-Planck equation for a species $A$ reduces to

$$J_A(x) = -D_A \frac{\partial c_A(x)}{\partial x}$$  \hspace{1cm} (1.30)

on applying the assumptions: that we have supporting electrolyte in sufficient concentration to eliminate migration and the experiment is conducted on a timescale
short enough to neglect convective mass transport. The charge flux may be related to the heterogeneous rate constant,

\[ J_A(x) = k^0 c_A(x) \quad (1.31) \]

Where \( k^0 \) is the heterogeneous rate constant (in \( \text{cm s}^{-1} \)).

Finally, diffusion with time and concentration gradient is related by Fick’s second law

\[ \frac{\partial c_A}{\partial t} = D \frac{\partial^2 c_A}{\partial x^2} \quad (1.32) \]

### 1.5 Diffusion geometries

The system we are now modelling has been shown to follow classical electrochemical methodology for both reversible and quasi reversible charge transfer reactions. Also, mass transport is limited by diffusion alone. The next step is to consider the possible diffusion patterns or geometries to and from the interface. Consider a simple reversible electron transfer reaction at a polarised interface

\[ O + e^- \rightarrow R \quad (1.33) \]

Three diffusion geometries may be considered:

#### 1.5.1 Linear diffusion

- Macroelectrodes, typically of a diameter larger than one hundred microns.

- Ultramicroelectrodes, when the diffusion layer, \( \delta \), is small in comparison to the dimension of the electrode. (figure 1-2).

- Ultramicroelectrode arrays when diffusion layers interact after a longer time period [64] (figure 1-3).
Figure 1-2: Short time linear diffusion at Ultramicroelectrodes

Figure 1-3: Long time linear diffusion at Ultramicroelectrode arrays
We may express the concentration for each species \( c_O(x, y, z, t) \), \( c_R(x, y, z, t) \) in cartesian coordinates with respect to time as

\[
\frac{\partial c_O}{\partial t} = D \left[ \frac{\partial^2 c_O}{\partial x^2} + \frac{\partial^2 c_O}{\partial y^2} + \frac{\partial^2 c_O}{\partial z^2} \right]
\]  

(1.34)
a three dimensional expression of Fick's second law (equation (1.32) above).

Assuming that the linear diffusion occurs in an homogeneous media one may reduce equation (1.34) to the one-dimensional form.

\[
\frac{\partial c_O(x,t)}{\partial t} = D \frac{\partial^2 c_O(x,t)}{\partial x^2}
\]  

(1.35)

For the reversible case Nicholson and Sham [65] obtained a solution to the above equation for a system subject to a linear potential sweep.

\[
E_t = E_i - \nu t
\]  

(1.36)

where \( E(t) \), the applied potential, is a function of time, the initial potential \( E_i \) and the sweep rate \( \nu \). The current response is given as

\[
i_{\text{planar}} = nFAc_0^b (\pi D_0 \sigma)^{1/2} \chi(\sigma t)
\]  

(1.37)

where \( \chi(\sigma t) \) is a dimensionless tabulated current function.

\[
\sigma = \frac{nF}{RT} \nu t
\]  

(1.38)

The peak current may be expressed by the Randles-Sevčík equation

\[
i_{\text{peak}} = (2.69 \times 10^5)n^{3/2}AD_0^{1/2}N^{1/2}c_0^b
\]  

(1.39)

1.5.2 Spherical diffusion

For a hemispherical electrode diffusion is again perpendicular to the electrode surface, giving a spherical diffusion pattern. For long times the behaviour of an
ultramicrodisc may be approximated to this diffusion geometry. We obtain for the diffusion equation in spherical polar coordinates,

\[
\frac{\partial c_0}{\partial t} = D \left[ \frac{\partial^2 c_0}{\partial r^2} + \frac{2}{r} \frac{\partial c_0}{\partial r} + \frac{1}{r^2} \frac{\partial^2 c_0}{\partial \phi^2} + \frac{\cot \phi}{r^2} \frac{\partial^2 c_0}{\partial \phi^2} \right] \tag{1.40}
\]

assuming that the diffusion geometry is spherically symmetric,

\[
\frac{\partial^2 c_0}{\partial \phi^2} = \frac{\partial^2 c_0}{\partial \theta^2} = 0 \tag{1.41}
\]

we obtain

\[
\frac{\partial c_0(r,t)}{\partial t} = D \left[ \frac{\partial^2 c_0(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial c_0(r,t)}{\partial r} \right] \tag{1.42}
\]

A solution to the above equations was derived by Reinmuth [66],

\[
i = i_{planar} + \frac{nFADc_0b\phi(\sigma t)}{r_0} \tag{1.43}
\]

with \(\phi(\sigma t)\) a tabulated current function for the spherical diffusion to the interface and \(i_{planar}\) as before. The long time (steady-state) limit is

\[
i_{ss} = \frac{nFADc_0b}{r_0} \tag{1.44}
\]

This is the limiting current for a sphere. The diffusion to an ultramicrodisc and ultramicroband may be grossly approximated to the spherical diffusion equations above. These yield only qualitative results as the diffusion may only be regarded as spherical after some time has passed. The resulting steady-state current is quantitatively different to that obtained from cylindrical diffusion considerations. We shall see later that the limiting current derived for a disc [67] is greater by a factor of \(4/\pi\) (see chapter 2).

1.5.3 Cylindrical diffusion

The diffusion to ultramicrodisc electrodes may be fully and accurately treated in cylindrical polar coordinates.

\[
\frac{\partial c_0}{\partial t} = D \left[ \frac{\partial^2 c_0}{\partial r^2} + \frac{1}{r} \frac{\partial c_0}{\partial r} + \frac{\partial^2 c_0}{\partial z^2} + \frac{1}{r^2} \frac{\partial^2 c_0}{\partial \phi^2} \right] \tag{1.45}
\]
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Assuming that the diffusion to the interface is axially symmetric, but allowing for edge effects [68], that play a major part in this diffusion geometry, the concentration profile may be expressed by

$$\frac{\partial c_0(r,z,t)}{\partial t} = D \left[ \frac{\partial^2 c_0(r,z,t)}{\partial r^2} + \frac{1}{r} \frac{\partial c_0(r,z,t)}{\partial r} + \frac{\partial^2 c_0(r,z,t)}{\partial z^2} \right]$$

(1.46)

Where $\frac{\partial c}{\partial r}$ is the concentration gradient in the radial direction and $\frac{\partial c}{\partial z}$ the concentration gradient in the axial direction.

Unlike the linear and spherical diffusion regimes, cylindrical diffusion may not be reduced to one dimension. The lowest order is two, the equation above. Thus, the numerical simulation is correspondingly more complex.

In summary, for extremely short times where the diffusion layer thickness $\delta$ is small with respect to the interfacial dimension, diffusion to an ultramicrodisc may be approximated by linear diffusion. For long times we may apply the spherical diffusion approximation, calculated in one-dimension, for a hemispherical interface of equivalent area to that of a disc. However, for a complete treatment, a more complex cylindrical diffusion geometry must be adopted to allow for the two dimensional variation of the concentration profile.

1.6 Examples of diffusion and charge transfer at a liquid-liquid ultramicrointerface

The current response to an applied potential is directly dependent on both the diffusion geometry and the charge transfer kinetics of an interface, as shown in the preceding two sections. An understanding of how different system designs behave enables one to predict the approximate form of the current-potential-time $(i - E - t)$ profile.

For all but the slowest charge transfer reactions the current response to an applied potential at a flat macroscopic liquid-liquid interface is limited by the
diffusion of ions to the interface as opposed to the charge transfer kinetics across the interface.

For a liquid-liquid interface supported at the end of an ultramicropipette we attain unidirectional enhanced mass transport [1] (fig. 1-4.1). Thus for diffusion of an ion into the ultramicropipette the diffusion geometry is cylindrical, similar to that of a disc. For diffusion out of the pipette where diffusion to the interface is restricted, the diffusion geometry is linear. For the cases of ion-ionophore complexation (fig. 1-4.2) and electron transfer (fig. 1-4.3) at a liquid-liquid interface, supported on the tip of an ultramicropipette, the charge transfer may exhibit a current response analogous to that of an ultramicrodisc. This is achieved by ensuring that the charge transfer is pseudo first-order due to an excess of the required species in the pipette near to the interface.

For this system the current response is asymmetric, being limited generally, by the kinetics of charge transfer across the interface and the rate of charge transfer.
Chapter 1. Introduction

Figure 1-5: Diffusion regimes at an Ultramicrohole

to the interface from inside the pipette. Only from inside the pipette, as we have greatly enhanced mass transport due to cylindrical diffusion outside the pipette.

A two-dimensional enhanced diffusion profile may be obtained by supporting the liquid-liquid interface in an ultramicro-hole in an extremely thin substrate [69] (fig 1-5). Assuming that the substrate is infinitely thin then we obtain a cylindrical diffusion regime on both sides of the interface. Here, the current response, apart from the cases mentioned below, is limited solely by the interfacial charge transfer kinetics.

For all of the above cases, when determining the current response, we must consider diffusion geometry, the kinetics of charge transfer and the rate of change of the applied potential. For small interfaces where the diffusion is cylindrical the current response to a steadily variable potential, cyclic voltammetry, or a stepped potential, chronoamperometry, reaches a steady state. If the potential is scanned rapidly enough to reduce the diffusion layer $\delta$ to a value comparable to the microscopic dimensions of the electrode, then diffusion to the interface must again be considered.
1.7 Summary

This chapter shows that both the liquid-liquid interface and the ultramicroelectrode have a number of useful benefits and a combination of the two, the liquid-liquid ultramicroelectrode, has many applications. The analogy between the metal-electrolyte and the liquid-liquid interface allows classical electrochemical methodology to be applied for both reversible and quasi-reversible charge transfer kinetics.

The following chapters aim to model, through numerical simulation, the peculiar diffusion regimes occurring at ultramicroelectrodes and provide a complete \( i - E - t \) profile for a number of systems, particularly chronoamperometry and cyclic voltammetry at both ultramicrohole and ultramicropipette electrodes.
Chapter 2

A review of the simulation of ultramicroelectrode response

2.1 Introduction

Many approaches have been undertaken to simulate ultramicroelectrode response. Both fully numerical and pseudo-analytical techniques have been applied. Pseudo-analytical techniques are methods either applicable only over a restricted range of experimental parameters or requiring numerical evaluation at some point.

Of the numerical methods, the most popular are explicit and implicit finite difference methods, developments of original work such as that of Crank and Nicolson [70] and Gourlay [71] on parabolic partial differential equations for the solution of heat transfer. Other approaches include the use of the Runge-Kutta method [72] and finite element methods such as Orthogonal Collocation, first introduced by Whiting and Carr [73].

Pseudo-analytical methods in electrochemistry originated with Saito [67], and generally follow the approach initiated by Nicholson and Shain [65] of solution of diffusion equations via Laplace Transforms and Bessel Functions to give an integral expression, numerically evaluated to solve boundary conditions.

Fully numerical and pseudo-analytical methods are often investigated in tandem as this allows a general numerical solution to be derived which may be com-
pared with the analytical solution over a range of parameters, within which the analytical solution is exact. In the work presented below emphasis is placed upon microscopic disc electrodes, for example, diffusion to platinum, gold, carbon fibre and carbon paste disc ultramicroelectrodes. The diffusion to ultramicrodiscs is of the same nature as diffusion to a liquid-liquid ultramicrointerface of equivalent geometry (see Section 1.3 and reference [15]).

The next section in this chapter places the refinements in modelling the behaviour of ultramicroelectrodes into an historical context. In the remaining sections pseudo-analytical and digital simulation methods are described, covering developments up to the present day. Included in the summary to this chapter on page 85 is a table comparing the complexity and accuracy of the many methods available and suggesting the most appropriate method for simulation of a range of ultramicrodisc experimental techniques.

2.2 Historical overview

Deviations of electrode current-time response from the ideal semi-infinite linear diffusion model were first noticed by Cottrell in 1902 [74]. Digital simulation methods to model this response were first introduced to electrochemistry by Randles in 1948 [75], using a simple finite difference method previously detailed by Emmons [76]. This initial approach yielded polarographic current-potential curves and a general current-potential relationship, an embryonic form of the Randles-Sevčik equation (eqn.(1.39)). A concerted effort towards the solution of electrochemical problems by digital simulation was not undertaken until 1964 with the work of Feldberg and Auerbach [77] using a simple finite-element method to model current reversal chronopotentiometry with following second order kinetics. This work was followed by a lengthy and detailed treatment of digital simulation by Feldberg in 1969 [78], that ended with a prophetic concluding caveat;
“Don’t overprogram, as the computer may mask the programmer’s inefficiency better than the programmer himself”

Further improvements were published by the same author three years later [79], detailing surface boundary phenomena, particularly multiple electron transfer and adsorption. Olmstead, Hamilton and Nicholson [80] gave a simple finite difference method for the cyclic voltammetric response for a dimerisation reaction at planar and spherical electrodes. In a consecutive paper Olmstead and Nicholson [81] used the same method to simulate a double potential step experiment for the study of a reduction-dimerisation reaction, the pseudo-analytical solution only being available up to the time at which the second potential step is applied.

Thus, although digital simulation techniques saw a wide application for a number of electroanalytical techniques, the electrode geometry generally used remained of a form that minimised edge effects or was simple to treat mathematically. (Both planar and spherical geometries may be simulated one-dimensionally, see Chapter 3). The diffusion regimes treated were of a simple nature, such as those resulting from a single potential step.

Deviations from the linear diffusion model were also noticed when using other electroanalytical techniques, notably cyclic voltammetry [82], where peak separation is seen to decrease as scan rate increases (see also Section 45 ). Lines and Parker suggested that the deviation from expected behaviour arose from diffusion toward and electron transfer at the edge of the electrode [82]. Lingane quantified experimentally the influence of the edge effect and [83] obtained for chronopotentiometry the expression

\[
\frac{it^{1/2}}{Ac^5} = \frac{nF \pi^{1/2} D^{1/2}}{2} \left[ 1 + 0.98 \left( \frac{Dt}{r_0^2} \right)^{1/2} \right]
\]

(2.1)

as an adaptation of the Sand equation. The second term within the square brackets accounts for the additional effect of diffusion to the edge of the electrode. Early theoretical attempts at quantifying the deviations from ideality, for example, when
Table 2-1: \( b \) values for the modified Cottrell equation for an ultramicrodisc.

<table>
<thead>
<tr>
<th>( b ) value</th>
<th>reference</th>
<th>method</th>
<th>author</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.49-2.51</td>
<td>[83]</td>
<td>experiment</td>
<td>Lingane</td>
</tr>
<tr>
<td>2.26</td>
<td>[84]</td>
<td>analytical</td>
<td>Soos and Lingane</td>
</tr>
<tr>
<td>2.12</td>
<td>[84]</td>
<td>experiment</td>
<td>Soos and Lingane</td>
</tr>
<tr>
<td>1.77</td>
<td>[85]</td>
<td>experiment</td>
<td>Ito</td>
</tr>
<tr>
<td>2.16-3.21</td>
<td>[86]</td>
<td>experiment</td>
<td>Dayton</td>
</tr>
<tr>
<td>1.92</td>
<td>[87]</td>
<td>experiment</td>
<td>Flanagan and Marcoux</td>
</tr>
<tr>
<td>2.26</td>
<td>[87]</td>
<td>analytical</td>
<td>Flanagan and Marcoux</td>
</tr>
<tr>
<td>1.83-2.14</td>
<td>[88]</td>
<td>experiment</td>
<td>Kakihana</td>
</tr>
<tr>
<td>1.75-1.98</td>
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<tr>
<td>1.77-3.21</td>
<td>[90]</td>
<td>analytical</td>
<td>Aoki and Osteryoung</td>
</tr>
<tr>
<td>1.77-2.26</td>
<td>[91]</td>
<td>simulation</td>
<td>Heinze</td>
</tr>
</tbody>
</table>

Table 2-1: \( b \) values for the modified Cottrell equation for an ultramicrodisc.

using chronoamperometry [84], again resulted in modification to the analytical solution. An additional term was introduced to the the Cottrell equation dependent on electrode radius, diffusion coefficient and time after the potential step, the term having a coefficient \( b \). (see equation (2.2) below). Soos and Lingane gave a value for \( b \) of 2.26, or more exactly, \( 4/\sqrt{\pi} \) [84], (see table 2-1).

\[
\frac{it^{1/2}}{nFACbD^{1/2}} = \frac{1}{\pi^{1/2}} \left[ 1 + b \left( \frac{Dt}{\tau_0^2} \right)^{1/2} \right] \quad (2.2)
\]

\( b \) was later found to be variable, dependent on the relative magnitude of the additional time dependent term [91]. Several different values were calculated for \( b \) by other workers using various mathematical methods and are given together with the method of calculation in table 2-1. The upper set of values are only incidentally accurate and those lying outwith the range, later found to be \( 4/\sqrt{\pi} \) (or 2.26) for shorter times to \( \sqrt{\pi} \) (or 1.77) for longer times, were attributed to factors dependent on the material of the interface [86]. Later work suggested this was not the case, the anomalous \( b \) values arose due to erroneous electrode area calculations due to fabrication problems [91,92]. The lower set of values in
table 2-1 present a much more logical range of \( b \) values, the origins of which are discussed in further detail in the following sections. The long time value of \( b, \sqrt{\pi} \), is in exact agreement with the steady-state current predicted by Newman in 1966 [93] and Saito in 1968 [67].

The first digital simulation of the chronoamperometric current at a finite disc electrode was performed by Flanagan and Marcoux in 1973 [87] using an explicit finite difference method. Fitting the simulated current-time response to that predicted by equation (2.2) yielded a value for \( b \) of 1.92. This was compared to the value of 2.12 ± 0.11 obtained experimentally by Lingane [83]. An analytical treatment presented in the paper by Flanagan and Marcoux [87] gives \( b \) equivalent to \( 4/\sqrt{\pi} \), the limiting short time value. For chronopotentiometry the coefficient of the additional term in the Sand equation (equation (2.1)) is given as 0.72 in comparison to 0.98 obtained experimentally by Lingane.

Kinetically controlled chronopotentiometry and chronoamperometry were also considered by Flanagan and Marcoux [87]. Working curves were given as a function of \( kr_0^2/D \) where \( k \) is the heterogeneous rate constant, \( r_0 \) the interfacial radius and \( D \) the diffusion coefficient of the initial species.

The above work takes us up to the end of the seventies. The remainder of this chapter concentrates on refinements and new methods developed during the last decade.

### 2.3 Pseudo-analytical approach

All of the solutions presented to date as analytical solutions, including those in the previous section and those below, are unable to describe the complete current-potential-time (\( i - E - t \)) response for any non-steady-state electroanalytical technique used with ultramicrodiscs, for example, cyclic voltammetry. The problem is not tractable using normal methods (via Laplace transformations and solution
of the resulting Bessel functions [65]). Each solution derived is accompanied with a restriction such as; validity over a limited time period [94,95] or reliance on a steady-state condition for diffusion to and from the interface [96,97,68]. A solution of limited applicability, a 'pseudo-analytical' solution, may be found or partial recourse to numerical methods may be sought.

An advantage of using a digital simulation method is that changes in electrode and diffusion geometry may be rapidly implemented by a few changes in the computer program. Also, kinetic parameters may be easily incorporated and concentration profiles are readily available due to the discrete nature of the simulation methods. Therefore, in this section reviewing the analytical, or more accurately, the pseudo-analytical methods, frequent references will be made to the digital simulation results, detailed in succeeding sections, that complete the description of ultramicroelectrode behaviour.

The pseudo-analytical approaches covered below are;

- Solutions over a limited time period for Chronoamperometry.
- Approximate and limiting value solutions for Voltammetry.
- Solutions based on a steady-state assumption.
- Solutions based on an uniform flux approximation.
- Solutions allowing for variable flux.

### 2.3.1 Solutions over a limited time period for Chronoamperometry

Following the analytical work of Soos and Lingane, Saito, and Flanagan and Marcoux mentioned previously [67,84,87] Kakihana et al. [89,98] present a chronoamperometric method to measure charge number \( n \) and diffusion coefficient \( D \), in
Chapter 2. A review of the simulation of ultramicroelectrode response

which they correct the error made by Flanagan and Marcoux [87]. An analytical approximation is made to equation (2.2).

\[
\frac{I_d}{\pi^{1/2}F \tau_{dc} n c D} = 1.7947 + \frac{0.9979}{\tau} + 0.4944e^{-0.7246/\tau}
\]

(2.3)

where \( \tau = (D t)^{1/2}/r_0 \). Diffusion coefficient values were obtained using an iterative method, fitting observed \( n c \) values from calculated curves to the known \( n c \) values from experimental data, yielding an approximation to \( D \). For \( \tau \leq 0.5 \) this work compares closely to later analytical work by Oldham [68] (eqn.(2.8)) and Aoki and Osteryoung [90] (eqn.(2.9)) and digital simulation by Heinze [91], detailed on page 75.

Oldham obtains a complete solution for chronoamperometry at a disc subject to radius-dependent time constraint (eqn. 2.6) [68]. The derivation is via an exact solution for diffusion to an infinitely thin sheet, using transformation geometry to change coordinate systems from cartesian to polar coordinates. A general expression is also given for the chronoamperometric current at an inlaid electrode of arbitrary geometry.

\[
i = nF c^b D \left( \frac{A}{\pi^{1/2}D^{1/2}t^{1/2}} + \frac{P}{2} \right)
\]

(2.4)

where \( A \) is the interfacial area and \( P \) the perimeter of the interface. Thus for a disc

\[
i = nF c^b D r_0 \left( \frac{r_0}{\pi^{1/2}D^{1/2}t^{1/2}} + 1 \right)
\]

(2.5)

Constraints in the derivation of equation (2.4) restrict the curvature of the interface to a minimum value.

\[r_0 \geq 4D^{1/2}t^{1/2}\]

(2.6)

Oldham also shows concentration contours for an ultramicrodisc and comments on the contrast between the smooth axial concentration profile and the rapid change in concentration values radially, moving out from the edge of the electrode. The
initial current at an ultramicroelectrode, radius $r_0$, is given as equivalent to that at a quarter sphere of radius $r_0$.

$$i \rightarrow \pi nF c^b Dr_0$$  \hspace{1cm} (2.7)

$$t \rightarrow 0$$

The long time current is claimed to be equivalent to the current at a hemisphere of radius $2r_0/\pi$, that is, the steady state current at a polarised inlaid disc radius $r_0$ is given as

$$i \rightarrow 4nF c^b Dr_0$$  \hspace{1cm} (2.8)

$$t \rightarrow \infty$$

The above expression is attributed to Newman [93].

Aoki and Osteryoung derive short and long time responses for a disc through use of a Weiner-Hopf [99] technique. Limits of applicability for both the short time response

$$i = \frac{4nF c^b Dr_0}{1 + \xi} \left( \frac{\pi^{1/2}}{2} x^{-1/2} + \frac{\pi}{4} + \frac{3\pi}{2^{10}} x - \frac{315\pi}{2^{21}} x^2 - \cdots \right)$$  \hspace{1cm} (2.9)

and the long time response

$$i \approx \frac{4nF c^b Dr_0}{1 + \xi} \left[ 1 + \frac{2}{\pi^{3/2}} x^{-1/2} + \left( \frac{16}{9\pi^{3/2}} - \frac{4}{\pi^{7/2}} \right) x^{-3/2} + \cdots \right]$$  \hspace{1cm} (2.10)

are not given. $x$ in this case is defined as $4Dt/r_0^2$ (compare with equation 2.3). $\xi$ is the exponential potential dependent term,

$$\xi = \exp \left( \frac{nF}{RT} (E - E^0) \right)$$  \hspace{1cm} (2.11)

$\xi$ is zero for complete concentration polarisation at the electrode surface. Due to a miscalculation of a residue the long time response, equation (2.10), is incorrect in all but the first term. The correct form, (for $\xi = 0$), reported by Shoup and Szabo [100] in 1982 and Hepel, Plot and Osteryoung [101] in 1983 is

$$i \approx 4nF c^b Dr_0 \left[ 1 + \frac{4}{\pi^{3/2}} x^{-1/2} + \frac{32}{\pi^{3/2}} \left( \frac{1}{9} - \frac{1}{\pi^2} \right) x^{-3/2} \right]$$  \hspace{1cm} (2.12)
and is given as accurate for $x > 1$. Shoup and Szabo [100] give an expression for short times,

$$i_{\text{lim} x \to 0} \simeq 4nF^bD_{\text{r}0} \left( \frac{\pi^{1/2}}{2} x^{-1/2} + \frac{\pi}{4} + 0.1x^{1/2} + \cdots \right)$$  \hspace{1cm} (2.13)

This compares with equation (2.9) by Aoki and Osteryoung and equation (2.8) by Oldham, although Shoup and Szabo note that Oldham’s approach does not appear general enough to obtain higher terms.

After Kakihana, [89,98] (equation (2.3) above) Shoup and Szabo use a similar function

$$i = 4nF^bD_{\text{r}0} \left[ \frac{\pi^{1/2}}{4} + \frac{\pi^{1/2}}{2} x^{-1/2} + \left( 1 - \frac{\pi}{4} \right) \exp \left( \frac{\pi^{1/2}/2 - 4\pi^{-3/2}}{1 - \pi/4} \right) \right]$$  \hspace{1cm} (2.14)

optimised to within 0.6% over all times. The first two terms equate the short time expansion of equation (2.14) to equation (2.13) and the coefficients of the exponential term equate the long time expansion of equation (2.14) to equation (2.12). Aoki and Osteryoung give a solution for the relation between current and potential at an ultramicrodisc [94], incorporating the corrections of Shoup and Szabo.

$$I = nF \frac{(c_{\text{o}} - c_{\text{R}})f(x)}{1 + \xi}$$  \hspace{1cm} (2.15)

with $f(x)$ given by two overlapping functions

$$f(x) = 4D_{\text{r}0} \left( 1 + 0.71835x^{-1/2} + 0.05626x^{-3/2} - 0.00646x^{-5/2} \right), \hspace{1cm} x > 0.88$$  \hspace{1cm} (2.16)

$$f(x) = 4D_{\text{r}0} \left( \frac{\pi}{4x} \right)^{1/2} + \frac{\pi}{4} + 0.094x^{1/2}, \hspace{1cm} x < 1.44$$  \hspace{1cm} (2.17)

connected at $x = 1.08$, where $x = 4Dt/r_0^2$.

A comparison of the corrected general solution with analytical data from Shoup, Szabo and Fleischmann et al. (page 60) and digital simulation results from Shoup and Szabo, Kakihana, Heinze, and Taylor et al. [102] is given in table 2–2 on page 82.
In concluding their paper Shoup and Szabo present an important contrast to the expected profile of the current decay at long times in that the Cottrell-type behaviour is not observed.

\[
i_{\text{lim}}_{x \to \infty} \neq \frac{nFAD^{1/2}c^b}{\pi^{1/2}t^{1/2}} + 4nFc^bDr_0 \tag{2.18}
\]

but has the form

\[
i_{\text{lim}}_{x \to \infty} = \left(\frac{8}{\pi^2}\right) \frac{nFAD^{1/2}c^b}{\pi^{1/2}t^{1/2}} + 4nFc^bDr_0 \tag{2.19}
\]

They also suggest that this may affect the analysis of results obtained from carbon fibres [86] where the radius was obtained from \( I \) vs. \( x^{-1/2} \) at long times. Typical carbon fibre results [86] of \( b = 3.21 \) (for a definition of \( b \) see equation (2.2)) calculated with equation (2.18). may be partially explained by recalculation using equation (2.19) to give \( b = 2.60 \), more in keeping with the expected result of \( 4/\sqrt{\pi} \).

### 2.3.2 Approximate and limiting value solutions for Voltammetry

Analytical solutions to the shapes of cyclic voltammograms for ultramicrodiscs were first presented by Aoki et al. [103] in 1984. A steady-state solution is given,

\[
i = \frac{4nFc^bDr_0}{(1 + e^{-\xi})}, \quad \xi = \left(\frac{nF}{RT}\right) (E_i + \nu t - E^{0'}) \tag{2.20}
\]

which is a limiting form of a general equation for cyclic voltammetry at an ultramicrodisc,

\[
i = 4nFc^bDr_0 \left(\frac{\rho^2}{16}\right) \int_0^\infty f(x) \text{sech}^2 \left(\frac{\rho^2 x}{8} - \frac{\xi}{2}\right) dx \tag{2.21}
\]

with \( f(x) \) given by two overlapping functions

\[
f(x) = 1 + 0.71835x^{-1/2} + 0.05626x^{-3/2} - 0.00646x^{-5/2}, \quad x > 0.88 \tag{2.22}
\]
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\[ f(x) = \left( \frac{\pi}{4x} \right)^{1/2} + \frac{\pi}{4} + 0.094x^{1/2}, \quad x < 1.44 \]  \hspace{1cm} (2.23)

connected at \( x = 1.08 \) and \( \rho \), a term dependent on experimental parameters;

\[ \rho = \left( \frac{nF \rho^2}{RTD} \right)^{1/2} \]  \hspace{1cm} (2.24)

(see also equations (2.15) - (2.17))

In the same manner that the linear diffusion solution for cyclic voltammetry must be evaluated numerically, so must the expression for an ultramicrodisc. Aoki et al. employ Simpson's method. The resulting curves for a range of \( \rho \) values are shown in figure 2-1, taken from reference [103]. Two useful approximate equations are presented for the analysis of voltammograms:

for maximum current

\[ \frac{i_m}{4nF \sigma^2 D_0} = 0.34e^{-0.66\rho} + 0.66 - 0.13e^{-11/\rho} + 0.351\rho \]  \hspace{1cm} (2.25)

and for half-maximum potential

\[ \frac{nF}{RT}(E_{m/2} - E_0') = -0.694\tan^{-1}(0.85\rho) \]  \hspace{1cm} (2.26)

\( \rho \) as defined in equation (2.24). A comparison between maximum currents from equation (2.25) and half maximum potentials from equation (2.26) with digital simulation values is given in table 5-1 on page 187. Equation (2.26) is plotted in figure 2-2, also from ref.[103].

An analytical solution for square wave voltammetry at ultramicrodisc electrodes is given by Whelan et al. [104]. The current response for reversible electron transfer is calculated by using functions given by Aoki in references [94, 103]. Voltammetric peak shape and position are independent of the dimensionless parameter \( p = 4Dt_{sw}/r_0^2 \) where \( D \) is the diffusion coefficient, \( t_{sw} \) the square wave period and \( r_0 \) the radius of the disc. However, peak current density is dependent on \( p \) and is not limited. A function is given for analysis of square wave voltammograms at ultramicrodiscs;

\[ \psi_{peak} = 0.846p^{1/2} + 1.06 + 0.25e^{-0.8p^{1/2}} \]  \hspace{1cm} (2.27)
Figure 2-1: Linear sweep voltammograms for $\rho = (1) 10, (2) 8, (3) 6, (4) 4, (5) 3, (6) 2, (7) 1, (8) 0.1$. The upper abscissa is for 25°C.
Figure 2-2: Variation of half-maximum potential with \( \rho \) (solid line) compared to a planar electrode (dashed line).
where $\psi_{\text{peak}}$ is the maximum value of the dimensionless normalised net current.

$$\psi = \frac{\Delta I}{nF \sigma_p r_0^2} \left( \frac{\pi t_{sw}}{D} \right)^{1/2}$$  \hspace{1cm} (2.28)

Equation (2.27) is quoted as valid for the step height of the base staircase, $nE_s = 10mV$ and the square wave amplitude, $E_{sw} = 50mV$ and has a relative error of less than 0.3\% [104].

Sinru et al. [105] developing the work of Aoki and Osteryoung [94], describe normal and reverse pulse voltammetry at ultramicrodisc electrodes. A rapid renewal of boundary conditions in both normal and reverse pulse modes is found within very short times due to the diffusion geometry of the electrode, thus, a superposition principle may be applied. Errors are given for the pulse limiting current with respect to pulse width and waiting time between pulses. Times for the current to fall to within 10\% and 5\% of the steady state value are given for a range of ultramicrodisc sizes.

Further work by Aoki et al. [95] aims to evaluate kinetic parameters from experimental current-potential curves in a manner similar to a polarographic log-log plot. Defining a kinetic parameter

$$\lambda = \frac{r_0}{D} (k_f + k_b)$$  \hspace{1cm} (2.29)

where $k_f$ and $k_b$ are the forward and backward rate constants respectively, and applying a Weiner-Hopf technique [99], as in previous papers, an expression is derived for the total current,

$$i = \frac{i_d}{(1 + e^{-\xi})} f_1$$  \hspace{1cm} (2.30)

where $i_d$ is the diffusion controlled limiting current, (see equation (2.9)), $\xi$ is defined in equation (2.20) and $f_1$ is evaluated as a convergent function of an infinite number of simultaneous equations, dependent on the kinetic parameter. An implicit expression for $f_k$ is given

$$\left[ \frac{\Gamma(k - 1/2)}{\Gamma(k)} \right] f_k + \frac{4}{\pi \lambda} \sum_{m=1}^{\infty} \left[ \frac{\Gamma(m + 1/2)}{(m - 1)!(2m - 2k + 1)} \right] f_m = \frac{\pi^{1/2}}{2k - 1}$$  \hspace{1cm} (2.31)
The infinity in equation (2.31) is replaced by a finite number $N$ and convergence is deemed sufficient for $N = 60$. Limiting behaviour, as $\lambda \to 0$, is given as

$$ f_1 \simeq \frac{\pi}{4} \lambda $$

(2.32)

Aoki et al. continue by using the Butler-Volmer equation to define

$$ k_f = k_s[(1 - \alpha)\xi] $$

(2.33)

$$ k_b = k_s[-\alpha\xi] $$

(2.34)

and introduce the potential independent kinetic parameter

$$ \Lambda = \frac{k_s r_0}{D} = \frac{\lambda \exp[(1 - \alpha)\xi]}{1 + e^{-\xi}} $$

(2.35)

Curves obtained from this expression are given in figure 2-3 (from ref.[95]) for variable $\Lambda$. Reversible, quasi-reversible and irreversible domains are given as $\Lambda \geq 10$, $10 \geq \Lambda \geq 0.2$, and $\Lambda \leq 0.2$ for an ultramicrodisc ($\alpha = 0.5, T = 25^\circ C$). 1

For the irreversible domain at an ultramicroelectrode the half wave potential is shifted by

$$ -\frac{59}{1 - \alpha} \times \log(\Lambda) \equiv -118 \times \log \left( \frac{k_s r_0}{D} \right) \ mV $$

(2.36)

for one decade variation in $\Lambda$. For the analysis of experimental current-potential curves an expression is given

$$ E = E^* - 2.3 \frac{RT}{(1 - \alpha)nF} \log \left[ \frac{(1 - (I/I_d)(1 + e^{-\xi}))^{1.11}}{I/I_d} \right] $$

(2.37)

1It is interesting to compare these values with the respective domains of $\Lambda \geq 15$, $15 \geq \Lambda \geq 10^{-2}(1 + \alpha)$, and $\Lambda \leq 10^{-2}(1 + \alpha)$ given by Matsuda and Ayabe [106] for semi-infinite linear diffusion to a planar electrode where $\Lambda$ is defined as,

$$ \Lambda = \frac{k_0}{D^{1/2}(nF/RT)^{1/2} \nu^{1/2}} $$
Figure 2-3: Log-plot for $\Lambda = (a) 30$, (b) 3, (c) 1, (d) 0.3, (e) 0.1, (f) 0.03, and (g) 0.01 at $\alpha = 0.5$ and 25°C.
where

\[ E^* = E^{\prime} - 2.3 \left[ \frac{RT}{(1 - \alpha)nF} \right] \log \left[ \frac{\pi k_s r_0}{4D} \right] \]  

(2.38)

### 2.3.3 Solutions based on a steady-state assumption

Bond et al. produce a comprehensive paper on electrochemical processes at an ultramicrodisc, with a major constraint of steady-state mass transport [97]. The solutions are based on a general integral expression combining a weighting function dependent on the particular electrochemical condition. The calculation of the weighting function is not facile due to the discontinuity imposed by the flux at the edge of the electrode [68], (a sharp transition from infinity to zero for a fully reversible reaction). A solution for extreme concentration polarisation gives concentrations as a function of the axial and radial parameters, \( z \) and \( r \).

\[ c_0(z, r) = \frac{2c^0}{\pi} \cos^{-1} \left( \frac{2r_0}{\left[ z^2 + (r_0 + r)^2 \right]^{1/2} + \left[ z^2 + (r_0 - r)^2 \right]^{1/2}} \right) \]  

(2.39)

and a solution for current density across a disc

\[ I_d(r) = \frac{2nFD_0 c_0}{\pi (r_0^2 - r^2)^{1/2}} \]  

(2.40)

From equation (2.40) and the expression for steady state current, \( i_d \), to an ultramicrodisc, (equation (2.9)) Bond et al. derive an expression for the ratio of current density at the centre of the disc to the average current density;

\[ \frac{I_d(0)}{I_d} = \frac{\pi r_0^2 I_d(0)}{i_d} = \frac{1}{2} \]  

(2.41)

For a reversible electrode reaction an expression is given for the current, \( i \)

\[ i = \frac{i_d}{\theta}, \quad \theta = \frac{1 + D_0}{KD_R} \]  

(2.42)

where

\[ \frac{1}{K} = \frac{C_0(r, 0)}{C_R(r, 0)} = \exp \left[ \frac{nF}{RT} (E - E^0) \right] \]  

(2.43)
This may be expressed in a form similar to a polarographic log plot.

\[
\frac{i_d - i}{i} = \frac{D_O}{K D_R} = \exp \left[ \ln \frac{D_O}{D_R} + \frac{nF}{RT} (E - E^0) \right]
\]  
(2.44)

To obtain local current density for the reversible case, divide equation (2.40) by \( \theta \), given in equation (2.42). Bond et al. also derive an expression similar to equation (2.39) for the steady-state concentrations for a reversible reaction.

\[
1 - \frac{c_0(z,r)}{c_0^b} = \frac{D_R c_R(z,r)}{D_O c_O^b}
\]

\[
= \frac{2 \sin^{-1} \left( \frac{2r_0}{(z^2 + (r_0 + r)^2)^{1/2} + [z^2 + (r_0 - r)^2]^{1/2}} \right)}{\pi (1 + \exp[nF(E - E_1)/RT])}
\]  
(2.45)

For kinetically controlled reactions the simple expression

\[
i = \pi n F c_0^b k r_0^2
\]  
(2.46)

is given. Equation (2.47) shows no \( r \) dependence, the current density for a purely kinetically controlled reaction is uniform across the surface of an ultramicrointerface. It is also noted that the current density is no longer infinite at the edge of the electrode. Two solutions are presented for irreversible reactions, the first with kinetics dominant which converges to complete kinetic control as \( \kappa \to 0 \), the second with diffusion dominant which converges to extreme concentration polarisation as \( \kappa \to \infty \). \( \kappa \) is defined as

\[
\kappa = \frac{\pi k r_0}{4 D_O}
\]  
(2.48)

where \( k \) is the forward (oxidation) rate constant and \( k' \) (see equation (2.52) below) the reverse (reduction) rate constant. A table of \( i/i_d \), the normalised irreversible current, against \( \kappa \) is obtained for the combined result of both approaches [97], the values calculated by each method being almost equivalent. It is worth noting
that a steady-state voltammogram is not symmetrical, being steeper in its section before the half-wave potential, \((E_{1/2})\). Applying the Butler-Volmer equation for irreversible conditions Bond et al. find for the half-wave potential

\[
\frac{\alpha n}{RT} (E_{1/2} - E) = \ln(\kappa) - 0.06985
\]  

(2.49)

Also, the irreversible charge transfer coefficient may be determined from the one-quarter and three-quarter potentials via a Tômes procedure (see refs. in [97]). Assuming a temperature of 25°C.

\[
\alpha n = \frac{2.34RT}{F(E_{1/4} - E_{3/4})} = \frac{60.0}{E_{1/4} - E_{3/4}} \text{ mV}
\]  

(2.50)

An expression is given to calculate the shift in half-wave potential with differing interfacial radii,

\[
\Delta E_{1/2} = \frac{RT}{\alpha n F} \Delta \ln(r_0)
\]

(2.51)

(see also the expression on page 48).

For quasi-reversible conditions Bond et al. derive similar functions to the irreversible case with the inclusion of the potential dependent parameter \(\theta\) (see equation (2.42)),

\[
\kappa \theta = \frac{\pi kr_0}{4D_0} \left[ 1 + \frac{D_0}{KD_R} \right] = \frac{\pi r_0}{4} \left[ \frac{k}{D_0} + \frac{k'}{D_R} \right]
\]

(2.52)

which becomes, on applying Butler-Volmer kinetics,

\[
\kappa \theta = \frac{\pi k^0 r_0}{4} \exp \left\{ \frac{-\alpha n F(E - E^0)}{RT} \right\} \left[ \frac{1}{D_0} + \frac{\exp\left\{n F(E - E^0)/RT\right\}}{D_R} \right]
\]

(2.53)

\[
= \frac{\pi k^0 r_0}{4D_0^{1-\alpha} D_R^\alpha} \left[ \exp \left\{ \frac{-\alpha n F(E - E_h)}{RT} \right\} + \exp \left\{ \frac{(1-\alpha)n F(E - E_h)}{RT} \right\} \right]
\]

(2.54)

\(E_h\) is the reversible half-wave potential and \(k^0\) the standard rate constant. A table of \(\kappa \theta\) versus \(\theta/\theta_d\) is calculated numerically in the same manner as the irreversible case and is also reproducible via a simple approximate expression later
given by Oldham and Zoski [107], accurate to 0.3% of the numerical method employed in reference [97].

\[
\frac{i_d}{\theta i} = 1 + \frac{\pi}{\kappa \theta} \left( \frac{2\kappa \theta + 3\pi}{4\kappa \theta + 3\pi^2} \right)
\]  

(2.55)

For the irreversible case $\theta$ is simply replaced by unity.

This simple extension of the irreversible to quasi-reversible case is also detailed by Cope and Tallman [108], using an integral equation method [109] to obtain solutions to chromoamperometric experiments at electrodes of arbitrary geometry. Diffusion limited, irreversible and reversible charge transfer reactions are all described as limiting cases of quasi-reversible reactions. Also, for $D_O/D_R = 1$, the reversible case may be expressed in terms of the solution for the diffusion limited reaction and the solution for the quasi-reversible reaction in terms of the solution for the totally irreversible reaction.

Oldham and Zoski [107] also discuss the applicability of the spherical model to steady-state voltammetry at a disc, in that the behaviour of an ultramicrodisc tends to that of an ultramicrosphere at long times. The problems in applying this approach to the simulation of ultramicrodisc response at short times are detailed in Chapter 3.

Bond, Oldham, Zoski and Myland [110] use the spherical approximation to develop a method to determine of kinetic parameters from a series of working curves or 'kinetic indicator diagrams', using ultramicrodiscs with a range of radii. Their approach is extremely versatile and presents a very useful method for rapidly obtaining kinetic parameters $\alpha$ and $k^0$ from quartile ($\frac{1}{4}, \frac{3}{4}$) potential values. Ranges for reversible, quasi-reversible and irreversible behaviour are given as $\kappa \geq 40$, $20 > \kappa \geq 0.2$, $\kappa < 0.1$ respectively, with $\kappa$ as given in equation (2.48).

For the 'kinetic indicator diagrams' to be most beneficial $\kappa$ should lie in the 'usefully' quasi-reversible range. Therefore within the range of ultramicroelectrode radii of 0.25 - 25 $\mu$m heterogeneous rate constants of $10^{-2}$ to 1 $\text{cm}^{-1}$ may be
measured. It is also notable that the method does not rely on the assumptions of uniform accessibility (equal flux over all of the electrode surface) or equal diffusion coefficients, but only on a steady-state approximation.

Although the method is restricted in its application only to steady-state systems, Zoski et al. [111] circumvent to an extent the problems in achieving the steady-state experimentally. A technique, 'convolutive forecasting', is described. It allows any voltammetric curves, irrespective of experimental method, reversibility or size of the electrode, to be reduced to a steady-state form. The constraints are, first, that the average diffusion current and electrode dimensions are required and second, the assumption that the behaviour of the disc tends to that of a hemisphere as \( t \to \infty \). The method is applicable and accurate for hemispherical ultramicroelectrodes. Experiments show an average 10% error when the method is applied to ultramicrodiscs.

Oldham [112] re-expresses the concentration and flux profiles obtained for a reversible reaction by Bond et al. [97] by using an oblate spheroidal coordinate system, previously introduced by Newman [93, 113].

\[
\begin{align*}
    r &= r_0 \cosh(\rho) \cos(\phi) \\
    z &= r_0 \sinh(\rho) \sin(\phi)
\end{align*}
\]

This may also be compared to earlier co-ordinate transformation work by Oldham [68]. The transformation described by equations (2.56) and (2.57) simplifies greatly the derivation and complexity of the final expressions. The concentration contours are ellipsoidal;

\[
\frac{r^2}{r_0^2 \cosh^2(\rho)} + \frac{z^2}{r_0^2 \sinh^2(\rho)} = 1
\]

and are given as functions of an inverse gudermannian function [114].

\[
\rho = \text{invgd} \left( \frac{\pi}{2} \cdot \frac{c_0 - c_O^e}{c_O^b - c_O^e} \right), \quad c_O^e \leq c_O \leq c_O^b
\]
Defining the surface concentration $c_O^s$ as

$$c_O^s = \frac{c_O^b}{1 + K} \tag{2.60}$$

with $K$ as in equation 2.43. Flux values are obtained from the orthogonal properties of the coordinate system.

$$-J_O = J_R = \frac{2KD_Oc_O^b\text{sech}(\rho)}{\pi(1 + K)r_0[\sinh^2(\rho) + \sinh^2(\phi)]^{1/2}} \tag{2.61}$$

with the surface flux $\rho = 0$ as

$$-J_O^s = J_R^s = \frac{2KD_Oc_O^b\csc(\phi)}{\pi(1 + K)r_0} \tag{2.62}$$

As found in earlier work using co-ordinate transformation geometry [68], Oldham notes that the flux at the electrode edge ($\rho = 0, \phi = 0$) is infinite for a reversible system. An alternative approach in the same coordinate system is presented by Birke [115] in terms of an inverse tangent function. It is applicable not only to ultramicrodiscs but any interface with an elliptical profile. The concentration values are given as

$$c_O = c_O^b - \frac{c_O^b}{(1 + \theta)} \left\{ \frac{1 - 2/\pi \tan^{-1}(\rho)}{1 - 2/\pi \tan^{-1}(\rho_0)} \right\} \tag{2.63}$$

$$c_R = \frac{D_Oc_O^b}{D_R(1 + \theta)} \left\{ \frac{1 - 2/\pi \tan^{-1}(\rho)}{1 - 2/\pi \tan^{-1}(\rho_0)} \right\} \tag{2.64}$$

where $\rho_o$ relates to the interfacial profile, increasing with the curvature of the interface. $\rho_o = 0$ for a disc [109].

### 2.3.4 Solutions based on an uniform flux approximation

Szabo [116], uses assumptions of a spatially uniform flux to the electrode and an average boundary condition method, detailed in an earlier paper [117], for an ultramicrodisc. A simple, approximate expression is obtained for the long time
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behaviour of the current at an electrode possessing a closed surface in an infinite insulating support. (See also page 59 for mixed boundary conditions)

\[
\frac{i}{nFDC} = l_o \left(1 + \frac{l_o}{(4\pi^3Dt)^{1/2}} \right)
\]  
\[ (2.65) \]

\[ l_o = 2\pi R \text{ for a hemisphere} \]
\[ = 4R \text{ for a disc} \]  
\[ (2.66) \]

\[ \simeq \pi^2(a + b)\ln(32a/(b - a) + e^{\pi^2/4}) \]
for a ring, inner radius a, outer radius b.  
\[ (2.67) \]

Fleischmann, Pons et al. present a number of papers describing the behaviour of ultramicrodisc and ultramicroring electrodes assuming uniform flux at the interface [118–124]. Initial work [118] notes that as the thickness of the electrode decreases, the mass transfer increases and the concentration variation over the electrode becomes less pronounced. Plots of dimensionless concentration parameter as a function of radial position for ring-disc systems are also given. Subsequent work by the above authors [120] gives an exact analysis of diffusion to ultramicrodisc and ultramicroring electrodes under steady-state diffusion conditions, constant concentration over the surface of the electrode and constant flux over the surface of the ring.

Work performed in 1988 by Fleischmann, Pons et al. [121–124] assuming an overall uniform surface flux condition, akin to a hemispherical electrode, derives solutions for a range of electrochemical techniques employing an ultramicrodisc. The analytical and numerical approach, involving the use of discontinuous integrals is closely allied to that of Bond et al. [97] (see page 50) and earlier work of Sarangapani and de Levie [125] (see page 63). However, different boundary conditions are applied, in contrast to the steady-state boundary condition applied by Bond in reference [97];

\[ \frac{\partial c}{\partial t} = 0 \]  
\[ (2.68) \]
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Fleischmann, Pons et al. use

\[
\left( \frac{\partial Q}{\partial r} \right)_{z=0} = 0 \quad \forall t, \ t > 0
\]  

(2.69)

where \( Q \) is the flux at the electrode surface. These conditions allow study of the 'unsteady' state. The approach is as follows [121]; solution of the time dependent diffusion equation in cylindrical polar coordinates with boundary conditions

\[
r > 0, \ z > 0, \ t = 0, \ c = c^b,
\]  

(2.70)

via a Laplace transformation and Bessel's differential equation gives

\[
\bar{c} = \frac{c^b}{s} - \int_0^\infty \omega(\lambda, q) e^{-f(\lambda, q)z} J_0(\alpha r) \, d\alpha
\]  

(2.71)

with

\[
f(\lambda, q) = (\alpha^2 + q^2)^{1/2}, \quad q = \left( \frac{s}{D} \right)^{1/2}
\]  

(2.72)

\( \omega(\lambda, q) \) is similar to the weighting function employed in reference [97] and is chosen to satisfy the boundary conditions given in equation (2.70).

Solution of equation (2.71) for a number of electroanalytical techniques gives a series of straightforward pseudo-analytical equations that may be used to predict ultramicroelectrode response.

For chronopotentiometry, integration over the surface of the disc gives an expression for the average concentration at \( z = 0 \),

\[
c_{AV} = c^b - \frac{2Qr_0}{D} \cdot \Phi_1 \left( \frac{Dt}{r_0^2} \right)
\]  

(2.73)

\( \Phi_1 \) is a dimensionless function and is given in tabular form in reference [121]. For long times and small flux values the transition time is negligible and a steady state value is obtained, [118]

\[
c_{AV} = c^b - \frac{8Qr_0}{3\pi D}
\]  

(2.74)
For large values of flux, \( Q \), a sharp transition time is observed as \( c_{AV} \to 0 \), thus
\[
\frac{2Qr_0}{Dc^b} \cdot \Phi_1 \left( \frac{Dt}{r_0^2} \right) = 1
\]  
(2.75)

A plot of square root of dimensionless transition time, \( \tau \)
\[
\tau = \left( \frac{Dt}{r_0^2} \right)^{\frac{1}{2}}
\]  
(2.76)
against dimensionless flux, \( \chi \),
\[
\chi = \frac{2Qr_0}{Dc^b}
\]  
(2.77)
is given by Fleischmann and Pons, [121]. This is in agreement with work by Aoki and Osteryoung [90] under the assumption of uniform surface concentration. The expression of Fleischmann and Pons is an improvement on reference [90] as it is exact (assuming constant flux) and is applicable over the entire time range.

Applying Butler-Volmer kinetics to the above derivation, using the expression for average concentration over the surface of the disc (equation (2.74)) and assuming equal concentrations of oxidised and reduced forms of the redox couple gives
\[
\frac{FQ}{i_0} + \frac{2Qr_0}{Dc^b} \cdot \Phi_1 \left( \frac{Dt}{r_0^2} \right) \left[ e^{-\alpha\xi} + e^{(1-\alpha)i} \right] = e^{-\alpha\xi} - e^{(1-\alpha)i}
\]  
(2.78)
with \( i_0 \) as the exchange current density and all other terms as described above. Thus the transients are a function of \( \alpha, \frac{FQ}{i_0}, \frac{2Qr_0}{Dc^b} \).

For linear sweep amperometry, similar expressions are derived. On applying a linear current ramp, \( Q(t) \),
\[
Q(t) = \gamma t
\]  
(2.79)
where \( \gamma \) is the flux sweep rate (\( mol cm^{-2} s^{-2} \)), we obtain
\[
\frac{4\gamma tr_0}{Dc^b} \cdot \Phi_3 \left( \frac{Dt}{r_0^2} \right) = 1
\]  
(2.80)
as an expression of transition time. $\Phi_3$ is tabulated, as a function of $Dt/r_0^2$ in reference [121]. Sweeping the current from zero results in a sharp transition in the potential time plot. For linear sweep amperometry with Butler-Volmer kinetics Fleischman and Pons obtain the expression,

$$ \frac{F\gamma t}{i_0} + \frac{4\gamma tr_0}{Dc_b} \cdot \Phi_3 \left( \frac{Dt}{r_0^2} \right) \left[ e^{-\alpha t} + e^{(1-\alpha)\xi} \right] = e^{-\alpha t} - e^{(1-\alpha)\xi} $$

(2.81)

Illustrations of the above equations for chronopotentiometry and linear sweep amperometry are given in reference [120] together with experimental results and an estimate of errors.

In a following paper Fleischmann, Daschbach and Pons [122] present a solution to the chronoamperometric response of a microdisc. The problem of mixed Dirichlet and Neumann boundary conditions is addressed; a concentration boundary condition over the electrode and a flux boundary condition over the insulator, in contrast to the two flux conditions applicable to the two cases above. This case is again tractable via discontinuous Bessel integrals with a uniform flux approximation, but only if a steady-state restriction is applied,

$$ Q(s) = \frac{(c^b - c_{AV})r_0}{2} \cdot \Phi_2 \left( \frac{r_0s^{1/2}}{D^{1/2}} \right) $$

(2.82)

(A digital solution for the same boundary conditions, but without recourse to a steady-state restriction is outlined on page 75). Note that this pseudo-analytical solution is restricted to the Laplace plane. $\Phi_2$ is again tabulated [122], but as a function of $s^{1/2}$, not $t$. The authors apply their previously derived results [118], of

$$ Q = \frac{3\pi D}{8r_0^2}(c^b - c_{AV}) $$

(2.83)

for the steady state and

$$ Q = \frac{D^{1/2}}{\pi^{1/2}t^{1/2}}(c^b - c_{AV}) $$

(2.84)

the expected behaviour at short times and obtain an approximate expression for equation (2.82) in Laplace space, for intermediate values of $\Phi_2$

$$ Q(s) \simeq \frac{1.3001D^{1/2}}{r_0s^{1/2}} + \frac{3\pi D}{4r_0^2s} + \frac{0.6999D^{1/2}/r_0}{1.79184D^{1/2}/r_0 + s^{1/2}} $$

(2.85)
which on inversion from the Laplace plane gives a flux to the surface

\[ Q \approx \frac{D(c^b - c_{AV})}{2r_0} \]  

\[ \left[ \frac{3\pi 2.000}{4 \pi^{1/2}} \left( \frac{r_0}{D} \right)^{1/2} - 1.2541 \exp \left( 1.79184 \frac{D^{1/2}}{r_0} \right)^{2} \text{erfc} \left( 1.79184 \frac{D^{1/2}}{r_0} \right) \right] \]

This is converted to dimensionless current by dividing by equation (2.83). A comparison is made to analytical solutions by Shoup and Szabo [100] and Aoki and Osteryoung [94] and digital simulation results from Shoup and Szabo, Kakihana, Heinze, and Taylor et al. [102] in table 2–2 on page 82.

Two points are worth noting with regard to the results of Fleischmann, Daschbach and Pons; firstly they assume Cotrellian behaviour at short times, whereas Shoup and Szabo show that this is not the case and the correct short time flux term (see equation (2.19)) differs by a factor of \(8/\pi^2\), secondly the solution presented by Fleischmann, Daschbach and Pons tends to a steady state value of

\[ \frac{i}{i_d} \to \frac{3\pi^2}{32} \]  

(2.87)

as opposed to the expected value of unity (\(i_d\) is the diffusion limited current (equation 2.9)). This occurs due to the incorrect application of equation (2.83), based on uniform flux, instead of

\[ Q = \frac{4D(c^b - c_{AV})}{\pi r_0} \]  

(2.88)

which leads to the correct steady-state value. Applying the above equation to the results of Fleischmann, Daschbach and Pons (i.e. multiplication by \(32/3\pi^2\)) gives an excellent agreement with previous work for long times (see table 2–2). The uniform flux approximation is not applicable at short times due to pronounced edge effects. However, Fleischmann, Daschbach and Pons again claim that constant flux conditions are more applicable.

The constant flux approximation is extended to rings by Li et al. [119] following a similar derivation to the above.

\[ Q(s) = \frac{(c^b - c_{AV})r_0}{2} \cdot \Phi_{12} \left( \frac{\gamma D^{1/2}}{r_0 s^{1/2}} \right), \quad \gamma = \frac{r_0 + \delta r}{r_0} \]  

(2.89)
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is obtained. $\Phi_{12}$ is given as a numerical evaluation of an integral also subject to uniform flux conditions and $r_0$ is the inner radius of the ring and $\delta r$ the ring width. It is shown that rings attain steady-state much more quickly than discs of equivalent dimensions. Experimental results shown for chronoamperometry for a series of different diameter rings and discs are in excellent agreement with the results predicted by the equations above.

The A.C. response of ultramicrodiscs derived by Fleischmann and Pons [123] is also subject to uniform flux conditions

$$D \left( \frac{\partial c}{\partial z} \right)_{z=0} = -Q \sin \omega t \quad 0 < r < r_0 \quad (2.90)$$

yielding, as before, expressions containing tabulated functions For the imaginary and real components of the flux we obtain

$$\mathfrak{S}(z) = \frac{RT}{\pi n F i_0 r_0^2} + \frac{4RT}{\pi n^2 F^2 D^{1/2} r_0^{1/2} \omega r_0^{2/3} c_b} \cdot \Phi_4 \left( \frac{r_0^2 \omega}{D} \right) \quad (2.91)$$

$$\mathfrak{R}(z) = \frac{4RT}{\pi n^2 F^2 D^{1/2} r_0^{1/2} \omega r_0^{2/3} c_b} \cdot \Phi_5 \left( \frac{r_0^2 \omega}{D} \right) \quad (2.92)$$

This work may be compared to the steady-state, non-uniform flux A.C. work performed earlier by Sarangapani and de Levie, detailed on page 63.

Coupled chemical reactions are also detailed by Fleischmann and Pons [124], illustrated by the CE mechanism. In this case the authors deem it necessary to make a spherical approximation to the diffusion at a microdisc (i.e. the disc behaves as a sphere of radius $\frac{3}{4} r_{\text{disk}}$). For the reaction

$$A \xleftrightarrow{k_1 \ k_2} B$$

$$B \xrightarrow{\text{ne}^-} C$$

with diffusion in the spherical polar coordinate system

$$D \left[ \frac{\partial^2 c}{\partial r^2} + \frac{2 \partial c}{r \partial r} \right] + k_1 - k_2 c_B = 0 \quad (2.94)$$
A derivation similar to other systems above gives

\[ \frac{Q^{1/2}}{2} = k_1 r_0 \Phi_2 \left( \frac{r_0 k_2}{D^{1/2}} \right) \]  

(2.95)

similar to the chronoamperometric response. An approximate analysis produces expressions for flux assuming constant surface concentration

\[ Q = \frac{k_1 r_0}{2} \frac{8}{\pi} \left( \frac{D}{r_0^2 k_2} \right) \left[ 1 + \frac{\pi}{4} \left( \frac{r_0^2 k_2}{D} \right)^{1/2} \right] \]  

(2.96)

However, equation (2.95) assumes a constant surface flux so the authors incorporate a factor that is the ratio of the constant flux and constant concentration mass transfer coefficients, \( \pi \), to give

\[ Q = \frac{k_1 r_0}{2} \frac{3\pi}{4} \left( \frac{D}{r_0^2 k_2} \right) \left[ 1 + \frac{\pi}{4} \left( \frac{r_0^2 k_2}{D} \right)^{1/2} \right] \]  

(2.97)

The above may be compared to equations (2.83) and (2.84). Close agreement of the hemispherical approximation with more complex mathematical treatments is shown (within 6.8%), both as a table and as a plot of relative errors with respect to the exact chronoamperometric result and the exact CE result. (One reference appears incorrectly in [124] (ref 3), the authors appear to be comparing something with itself).

Some of the conclusions drawn by the authors of this first short series of papers [121-124] are open to question, such as the derivation of an extension to the Cottrell equation that is in contradiction to the conclusions of Shoup and Szabo [100] and the assumed superiority of the uniform flux approximation. One very useful conclusion is that the use of average concentration values, \( c_{AV} \), over the surface of an ultramicroelectrode may avoid involved mathematical complications or approximations.

### 2.3.5 Solutions allowing for variable flux

Sarangapani and De Levie [125] treat diffusion associated with the steady state A.C. response of a disc and obtain an expression for non-uniform radial flux. It
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is notable that this work was performed in 1979, some time before similar work described in this chapter. The solution is obtained via discontinuous integral of Bessel functions (see also the detailed contributions from Pons and Fleischmann on page 61). The ratio of the AC current to the alternating interfacial current is given as

\[
\frac{i_{\sim}}{c_{\sim}} = 2\pi nFDr_0\int_0^1 \frac{\rho \, d\rho}{S(\rho, \nu)}, \quad \rho = \frac{r}{r_0}, \quad \nu = \frac{j\omega r_0^2}{D}
\]  

(2.98)

\(S(\rho, \nu)\) is a discontinuous integral of a Bessel function [125]. The AC concentration amplitude \(c_{\sim}\) is independent of the radial parameter \(\rho\). From equation (2.98) above we may obtain the familiar expressions for diffusion to a plane

\[
\left(\frac{i_{\sim}}{c_{\sim}}\right)_p = \pi nFDr_0\nu^{1/2}
\]

(2.99)

and to a hemisphere of radius \(r_0\)

\[
\left(\frac{i_{\sim}}{c_{\sim}}\right)_h = 2\pi nFDr_0(\nu^{1/2} + 1)
\]

(2.100)

The non-uniform radial flux across the surface of a disc may be obtained via

\[
\frac{i_{\sim}}{i_{\sim,av}} = \frac{1}{2S(\rho, \nu)\int_0^1 \frac{\rho \, d\rho}{S(\rho, \nu)}}
\]

(2.101)

Note that at \(\rho = 0\) (at the centre of the disc) the current is exactly half the average current \(i_{\sim,av}\). The same result of 1/2 has also been derived by Oldham, in 1981 [68], for steady-state conditions at an ultramicrodisc.

A later series of three papers by Fleischman, Daschbach, Pons et al. [126–128] introduce Neumann's integral theorem, which allows solution for a variable flux over the electrode surface.

\[
D \left(\frac{\partial c}{\partial z}\right)_{z=0} = Q(y), \quad 0 < y < r_0
\]

(2.102)

under the constraint of steady-state conditions as mentioned on page 50. A general solution is first derived from discontinuous Bessel integrals, as in previous
papers by the same authors. Applying Neumann’s integral theorem in one variable gives
\[ c(r, z) = \int_0^\infty \alpha \, d\alpha \int_0^{r_0} \frac{e^{-\alpha z}}{\alpha} \frac{Q(y)}{D} J_0(\alpha r) \, J_0(\alpha y) \, y \, dy \]  
(2.103)
where \( \alpha \) is a variable of integration and \( y \) is the radial position in the plane of the disc and at the electrode surface
\[ c(r) = \int_0^\infty \int_0^{r_0} \frac{Q(y)}{D} J_0(\alpha r) \, J_0(\alpha y) \, y \, dy \, d\alpha \]  
(2.104)
By expressing the flux as a Fourier series
\[ -Q \left( \frac{r}{r_0} \right) \]  
(2.105)
\[ = \frac{1}{(r_0^2 - r^2)^{1/2}} \left[ d_0 + d_1 \left( \frac{r_0^2 - r^2}{r_0^2} \right)^{1/2} + d_2 \left( \frac{r_0^2 - r^2}{r_0^2} \right) + \cdots + d_n \left( \frac{r_0^2 - r^2}{r_0^2} \right)^{n/2} \right] \]
Fleischmann, Daschbach and Pons find that the first two terms of the above expression give respectively, the diffusion controlled limit a high overpotentials and the kinetically controlled limit at low overpotentials. Thus, they conclude that a short Fourier series should give adequate accuracy at median values of overpotential. A treatment for quasi-reversible steady-state reactions is presented, solutions are given as function of a variable \( g_j \)
\[ g_j = \frac{1}{4Dc^b} \frac{i_0}{i_d} \]  
(2.106)
which determines the behaviour of the system. In turn, \( g_j \) is a function of a dimensionless kinetic variable expressed as
\[ \frac{i_0^2}{i_d^2} \]  
(2.107)
with \( i_0 \) the charge transfer current and \( i_d \), the diffusion limited current as defined in equation (2.9). Employing a general expression for concentration at the surface of the electrode, via equation (2.104), the flux is given as
\[ Q \left( \frac{r}{r_0} \right) = \frac{4Dc^b}{r_0 \left( 1 - r^2/r_0^2 \right)^{1/2}} \sum_{j=0}^{n} g_j \left( 1 - \frac{r^2}{r_0^2} \right)^{j/2} \]  
(2.108)
The total current over the surface of a disc may be obtained from

\[ 2\pi DF \int_0^{r_0} \left( \frac{\partial c}{\partial z} \right)_{z=0} r \, dr = 8\pi DF c_b r_0 \sum_{j=0}^{n} \frac{g_j}{j+1} \]  

(2.109)

This expression is solved by evaluation of \( g_j \) at \( (n+1) \) positions on the disc to give \( (n+1) \) coefficients \( d_j \) via equation (2.106) to substitute into equation (2.106) and solve the resulting simultaneous equations. Convergence is found satisfactory for \( n = 8 \) [126]. The variation or error of \( g_j \) over a range of overpotentials or kinetic parameters is smaller than that obtained using the approach of Bond et al. [97]. This occurs, according to Fleischmann, Daschbach and Pons, because a single Fourier series is applied throughout as opposed to a combination of two overlapping series employed by Bond et al. [97]. Illustrations of the errors associated with their technique [126] are presented for differing mass transfer coefficients, \( k_m \), in equations (2.112) - (2.114) below. For constant flux,

\[ (k_m)_Q = \frac{3\pi D}{8r_0} \]  

(2.110)

and for constant concentration,

\[ (k_m)_c = \frac{4D}{\pi r_0} \]  

(2.111)

Using the former flux limited mass transfer coefficient (equation(2.110)) yields the incorrect limiting current (as mentioned above on page 60). The resulting error is [127],

\[ \frac{(k_m)_c - (k_m)_Q}{(k_m)_c} = 7.5\% \]  

(2.112)

The concentration limited mass transfer coefficient should be used in this case and in high overpotential situations, but errors occur where kinetic control is at a maximum, at \( E_1 \). Overall errors are reduced to approximately 3.5% by using an average expression

\[ k_m = \frac{(k_m)_c + (k_m)_Q}{2} \]  

(2.113)
which may be reduced to less than 2.5% via

\[ k_m = \left( (k_m) Q \left( \frac{i_d - 1}{i_d} \right) + (k_m) c \right) \quad (2.114) \]

This gives an approximation to equation 2.109 of

\[
\begin{align*}
\left\{ \frac{3\pi^2}{32} - \pi \left[ e^{-\alpha \xi} + e^{(1-\alpha)\xi} \right] \left( \frac{i_0 r_0^2}{|i_d|} \right) \pm \left[ e^{-\alpha \xi} - e^{(1-\alpha)\xi} \right] \left( \frac{i_0 r_0^2}{|i_d|} \right) \right\} \frac{i}{i_d} \\
+ \left( \frac{i}{i_d} \right)^2 \left[ e^{-\alpha \xi} - e^{(1-\alpha)\xi} \right] \left( \frac{i_0 r_0^2}{|i_d|} \right) = 0
\end{align*}
\]

In comparison to the exact solution, this approximation gives minimal errors up to the half-wave potential (kinetic control) and zero errors for the steady state values.

Tertiary current distribution is also treated. The effects of the potential drop in the solution are given by the equation

\[ D \left( \frac{\partial c}{\partial z} \right) = kc = k_0 e^{-\alpha EF/RT} e^{-\alpha\phi(r)F/RT} c \quad (2.116) \]

and the resulting effects of solution conductivity on flux are calculated. The importance of this effect is noted, as many uses of electrodes are found in highly resistive solvents. The tertiary current distribution for irreversible electrode reactions under the boundary condition is given as

\[ D \left( \frac{\partial c}{\partial z} \right) = kc = k_0 e^{-\alpha EF/RT} e^{-\alpha\phi(r)F/RT} c \quad (2.117) \]

incorporating a variable heterogeneous rate constant over the electrode, \( kc \). The radially dependent variable \( \phi(r) \) is expressed as

\[ \phi(r) = \frac{z F r_0}{\kappa} \sum_{j=0}^{n} d_j e_j f_j \left( \frac{r}{r_0} \right) \quad (2.118) \]

There exists no unique value of potential drop over the surface of the electrode.

Also, for a typical electrochemical experiment the dimensionless parameter has a range from 0.1 to 5000 [127].

\[ 0.1 \leq \frac{\kappa RT}{\alpha z F^2 D c} \leq 5000 \quad (2.119) \]
The final paper of the series [128] considers chronoamperometry at ultramicro-
electrodes, assuming Cottrell behaviour at short times and allowing for variable
flux. A potential distribution at short time is presented for resistive solvents and
and a current distribution for linear sweep voltammetry is also given.

The Laplace transform is performed assuming steady-state boundary condi-
tions. and the behaviour (Cottrell) at short times may be given by

$$d_1(s) = \frac{r_0c^\infty}{s^{1/2}}$$  \hspace{1cm} (2.120)

$$d_0 = d_2 = d_3 = \ldots = d_n = 0$$  \hspace{1cm} (2.121)

greatly simplifying the solution of the simultaneous equations as outlined above.

Equations are also given for CE and EC catalytic reactions under steady-state
conditions [128]. Working curves are also calculated for time limited flux (see
also page 61). Flux, concentration distribution and total rate of reaction are
determined in the Laplace plane, with edge flux remaining finite due to potential
distribution, as infinite flux would correspond to an infinite value of overpotential.

2.4 Digital Simulation approach

The simulation of electrical response of a system by digital methods is neces-
sary when no analytical or pseudo-analytical solution is available for the complete
current-potential-time \((i - E - t)\) regime.

The discretisation approach may either be one of finite differences or finite
elements, commonly referred to as the 'point' or 'box' methods respectively. As
mentioned in the introduction to this chapter,

Pioneering work on digital simulation in electrochemistry was carried out by
Randles in 1948 [75] using a finite difference method. This work was adopted and
refined by others, particularly Feldberg [77–79,129] (see also pages 34 and 35). Beginning in 1964, Feldberg used a simple finite-element method to model current reversal chronopotentiometry with following second order kinetics [77]. This work was followed in 1969, by a lengthy and detailed treatment of digital simulation [78]. Further improvements were published by the same author three years later [79], detailing surface boundary phenomena, particularly multiple electron transfer and adsorption. Work has also been performed to simulate edge effects at disc electrodes using a two-dimensional simulation in cylindrical coordinates [87]. All of the above models used the finite element approach.

Olmstead, Hamilton and Nicholson [80] gave a simple finite difference method for the cyclic voltammetric response of planar and spherical electrodes for a dimerisation reaction. In a consecutive paper Olmstead and Nicholson [81] used the same method to simulate a double potential step experiment for the study of a reduction-dimerisation reaction. Simulation of this technique was repeated by Hanafey et al. in 1978, in a paper detailing the double potential step current, charge and absorbance responses for a large range of electrochemical mechanisms [130].

A comparison of the point and box methods was undertaken by Britz in 1980 [131] with the point method being found more efficient, a conclusion arrived at following correspondence between Britz and Feldberg in 1979 [132]. On this basis, the majority of the following work detailed uses the point method. However, it is worth noting the advantage the box method presents in considering fluxes in separate volumes, making it still worthy of consideration when difficult flux patterns are encountered.

Explicit finite difference work exhibits a stability constraint of

$$n\lambda \leq 0.5$$ (2.122)

where \(n\) is the dimensionality of the simulation and \(\lambda\) is defined in equation (2.124) below. For a detailed simulation of diffusion to an ultramicrodisc, a two-dimensional simulation method must be used. An explicit two-dimensional method
would have a stability criteria of

$$\lambda \leq 0.25$$  \hspace{1cm} (2.123)

The major restriction on the explicit method is the variable, $\lambda$.

$$\lambda = \frac{D\delta t}{\delta x^2}$$  \hspace{1cm} (2.124)

This produces instabilities for either very small spatial increments or long time periods. Translated into practical terms, this precludes simulations with slow sweep rates or very small electrodes. For example, a typical electrochemical experiment with sweep rate, $\nu = 0.01 Vs^{-1}$, and duration of the experiment, $t = 4 sec$, giving a potential range of $E_v \pm 0.2 V$, $nt = 1000$, giving $\delta t = 0.004$, radius of electrode $= 50 \mu m$ and number of increments on the electrode $= 100 \rightarrow \delta r = 5 \times 10^{-5} cm$. Diffusion coefficient $= 1 \times 10^{-5} cms^{-1}$.

Using equation (2.124) above, $\lambda$ has a value of 8. This is too large for the algorithm to remain stable. For $\lambda = 0.5$, $nt = 160,000$, an unacceptably large number of time steps. This extremely large number of time iterations is often prohibitive due to the large amount of computer time required, although a lengthy simulation of this nature was undertaken by Flanagan and Marcoux in 1973 [87] and repeated, with amendments, by Kakihana et al. in 1981 [98]. A simulation algorithm offering consistency, convergence and stability for larger $\lambda$ values is required to provide a more efficient method.

The problem of a large number of iterations required to ensure an accurate algorithm may be partly overcome by use of an expanded grid method, of which there are several variations (For a basic description see the digital simulation text book by Britz [133]). Magno [134] uses a small diffusion layer dependent on

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\(^1\)Consistency, convergence and stability are investigated further in section 4.5.3 on page 161
\( m(Dt)^{1/2} \), \( m \) is an integer. This method is a expanded time grid. The exponentially expanded space grid, introduced by Joslin and Pletcher [135], and developed by Seeber and Stefani [136] and also by Feldberg [129], uses an expansion of the form,

\[
\delta x_i = \delta x_0 e^{K(i-1)}
\]  

(2.125)

Where \( K \), the expansion coefficient, can take values from 0 (a uniform grid), to a maximum of 0.5. This method has been further refined by Sandifer and Buck [137], who take a flux average at times \( t \) and \( t + \delta t \).

Seeber and Stefani discuss both expanded space and expanded time grids [136] and calculate, for a range of electrochemical techniques, the optimum number of iterations in each grid to achieve an accurate simulation. Work by Reller et al. [138] uses a non-uniform time discretisation and an expanding space-grid of the Joslin and Pletcher type both on the electrode and in solution. The maximum density of points being at the electrode boundary, as required. The method is applied to arrays of disc microelectrodes and shows a great saving in computation time when compared to earlier uniform grid simulations by the same authors [139]. Arrays of band electrodes have also been simulated using a 2D expanded space grid method giving results, for a single band, to within 3% of a numerical solution [140].

An expanding grid for the time parameter is useful for chronoamperometry but is not applicable to cyclic voltammetry as the concentration profile changes slowly at first, then with increasing rapidity as the half wave potential is reached. The rate of change then decreases until the scan is reversed. The time grid expansion for cyclic voltammetry would require a more complex expansion equation, utilising smaller increments for the area of maximum rate of change and larger grid increments for the limiting overpotentials. This equation would be similar to that used for the radial spatial expansion at disc interfaces. (see Section 4.4, page 143 on expansion in cylindrical coordinates.)
Chapter 2. A review of the simulation of ultramicroelectrode response

The following sections offer a series of alternative simulation methods based on finite differences together with comparisons of their associated and relative efficiencies and also a measure of accuracy when compared to the pseudo-analytical methods detailed in the previous section. The methods covered are:

- Crank-Nicolson method
- A.D.I. method
- Hopscotch method
- Orthogonal Collocation
- Runge-Kutta Integration and other methods

It is worth noting at this stage, that the two major factors effecting the accuracy and efficiency of a digital simulation are the location and density of the points and the time-dependent calculation of the resulting flux between these points of differing concentration. A lack of correlation between the rate of propagation of the simulation and the real response will, in the majority a cases, lead to errors. All of the the more advanced methods described below use methods allowing variable time or spatial increments as the simulation progresses.

2.4.1 Crank-Nicolson method

A semi-implicit method such as that of Crank and Nicolson \[70\] offers stability for large values of \( \lambda \), reducing simulation time and yielding increased accuracy. The basic equation is based on a implicitly and explicitly determined central difference expressions, a discretised form of Ficks second law,

\[
\frac{\partial c}{\partial t} \approx \frac{D}{2\delta x} \left( \frac{c'_{i+1} - c'_i}{\delta x} - \frac{c'_i - c'_{i-1}}{\delta x} + \frac{c_{i+1} - c_i}{\delta x} - \frac{c_i - c_{i-1}}{\delta x} \right) \quad (2.126)
\]

\[
= \frac{D}{2\delta x^2} (c'_{i-1} - 2c'_i + c'_{i+1} + c_{i-1} - 2c_i + c_{i+1}) \quad (2.127)
\]
A full description of this method (applied to one-dimensional diffusion in solution) is given in Chapter 3. Early examples of work performed using the Crank-Nicolson (C-N) method are a generalised numerical method for stationary electrode polarography by Booman and Pence in 1965 [141], and a fully implicit method to simulate spectro-electrochemical working curves by Winograd in 1973 [142].

More recently, the two most widely discussed refinements to the C-N method are the 'half-box' shift (a dislocation of simulation points by \( \delta x/2 \)), and implicit determination of boundary conditions.

Following the work of Feldberg [78, 79], a \( \delta x/2 \) shift is used widely by Heinze [91, 143–146] for both C-N and ADI work (section 2.4.2 below), and is also detailed in the text book by Britz [133] together with a number of suitable grid expansions for the C-N method. Lasia [147] assesses a number of approaches to calculate flux for both explicit and implicit (C-N) finite differences, comparing the \( \delta x/2 \) to the \( \delta x \) method (no shift of simulation points). Although Britz suggests that the \( \delta x/2 \) method gives marginally better results Lasia shows for DPSV the \( \delta x \) method gives better results and for LSV there is no difference between the two. It is nowadays generally agreed that the 'half-box' method conveys little advantage and that the method has now been superseeded by the \( n \)-point polynomial method [148] detailed below.

A paper by Heinze, Storzbach and Mortensen, [149] introduces implicitly calculated boundary conditions, \( C'_0 \), now accepted as an essential part of any Crank-Nicolson scheme where the boundary concentration values are time-dependent. One example is cyclic voltammetry, where the boundary values needed to calculate the new concentration values in every \( \delta t \) loop must be known before the new iteration begins. To achieve this the flux at the electrode surface and the surface concentra-

\(^1C'_0\) denotes the concentration value at the electrode, \((x = 0)\), with the ' signifying time \( t + \delta t \), C is dimensionless concentration \( c/c^\circ \).
tions are computed simultaneously with the 'bulk' concentrations as part of the C-N algorithm. An expression for the new boundary concentration (of a species A) is obtained by Heinze et al. [149],

\[ C'_{A,0} - C_{A,0} = \frac{\lambda}{2} \left( 8C'_{A,1} - 8C'_{A,0} - \frac{4\delta x}{D_A} f'_{A,0} \right) + \left( 8C_{A,1} - 8C_{A,0} - \frac{4\delta x}{D_A} f_{A,0} \right) \]  

and likewise for B. In the above expression and those below a 'half-box' shift is used. The flux at the boundary is given by a Butler-Volmer expression relating the concentrations of the redox couple A, B. This is used to obtain a fully implicit expression

\[ f'_{A,0} = k'_f C'_{A,0} - k'_b C'_{B,0} \quad (2.129) \]

\[ f'_{A,0} = -f'_{B,0} \quad (2.130) \]

where \( k'_f \) and \( k'_b \) are the rate constants for the forward and backward charge transfer. Heinze et al. note that multiplication of very small concentration by large \( k' \) factors may produce rounding errors and that the \( C_{A,0}, C_{B,0} \) do not appear symmetrically in the difference equation, leading to inaccuracies. This problem is overcome by expressing the fluxes as a three point approximation

\[ f'_{A,0} = \frac{D_A}{3\delta z} (-C'_{A,2} + 9C'_{A,1} - 8C'_{A,0}) \quad (2.131) \]

\[ f'_{B,0} = \frac{D_B}{3\delta z} (-C'_{B,2} + 9C'_{B,1} - 8C'_{B,0}) \quad (2.132) \]

then combining equations (2.129) to (2.132) to give an improved flux expression

\[ f'_{A,0} = -f'_{B,0} \]

\[ r = \frac{k'_f (9C'_{A,1} - C'_{A,2}) - k'_b (9C'_{B,1} - C'_{B,0})}{8 + 3k'_f \delta z/D_A + 3k'_b \delta z/D_B} \quad (2.133) \]
(Note that in reference [149] the first minus signs are missing from equations (2.131) and (2.132)). An error of less than 0.01% for \( \lambda \) values between 100 and 0.1 is shown in comparison to the analytical result for homogeneous kinetics at a semi-infinite planar interface. The treatment is extended to multiple electron transfer with continued accuracy. Lasia [150] discusses some of the approximations used in Heinze's work and suggests a number of methods to further improve the accuracy of the method. Other work by Lasia using the C-N method, simulates anomalous values of charge transfer coefficients [151] and study of the CEE mechanism by voltammetry and chronoamperometry [152]. These do not appear to have included an implicit determination of boundary conditions.

A refined implicit \( C'_0 \) method is presented by Britz as a paper [148] and later in the second edition of an excellent book on digital simulation in electrochemistry [133]. This method is a development of the work of Heinze et al. [149], in that a discretised Fick equation at the interface is no longer used and the three point approximations to the flux (equations (2.131) and (2.132) are replaced by a polynomial expansion for the concentration gradient at the interface.

\[
\left. g_0(n) \right|_i \simeq \frac{1}{a_n h} \sum_{i=0}^{n-1} b_{n,i} C_i
\]

(2.134)

where \( g_0 \equiv \left. \left( \frac{\partial C}{\partial x} \right) \right|_{x=0} \) Equation (2.134) is a development of a Taylor expansion \( a_n \) and \( b_{n,i} \) are integer coefficients and are given as a table in reference [148]. The method is detailed by Britz for one-dimension only, but may be easily extended to two dimensions. For details see reference [102] or Chapter 5.

The refined implicit \( C'_0 \) method is applied to electrochemical techniques by Britz, Heinze et al. [153]. Greatly improved simulation efficiency of one or two orders of magnitude is shown over both the explicit finite-difference method and the C-N method lacking implicit determination of boundary conditions.

Some of the possible inaccuracies of the C-N method are detailed in the work of Britz and Thomsen [154]. Ignorance of the implicit \( C'_0 \) refinement may lead to compounded errors in excess of those associated with an explicit method and may
also lead to instability in the C-N algorithm in the short time domain. Further details of errors produced due to instability are given in section 4.5.3

### 2.4.2 ADI method

The Alternating Direction Implicit (ADI) method proposed by Peaceman and Rachford in 1955 [155] has proved a popular method for the simulation of ultramicroelectrode response [91, 133, 143-146]. It is essentially a two dimensional adaptation of the Crank-Nicolson method, presenting a similar symmetric algorithm. Concentration is expressed as a function of cylindrical coordinates and time, $C(\delta r, j\delta z, k\delta t)$. The ultramicrodisc is assumed to be symmetric so the simulation may be reduced to two dimensions.

For odd time steps ($k = 1, 3, 5, \ldots$), the concentrations are determined fully implicitly in one direction and explicitly in the perpendicular direction. Conversely, for even time steps ($k = 2, 4, 6, \ldots$), concentrations are calculated explicit and fully implicit respectively. A full description of this method (applied to two-dimensional diffusion in solution) is given in Chapter 4. The original work of Peaceman and Rachford [155], shows that for a rectangular region in cartesian coordinates the ADI method is about twenty-five times more efficient than the explicit method and about seven times more efficient than the C-N method overheads - CHPT twoD

Heinze [144] uses the ADI method with chronoamperometric boundary conditions to investigate the current-potential response of an ultramicrodisc. A series of working curves are presented which enable a very accurate estimate (error $< 1\%$) to be made of the diffusion coefficient of the electroactive species. Experimental results [144] show good agreement with the simulations.

In a similar paper [91], Heinze simulates a full chronoamperometric response yielding variable values of $b$ for equation (2.2). $b$ is shown to increase as the parameter $\tau = (Dt/r_o^2)^{1/2}$ increases. A table of $b$ values is given for $\tau = 0.002$
(b = 1.772) to \( \tau = \infty \) (b = 2.2567). The simulation also produces current values comparable to the theoretical results of Shoup and Szabo [100], Aoki and Osteryoung [94], Fleischmann et al. [122] and digital simulation results from Shoup and Szabo [100], Kakihana [98], and Taylor et al. [102] given in table 2–2 on page 82.

The advantages of digital simulation over a pseudo-analytical method are apparent in this application of the ADI method to simulate chronoamperometry. For each of the simulation points on the disc the concentration of the electroactive species A is zero, using the redox couple,

\[
A^{n\text{e}^-} \rightarrow B
\]  

(2.135)

as before, and for each of the simulation points on the insulating surface surrounding the ultramicroelectrode the flux perpendicular to the surface is zero. These mixed Dirichlet and Neumann boundary conditions may easily be incorporated into the algorithm [91] and calculated as part of the ADI scheme to yield the flux values over the active part of the interface.

Heinze uses 30 equally spaced simulation points on the active interface. The total current flowing at any time is given by summing the individual fluxes at each simulation point.

\[
\frac{i}{nFA} = \sum_{i=1}^{n_r} \frac{f^z_{A,i}(2i-1)c^b_A}{n_r^2} + \frac{f^*_{A,n_r}(n_r - 0.5)c^b_A}{2n_r^2}
\]  

(2.136)

as the current density for an ultramicrodisc increases markedly towards the perimeter of the disc the fractional currents in the outer range of the interface are too small. The use of a spline interpolation to increase the number of simulation points is suggested as a method of increasing accuracy. The outer 3 points are sub-divided into 30 and the fluxes recalculated (\( f^{**}_{A,i} \)).

\[
\frac{i}{nFA} = \sum_{i=1}^{n_r-3} \frac{f^z_{A,i}(2i-1)c^b_A}{n_r^2} + \sum_{i=1}^{30} \frac{f^{**}_{A,i}(n_r - 3.05 + 0.1l)c^b_A}{5n_r^2}
\]  

(2.137)

(In reference [91] the number 3.05 is incorrectly calculated as 3.1).
Chapter 2. A review of the simulation of ultramicroelectrode response

A successive paper by Heinze [143] details the boundary conditions necessary for cyclic voltammetry;

\[ f_{A,i,0}^z = \frac{D_A}{3\delta z}(-c_{A,i,2} + 9c_{A,i,1} - 8c_{A,i,0}) \] (2.138)

\[ f_{A,i,0}^z = k_f c_{A,i,0} - k_b c_{B,i,0} \] (2.139)

\[ f_{B,i,0}^z = \frac{D_B}{3\delta z}(-c_{B,i,2} + 9c_{B,i,1} - 8c_{B,1,0}) \] (2.140)

\[ f_{B,i,0}^z = -f_{A,i,0}, \quad \forall i, \quad i = 1\ldots n_r \] (2.141)

\[ f_{A,i,0}^z = f_{B,i,0}^z = 0, \quad \forall i, \quad i > n_r \] (2.142)

and as above, the \( c_{A,i,0} \) and \( c_{B,i,0} \) values can be eliminated to give

\[ f_{A,i,0}^z = \frac{k_f(9c_{A,i,1} - c_{A,i,2}) - k_b(9c_{B,i,1} - c_{B,i,0})}{8 + 3k_f\delta z/D_A + 3k_b\delta z/D_B} \] (2.143)

The author states that 'as only the component perpendicular to the the electrode is active, it is sufficient to give the equations in an explicit formation'. This both neglects radial diffusion to edge of the electrode, an substantial component in the case of ultramicroelectrodes, and could propagate errors similar to those detailed for the C-N method in the previous section. The total simulated current is expressed as a dimensionless function

\[ \pi^{1/2} \chi(\xi, t) = \frac{\phi_{tot}}{c_A^\infty(D_A \xi)^{1/2}} \] (2.144)

where \( \phi_{tot} \) is equivalent to the total flux over the electroactive surface, calculated in the same manner as equation (2.137)

\[ \xi = \frac{nF}{RT \nu} \] (2.145)

From the standard definitions of \( k_f \) (eqn. (2.33)) and \( k_b \) (eqn. (2.34)) and equation (2.143) Heinze notes that the current function becomes independent of \( k_s \) and \( \alpha \).
with increasing charge transfer rate. However with decreasing charge transfer rate the voltammetric curve changes markedly in magnitude and form. To investigate quasi-reversible charge transfer the author defines a parameter $\psi$,

$$\psi = \left(\frac{D_A}{D_B}\right)^{a/2} \cdot \left(\frac{k_s}{\pi \xi D_A}\right)^{1/2}$$ (2.146)

For values of $\psi > 20$, the charge transfer is reversible and for values $\psi < 10^{-4}$ the system may be considered irreversible. Intermediate values give rise to quasi-reversible charge transfer. The effect of both the kinetic parameter $\psi$ and the scan rate $\nu$ on the shape of the voltammetric response may be predicted from two very informative sets of working curves presented in reference [143].

The effect of radial diffusion on the voltammetric response is quantified using a modified form of the equation for a planar interface, in the same manner as the Cottrell equation ([91] and above)

$$\pi^{1/2} \chi(\xi, t) = \pi^{1/2} \chi_{\text{planar}}(\xi t) + \sigma \rho(\xi t)$$ (2.147)

$$\sigma = \left(\frac{D}{\xi R^2}\right)^{1/2}$$ (2.148)

The concluding remarks of Heinze's paper suggest a very elegant method to determine heterogeneous rate constants. From the working curves presented it can be seen that the voltammetric peak separation may be consistently predicted by the equation

$$\Delta E_p = 59 + \Delta \sigma \Delta E_p + \Delta \psi \Delta E_p \pm 2 \text{ [mV]}$$ (2.149)

If the ultramicroelectrode radius and diffusion coefficient are known then the diffusion increment $\Delta \sigma \Delta E_p$ for each increment may be identified and subtracted from the experimental peak separation giving $\Delta \psi \Delta E_p$. From this, and equation (2.149) above, one may calculate the heterogeneous rate constant.

Heinze and Storzbach [145] present a paper implementing the above ADI method to solve homogeneous chemical kinetics at ultramicroelectrodes. An expanded grid is used beyond the electrode in addition to the spline interpolation
fitted to the 3 perimetric concentration values the electrode to. It is not stated if expanded grid increases the accuracy of the flux calculation. This work is also presented as part of a collection of papers on the study of microelectrode response [146].

Britz details the ADI method in his textbook [133] but uses a half-implicit/explicit method. This gives discretised expressions less symmetrical than the usual implicit/explicit ADI method leading to a less accurate simulation.

No workers appear to have used the obvious combination of the three techniques; ADI implicit determination $C_0'$ and an expanded space grid to simulate the response of an ultramicroelectrode in two dimensions. This simulation is discussed further in Chapters 4 and 5.

### 2.4.3 Hopscotch method

The Hopscotch method was proposed by Gourlay [71] as a fast method for the solution of P.D.E.s. Following the early work of Gordon [156], Gourlay introduced a local redefinition of variables to give a fast computing algorithm. Convergence of the method occurs for

$$\frac{\Delta t}{(\Delta x)^2}, \quad \frac{\Delta t}{(\Delta y)^2}, \quad \text{constant as } \Delta x, \Delta y, \Delta t \to 0$$  \hspace{1cm} (2.150)

Convergence time is proportional to the number of simulation points $N$. The algorithm is fully explicit and unconditionally stable for all $\lambda$. Gourlay claims that the method presents comparable speed and accuracy to the ADI method and is shown to be equivalent to the ADI method as described by Peaceman and Rachford. The Hopscotch method requires less computer storage space, as a n-dimensional problem always is reduced to a 2-stage process. However, Heinze [146] maintains that the ADI is slightly more efficient and accurate and more amenable to direct incorporation of kinetic parameters.
Shoup and Szabo [157] rate Hopscotch as one of the fastest of all methods but agree that the ADI method is more accurate. This may be due to the ability of ADI to incorporate implicit boundary conditions 4.5.4 whereas Hopscotch is an overall explicit method.

The mechanism of the Hopscotch algorithm is as follows; In one dimension, starting at \( C_1 \), points are alternatively calculated explicitly for \( C_i \), \( i = 1, 3, 5 \ldots \)

\[
C_i^{k+1} = C_i^k + \lambda (C_{i-1}^k - 2C_i^k + C_{i+1}^k) \tag{2.151}
\]
or implicitly \( C_i \), \( i = 2, 4, 6 \ldots \)

\[
C_i^{k+1} = C_i^k + \lambda (C_{i-1}^{k+1} - 2C_i^{k+1} + C_{i+1}^{k+1}) \tag{2.152}
\]

which rearranges to

\[
C_i^{k+1} = \frac{C_i^k + \lambda (C_{i-1}^{k+1} + C_{i+1}^{k+1})}{1 + 2\lambda} \tag{2.153}
\]

If we start at \( k = 0 \) (\( t = 0 \)) and calculate \( C_i^{k+1} \) explicitly, for \( k = 1 \) (\( t = \delta t \)) \( C_i' \) is calculated implicitly. On each succeeding time step the determination of concentration values implicitly or explicitly swap, conferring a stability for all \( \lambda \). This method is overall explicit as all \( C_i^{k+1} \) values in equation (2.153) may be calculated after the \( C_i^{k+1} \) values in equation (2.151).

Extension of the Hopscotch algorithm to two dimensions gives the following discrete equations, for \( (i + j + k) \) odd,

\[
C_{i,j}^{k+1} = C_{i,j}^k + \lambda_R (C_{i-1,j}^k - 2C_{i,j}^k + C_{i+1,j}^k) + \lambda_Z (C_{i,j-1}^k - 2C_{i,j}^k + C_{i,j+1}^k) \tag{2.154}
\]

and for \( (i + j + k) \) even

\[
C_{i,j}^{k+1} = \frac{C_{i,j}^k + \lambda_R (C_{i-1,j}^k + C_{i+1,j}^k) + \lambda_Z (C_{i,j-1}^k + C_{i,j+1}^k)}{1 + 2\lambda_R + 2\lambda_Z} \tag{2.155}
\]

The alternating calculation of points explicitly or implicitly with increasing time or space increments may be visualised as a chess board switching from black to
white with each time step. Using the above method, Shoup and Szabo simulate chronoamperometric current at a finite disc electrode [100]. The results are compared to simulations by Kakihana [98], Heinze [91], and Taylor, Girault and McAleer [102] in table 2–2 together with pseudo-analytical solutions from a number of authors.

The Hopschoch method has been further improved by Shoup and Szabo [157]. This later version of the algorithm is approximately twice as fast as the form detailed above. The improvement is based on the premise that concentrations are only required near the electrode, for example, to calculate the current. The special points are denoted $i^*, j^*$. The calculation of new concentration values is as follows;

1. For $(i + j + k)$ odd,

$$C_{i,j}^{k+1} = C_{i,j}^{k} + \lambda_R(C_{i-1,j}^{k} - 2C_{i,j}^{k} + C_{i+1,j}^{k}) + \lambda_Z(C_{i,j-1}^{k} - 2C_{i,j}^{k} + C_{i,j+1}^{k})$$

(2.156)

this is an initial step and occurs only once.

2. For the special points where $(i^* + j^* + k)$ is odd the new concentration value $C_{i^*,j^*}^{k+1}$ is stored in a special array $S_{i^*,j^*}^{k+1}$ and for $(i^* + j^* + k)$ is even,

$$C_{i^*,j^*}^{k+1} = \frac{C_{i^*,j^*}^{k} + \lambda_R(C_{i^*-1,j^*}^{k} + C_{i^*,j^*+1}^{k}) + \lambda_Z(C_{i^*,j^*-1}^{k} + C_{i^*,j^*+1}^{k})}{1 + 2\lambda_R + 2\lambda_Z}$$

(2.157)

and the new value for $C_{i^*,j^*}^{k+1}$ is also stored as $S_{i^*,j^*}^{k+1}$.

3. For all points with $(i + j + k)$ even, two time steps are taken

$$C_{i,j}^{k+2} = 2C_{i,j}^{k+1} - C_{i,j}^{k}$$

(2.158)

$C_{i,j}^{k+1}$ is calculated as in equation (2.155).

4. Increment $k$ by 1 and return to step 2.

This method has been applied to both the Cottrell problem and chronoamperometry at a finite disc. The first Hopscotch method detailed above takes an equivalent
Chapter 2. A review of the simulation of ultramicroelectrode response

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<td>1.180</td>
<td>1.091</td>
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<tr>
<td>3.3</td>
<td>0.1329</td>
<td>1.012</td>
<td>1.094</td>
<td>1.109</td>
<td>1.108</td>
<td></td>
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<td>10.0</td>
<td>0.04431</td>
<td>0.9418</td>
<td>1.018</td>
<td>1.036</td>
<td>1.036</td>
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<td></td>
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<tr>
<td>16.7</td>
<td>0.02569</td>
<td>0.9352</td>
<td>1.011</td>
<td>1.022</td>
<td>1.022</td>
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<tr>
<td>20.0</td>
<td>0.01963</td>
<td>0.9335</td>
<td>1.009</td>
<td>1.018</td>
<td>1.018</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>0.01772</td>
<td>0.9319</td>
<td>1.007</td>
<td>1.014</td>
<td>1.014</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33.3</td>
<td>0.01329</td>
<td>0.9302</td>
<td>1.005</td>
<td>1.011</td>
<td>1.011</td>
<td></td>
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<td></td>
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<tr>
<td>50.0</td>
<td>0.00886</td>
<td>0.9285</td>
<td>1.003</td>
<td>1.007</td>
<td>1.007</td>
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<td></td>
</tr>
<tr>
<td>100.0</td>
<td>0.00443</td>
<td>0.9269</td>
<td>1.002</td>
<td>1.004</td>
<td>1.004</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2-2: Analytical solutions, Hopscotch, Explicit F-D and ADI simulations
of computer time per iteration to run as the explicit finite difference method. The second, faster Hopscotch method takes half as much time per iteration. Hopscotch also has the added advantage that although fully explicit, it is not limited to the stability constraint of

$$n\lambda \leq 0.5$$  \hspace{1cm} (2.159)

Shoup and Szabo also apply this efficient Hopscotch method to other diffusion geometries such as an array of ultramicrodiscs [158] and an ultramicrodisc on top of a finite insulating cylinder [159].

Ruzic and Shoup and Szabo engage in a debate as to the merits of the Hopscotch method over the simpler explicit finite difference method. Ruzic suggests that a generalised form of the explicit F-D equation may be applied in most cases with equal accuracy [160]. Shoup and Szabo respond by comparing Hopscotch and an exact solution for the Cottrell problem, showing the superior accuracy and efficiency of their method over explicit F-D [161]. Later work has been carried out combining Hopscotch with space grid transformation. Feldberg [162] shows the importance of using an expanded grid to overcome propagational inadequacy (the system evolving faster than the simulation) and Amatore, Deakin and Wightman [163] use a very elegant conformal map transformation to simplify the problem of the non-uniform current distribution across an ultramicroband electrode.

### 2.4.4 Orthogonal Collocation

Orthogonal Collocation (OC) is an overly complex mathematical method featured in a number of papers by Speiser, Pons et al. on the simulation of edge effects in electroanalytical experiments [164–167], a development of earlier work by Speiser [168, 169].

The complexity is evidenced in the four papers by Speiser, Pons et al. presenting solutions for cyclic voltammetry and chronomperometry for a range of
electroanalytical techniques and mechanisms. Britz [133] offers a whimsical insight into the complexity of the OC method and recommends as initial reading, the first paper on the use of the OC method by Whiting and Carr [73]. The OC method is based on a trial function (set of weighted polynomials) that satisfies both diffusion and kinetic terms of relevant mass transport equations.

Magno et al. [134] compare expanded space grids, expanded space and time grids and OC with the simple F-D method on a regular space grid. The space grid is the type given by equation 2.125, the work of Feldberg using finite elements. Limitations on the use of OC for simulation of coupled chemical reactions are also outlined.

### 2.4.5 Runge-Kutta Integration and other methods

Third order Runge-Kutta Integration is equivalent to the Crank-Nicolson method [89], but the algorithm has been found to be unstable for large rate constants (beyond $k \times \tau = 10$). An application to electrochemistry is given by Barker et al. [170] in modelling second order electron transfer reactions. Although this method has been applied to a number of electrochemical techniques, it has not as yet been used to simulate ultramicroelectrode response.

A range of other digital simulation and pseudo-analytical methods have been used to simulate ultramicroelectrode response such as finite-element Galerkin methods [171, 172] and non-linear regression analysis [173]. More recently, eigenvector - eigenvalue solutions have been proposed [174, 175]. The DuFort-Franklin method and Larkin’s procedures [176], particularly the Saul’yev algorithm [177], have also proved useful [178].
2.5 Summary

To decide on what is the "best" method to model ultramicroelectrode response would not result in a single answer. Suggestions as to the optimum methods balancing accuracy, speed and simplicity can be taken from table 2-3.

A number of articles [147, 161, 134, 179, 95, 116, 180–182] comparing various methods of predicting ultramicroelectrode response give some insight as to the relative merits of the many techniques.

The following protocol is suggested;

- If only a limiting value solution or a solution over a limited time period is required then a simple pseudo-analytical expression will suffice (sections 2.3.1 and 2.3.2).

- More complex expressions are available for the complete \((i - E - t)\) regime but only if assumptions such as constant flux or steady-state behaviour are applicable (sections 2.3.3, 2.3.4 and 2.3.5).

- If a complete \((i-E-t)\) response without recourse to the assumptions above is required a digital simulation technique must be used. The complexity of the technique used depends on the degree of accuracy required. It appears that optimum combinations of speed, simplicity and accuracy are the Crank-Nicolson (C-N) method for one dimensional simulations (section 2.4.1) and the Alternating Direction Implicit method (ADI) method for two dimensional simulations (section 2.4.2), both using an expanded space grid.

The accuracy of the digital simulation may be confirmed by comparing the results to exact analytical solutions where available on the \((i - E - t)\) surface.
### Table 2-3: Table of simulation methods and relative accuracy

<table>
<thead>
<tr>
<th>Method</th>
<th>Accuracy</th>
<th>Speed</th>
<th>Simplicity</th>
<th>Example of use</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additional 'b'term in Sand equation</td>
<td>Low</td>
<td>fast</td>
<td>very simple</td>
<td>[84]</td>
<td>36</td>
</tr>
<tr>
<td>Additional 'b'term in Cottrell equation</td>
<td>Low</td>
<td>fast</td>
<td>very simple</td>
<td>[84]</td>
<td>37</td>
</tr>
<tr>
<td>Empirical equation</td>
<td>limited to $1.23 \leq r_d/(D t^{1/2}) \leq 33.3$</td>
<td>fast</td>
<td>simple</td>
<td>chronoamperometry</td>
<td>40</td>
</tr>
<tr>
<td>Empirical equation</td>
<td>$r_0 \geq 4D^{1/2}t^{1/2}$</td>
<td>fast</td>
<td>simple</td>
<td>chronoamperometry</td>
<td>40</td>
</tr>
<tr>
<td>Empirical equation</td>
<td>long time only</td>
<td>fast</td>
<td>simple</td>
<td>chronoamperometry</td>
<td>42</td>
</tr>
<tr>
<td>Empirical equation</td>
<td>short time only</td>
<td>fast</td>
<td>simple</td>
<td>chronoamperometry</td>
<td>42</td>
</tr>
<tr>
<td>Approximate equation</td>
<td>error &lt; 0.6% over all time</td>
<td>fast</td>
<td>simple</td>
<td>chronoamperometry</td>
<td>42</td>
</tr>
<tr>
<td>Approximate equation</td>
<td>long time only</td>
<td>fast</td>
<td>simple</td>
<td>voltammetry half-max. potential</td>
<td>44</td>
</tr>
<tr>
<td>Approximate equation</td>
<td>error &lt; 0.3%</td>
<td>fast</td>
<td>simple</td>
<td>Rev. Sq. Wave voltammetry max. current</td>
<td>47</td>
</tr>
<tr>
<td>Approximate equation</td>
<td></td>
<td>fast</td>
<td>simple</td>
<td>Kinetics from current-potential plots</td>
<td>48</td>
</tr>
<tr>
<td>Approximate equation</td>
<td></td>
<td>fast</td>
<td>simple</td>
<td>Kinetics from Cyclic voltammetry</td>
<td>48</td>
</tr>
<tr>
<td>Table of calculated values</td>
<td>exact (assuming st-state)</td>
<td>fast</td>
<td>simple</td>
<td>Kinetics from Cyclic voltammetry</td>
<td>51</td>
</tr>
<tr>
<td>Approximate equation</td>
<td>error &lt; 0.3% (assuming st-state)</td>
<td>fast</td>
<td>simple</td>
<td>Kinetics from Cyclic voltammetry</td>
<td>53</td>
</tr>
<tr>
<td>Convolution to st-st</td>
<td>assumes hemispher. geom.</td>
<td>mod.</td>
<td>mod.</td>
<td>Any voltammetry</td>
<td>54</td>
</tr>
<tr>
<td>Plot of Flux vs Time</td>
<td>assume uniform surface flux</td>
<td>mod.</td>
<td>complex</td>
<td>Chronopotentiotmetry flux vs. t</td>
<td>58</td>
</tr>
<tr>
<td>Empirical equation</td>
<td>assume uniform surface flux</td>
<td>mod.</td>
<td>complex</td>
<td>LS amperometry potential-time values</td>
<td>59</td>
</tr>
<tr>
<td>Empirical equation</td>
<td>assume uniform surface flux and st-state</td>
<td>mod.</td>
<td>complex</td>
<td>chronoamperometry</td>
<td>59</td>
</tr>
<tr>
<td>Approximate equation</td>
<td>error = 7.5% (assuming constant flux)</td>
<td>low</td>
<td>fast</td>
<td>limiting kinetic current</td>
<td>65</td>
</tr>
<tr>
<td>average expression</td>
<td>error = 3.5% (average flux and conc)</td>
<td>low</td>
<td>fast</td>
<td>limiting kinetic current</td>
<td>65</td>
</tr>
<tr>
<td>average expression</td>
<td>error &lt; 2.5% (average flux and conc)</td>
<td>low</td>
<td>fast</td>
<td>limiting kinetic current</td>
<td>66</td>
</tr>
<tr>
<td>Approximate equation</td>
<td>minimal errors</td>
<td>fast</td>
<td>mod.</td>
<td>total disc current vs potential</td>
<td>66</td>
</tr>
<tr>
<td>Approximate equation</td>
<td>errors &lt; 3% of numerical soln.</td>
<td>fast</td>
<td>mod.</td>
<td>curr-time plot (microband arrays)</td>
<td>70</td>
</tr>
<tr>
<td>Approximate equation</td>
<td>errors &lt; 1% of available analytical solns.</td>
<td>fast</td>
<td>mod.</td>
<td>chronoamperometry</td>
<td>75</td>
</tr>
</tbody>
</table>

Table 2-3: Table of simulation methods and relative accuracy
Once a method of simulation has been decided upon, fitting the simulation to experimental results may be via simplex optimisation [183]. Examples being the work by Hanafey et al. [130], Zhaohui et al. [184] or Section 6.4.4. Finally, although the work presented has been wide ranging and extremely successful, no one has, as yet, addressed the problem of charge transfer, either diffusion or kinetically controlled, across a liquid-liquid ultramicrorinterface. Solution of this problem is the subject of the following chapters.
Chapter 3

The numerical method: Crank-Nicolson

3.1 Introduction

In the review of simulation methods in the previous chapter (page 71), the Crank-Nicolson (C-N) method is shown to be the most appropriate method for a one-dimensional simulation of ultramicroelectrode response. In this chapter, the C-N method is explained and equations are derived for both linear and spherical diffusion in one dimension. The use of the two-dimensional Alternating Direction Implicit (ADI) method is discussed in Chapter 4.

The numerical technique used in the C-N method is that of finite differences, where the second order partial differential equation

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

(3.1)

is expressed as a set of concentration values at distinct points on a space-time grid (fig. 3-1). The discrete explicit form of the one-dimensional equation above is

$$\frac{c_i' - c_i}{\delta t} = D \frac{c_{i-1} - 2c_i + c_{i+1}}{\delta x^2}$$

(3.2)
Figure 3-1: The space-time grid for one-dimensional C-N

Where \( c_i' - c_i \) denotes the concentration change at point SiS after a time step \( \delta t \). To obtain the equation above we must combine the forward and reverse difference expressions for the first derivative of concentration with respect to distance and the forward difference expression for concentration with respect to time.

3.2 Definition of variables

In the discretisation of the second order partial differential equation in its various forms for different diffusion regimes, we define a dimensionless factor \( \lambda \),

\[
\lambda = D \frac{\delta t}{\delta x^2} \quad (3.3)
\]

where \( \delta x \) is the spatial increment, \( \delta t \) the time step and \( D \) the diffusion coefficient. For a one-dimensional explicit expression \( \lambda \) must be less than or equal to 0.5 for the algorithm to remain stable. For two dimensions \( \lambda \) must be less than or equal to 0.25. If \( \lambda \) is greater than these values then the error associated with each iteration grows in magnitude. In the words of Britz [133], ”The choice of \( \lambda \) has a bearing on accuracy of as well as the time taken for a simulation”.
Chapter 3. The numerical method: Crank-Nicolson

It helps to transform the variables in equation (3.2) into dimensionless parameters, to give equations with solutions that are more widely applicable than the specific solution of a dimensioned equation. Time becomes dimensionless by dividing by \( \tau \), the length of time of the experiment. The distance variable \( x \) becomes \( X \) by dividing by \( \delta \), the Nernst diffusion layer thickness, and concentration likewise, by dividing \( c \) by \( c^b \), the unchanging bulk concentration.

\[
T = \frac{t}{\tau}, \quad X = \frac{x}{\delta}, \quad C = \frac{c}{c^b} \tag{3.4}
\]

A common set of boundary conditions for an electrochemical experiment (potential step) would then be,

\[
\begin{align*}
T < 0 \quad & : \quad C = 1 \quad \forall X \\
T \geq 0 \quad & : \quad C = 0 \quad X = 0 \\
& \quad C = 1 \quad X \to \infty
\end{align*} \tag{3.5}
\]

Fick's First Law states that the flux passing a point (mol sec\(^{-1}\)) is equivalent to the negative concentration gradient at that point, multiplied by the area over which it is measured, times the diffusion coefficient of the species,

\[
\vec{j} = -\delta A D \frac{\partial C}{\partial X} \tag{3.6}
\]

An important, measurable quantity is the interfacial current. The interfacial current is equivalent to molar flux at the electrode multiplied by the number of electrons transferred for each molecule or ion, times the Faraday constant,

\[
i = nFAD \left( \frac{\partial C}{\partial X} \right)_{X=0} \tag{3.7}
\]

Dividing through by area to gives the above in terms of current density,

\[
I = nFD \left( \frac{\partial C}{\partial X} \right)_{X=0} \tag{3.8}
\]

Calculation of diffusion current

Using the dimensionless parameter for applied potential, \( p \),

\[
p = \frac{nF}{RT} (E - E^o) \tag{3.9}
\]
we may express the ratio of concentrations of for example, species $A$ and species $B$ at the interface as related by the Nernst equation

$$\frac{C_{A,0}}{C_{B,0}} = \exp(-p)$$  \hspace{1cm} (3.10)

The discretised form of the current equation

$$i = nFAD \frac{C_1 - C_0}{\delta X}$$  \hspace{1cm} (3.11)

is equivalent for species $A$ and $B$ assuming that their diffusion coefficients are equal. From equations (3.10) and (3.11) we may obtain an expression in $C_{A,1}$ and $C_{B,1}$ only,

$$i = \frac{C_{A,1} - C_{B,1}\exp(-p)}{\delta X(1 + \exp(-p))}$$  \hspace{1cm} (3.12)

then for a given potential we may predict the the concentration profile as we are able to simulate $C_i$ for all $i = 1, n$ iteratively from equation (3.2) (see Section 3.6). For a more accurate determination of the current, a 5-point polynomial method may be used [148]. This is covered in detail in Chapter 5.

### 3.3 Boundary conditions

For determination of the concentration at a boundary where the concentration is not known at all times, for example, the insulating surface around the interface, the standard discretised differential equation (3.2) may not be used as the $C_{i-1}$ value does not exist. An alternative expression must be found. We may assume the current and therefore the concentration gradient, perpendicular to the boundary is zero. This is reasonable as no current is flowing into the insulating surface.

$$\frac{C_1 - C_0}{dX} = 0$$  \hspace{1cm} (3.13)

Thus $C_0 = C_1$. If there are polarised interfaces in the vicinity of these insulating surfaces there may be a diffusional flux both perpendicular and parallel to the surface. Accounting for diffusional flux parallel to the boundary leads to a differential
equation that differs to the differential equation for diffusion in the bulk of the solution. This differential equation must be solved to give boundary concentration values that may be used as $C_0$ values when calculating $C_i \forall i, i = 1, n$.

### 3.4 Simplification of the diffusion equations

For a three dimensional diffusion case

$$\frac{\partial C}{\partial T} = D \left( \frac{\partial^2 C}{\partial X^2} + \frac{\partial^2 C}{\partial Y^2} + \frac{\partial^2 C}{\partial Z^2} \right)$$

(3.14)

The diffusion coefficient is usually found to be equivalent in all directions throughout the solution, unless in anisotropic media. Often it is possible to obtain the concentration invariant with $y$ and $z$, reducing the above equation to

$$\frac{\partial C}{\partial T} = D \left( \frac{\partial^2 C}{\partial X^2} \right)$$

(3.15)

For a cylindrical system we employ cylindrical coordinates, $z$ along the cylinder axis, $r$, radial distance from the axis, and $\theta$, angle of rotation about the axis. As diffusion is normally independent of $\theta$, the diffusion equation may be expressed as,

$$\frac{\partial C}{\partial T} = D \left( \frac{\partial^2 C}{\partial Z^2} + \frac{\partial^2 C}{\partial R^2} + \frac{1}{R} \frac{\partial C}{\partial R} \right)$$

(3.16)

For a spherical system with no concentration gradient other than away from the centre we obtain

$$\frac{\partial C}{\partial T} = D \left( \frac{\partial^2 C}{\partial R^2} + \frac{2}{R} \frac{\partial C}{\partial R} \right)$$

(3.17)

For the case of very small circular interfaces a quasi-spherical approximation may be made in that diffusion to the circular interface is assumed to be equivalent to the diffusion to a spherical interface of the same surface area (see Section 3.7), reducing equation (3.16) to the one dimensional form, equation (3.17).
3.5 Expansion of the space grid

If one considers the concentration profile over a distance of 106 (10 x the Nernst diffusion layer), a large proportion of the concentration values will be almost equivalent to the bulk concentration. The concentration values show a rapid increase with distance near to the electrode and a much less pronounced change with each spatial increment further into the bulk solution.

A sensible approach is to use increasing intervals on increasing distance from the electrode, retaining accuracy where the concentration change is rapid and saving computer time by eliminating unnecessarily small increments where the concentration changes very slowly. This will reduce the total number of steps without losing accuracy.

The division of the space grid into unequal intervals employs a transformation function to give an equal concentration gradient between points. This function will always approximate to an ideal solution as the concentration profile is seldom stationary. Nevertheless, a wise choice of transformation function improves accuracy near the electrode, reduces the required number of simulation points and decreases computer time.

The use of an expanded grid further improves the use of the Crank-Nicolson method to solve the discretised diffusion equations.

Joslin and Pletcher [135] first used a space grid expansion to model diffusion at a platinum microelectrode.

\[ Y = \frac{aX}{aX + 1} \]  
(3.18)

This algorithm was later refined by Feldberg [107]. The coefficient \( a \) normally has a value between 0.2 and 2. Other suitable functions have been found possessing comparable accuracy, but are not as ammenable to transformation into the expanded grid coordinates [133].
Chapter 3. The numerical method: Crank-Nicolson

Grid transformation functions may be incorporated into the diffusion equations (3.15) and (3.17) using the inverse of an expansion equation, for example, equation (3.19) inverted,

\[ X = g(Y) = \frac{Y}{a(1 - Y)} \]  

(3.19)

and the relationships,

\[ \frac{\partial C}{\partial X} = \frac{\partial Y}{\partial X} \frac{\partial C}{\partial Y} \quad \text{or} \quad \frac{\partial C}{\partial R} = \frac{\partial Y}{\partial R} \frac{\partial C}{\partial Y} \]  

(3.20)

to give

\[ \frac{\partial C}{\partial T} = \frac{D}{g'(Y)} \left[ \frac{1}{g'(Y)} \frac{\partial^2 C}{\partial Y^2} + \frac{\partial}{\partial Y} \left( \frac{1}{g'(Y)} \frac{\partial C}{\partial Y} \right) \right] \]  

(3.21)

for a linear expression (from equation (3.16)) and

\[ \frac{\partial C}{\partial T} = \frac{D}{g'(Y)} \left[ \frac{1}{g'(Y)} \frac{\partial^2 C}{\partial Y^2} + \left( \frac{\partial}{\partial Y} \left( \frac{1}{g'(Y)} + \frac{2}{g(Y)} \right) \right) \frac{\partial C}{\partial Y} \right] \]  

(3.22)

to give a spherical expression (from equation (3.17)). The use of this transformation with cylindrical coordinates is detailed in Chapters 4 and 5.

3.6 Implementation of the C-N method

Consider a three-dimensional representation of concentration, time and distance (fig. 3–1). From the explicit discretised form of Fick’s second law, equation (3.2), we may obtain an estimate of the new value of the concentration \( C'_i \). This is a forward difference expression

\[ \frac{C'_i - C_i}{\delta T} = \frac{D}{\delta X^2} \left( C_{i-1} - 2C_i + C_{i+1} \right) \]  

(3.23)

An approximation to the tangent at point \( C_i \) is given by this expression, with an associated error, \( E_{\text{explicit}} \) (fig 3–2). An alternative would be to use the fully implicit expression

\[ \frac{C'_i - C_i}{\delta T} = \frac{D}{\delta X^2} \left( C'_{i-1} - 2C'_i + C'_{i+1} \right) \]  

(3.24)
Figure 3-2: The reduction of error by using a half-implicit method
which is an approximation to the tangent at point $C_i'$, also with an associated error, $E_{\text{implicit}}$. This latter approach is stable for all values of $\lambda$ but, obviously, not very accurate. The sensible approach is to combine both explicit and implicit equations to obtain an approximation to the tangent at the mid-point $C_i (T + \frac{\delta T}{2})$

Thus we obtain the discretisation formula

$$\frac{C_i' - C_i}{\delta T} = \frac{1}{2} \frac{D}{\delta x^2} (C_{i-1} - 2C_i + C_{i+1} + C_{i-1}' - 2C_i' + C_{i+1}')$$  (3.25)

This half-implicit method has great accuracy and stability for all values of $\lambda$ (see Section 3.8).

### 3.6.1 Linear diffusion

To obtain a set of $C_i$ values at time $T + \delta T$, for all $i$, $(i = 1, n)$ we use the previous set of $C_i$ values at time $T$. Using equation (3.3) we may express equation (3.25) as

$$C_i' - C_i = 0.5\lambda (C_{i-1} - 2C_i + C_{i+1} + C_{i-1}' - 2C_i' + C_{i+1}')$$  (3.26)

Collecting terms gives

$$\frac{-\lambda}{2} C_{i-1} + (\lambda + 1)C_i' - \frac{\lambda}{2} C_{i+1}' = -\frac{\lambda}{2} C_{i-1} + (-\lambda + 1)C_i + \frac{\lambda}{2} C_{i+1}$$  (3.27)

This may be expressed as

$$C_{i-1}' + aC_i' + C_{i+1}' = b_i$$  (3.28)

where

$$a = -\frac{2}{\lambda}(\lambda + 1)$$  (3.29)

and

$$b_i = -C_{i-1} + \frac{2}{\lambda}(\lambda - 1)C_i - C_{i+1}$$  (3.30)
Equation (3.28) can be written for all \(i, i = 1, n\), to give set of simultaneous equations

\[
\begin{align*}
C'_0 + aC'_1 + C'_2 &= b_1 \\
C'_1 + aC'_2 + C'_3 &= b_2 \\
&\vdots \\
C'_{i-1} + aC'_i + C'_{i+1} &= b_i \\
&\vdots \\
C'_{n-1} + aC'_n + C'_{n+1} &= b_n
\end{align*}
\]  

(3.31)

which have solutions for all \(C'_i\), as we have \(n\) unknowns and \(n\) equations. \(C'_0\) is the boundary condition that is known (or determined as detailed in Section 3.3). \(C'_{n+1}\) is equivalent to the bulk concentration, unaffected by the electrochemical change and therefore a known constant. Reducing the above series of equations to two unknowns gives, for the last equation,

\[
C'_{n-1} + aC'_n = b_n - C'_{n+1}
\]

or

\[
C'_n = \frac{b_n - C'_{n+1} - C'_{n-1}}{a}
\]

(3.32)

Substitute into the second from last equation in (3.31)

\[
C'_{n-2} + \frac{a^2 - 1}{a} C'_{n-1} = \frac{a b_{n-1} - b_n + C'_{n+1}}{a}
\]

(3.33)

yielding a second set of simultaneous equations

\[
\begin{align*}
C'_0 + a'_1 C'_1 &= b'_1 \\
C'_1 + a'_2 C'_2 &= b'_2 \\
&\vdots \\
C'_{i-1} + a'_i C'_i &= b'_i \\
&\vdots \\
C'_{n-1} + a'_n C'_n &= b'_n
\end{align*}
\]  

(3.34)
This leads to a general recursive expression with equation (3.31.i) used to obtain $C'_{i-1}$

$$C'_{i-1} = b'_i - a'_i C'_i$$  \hspace{1cm} (3.35)

substitution of (3.35) into (3.31.i - 1) gives

$$C_{i-2} + (a'_{i-1} - \frac{1}{a'_i})C'_{i-1} = b_{i-1} - \frac{b_i}{a'_i}$$  \hspace{1cm} (3.36)

This is equation (3.34.i - 1), such that

$$a'_{i-1} = a_{i-1} - \frac{1}{a'_i}$$

$$b'_{i-1} = b_{i-1} - \frac{b_i}{a'_i}$$  \hspace{1cm} (3.37)

Using $i = n$, we may calculate the initial value of $a'_n$ and $b'_n$ as

$$a'_n = a$$

$$b'_n = b_n - C'_{n+1}$$  \hspace{1cm} (3.38)

Once the $a'_n$ and $b'_n$ coefficients have all been calculated in this manner we may use (3.34) with $i = n$ and $C'_{n+1} = c^b$ to give all $C'$ values down to $C'_0$. This is an improved method of Gaussian elimination over the method listed in the first edition of the text book by Britz as it removes the necessity of assuming a value for the $C'_0$ boundary condition and employs the known $c^b$ value instead. The above method is adopted in the second edition in by Britz in 1988 [133].

### 3.6.2 Linear diffusion - expanded grid

From the expanded grid form of the linear diffusion equation (3.21) we obtain the discretised expression,

$$\frac{C'_i - C_i}{\delta T} = \frac{Da^2(1 - Y)^4}{2\delta Y^2} \left[ C'_{i+1} - 2C_i + C_{i-1} + C'_{i+1} - 2C'_i + C'_{i-1} \right]$$

$$- \frac{Da^2(1 - Y)^4}{2\delta Y^2} \left[ \frac{\delta Y}{1 - Y}(C'_{i+1} - C_{i-1} + C'_{i+1} - C'_{i-1}) \right]$$  \hspace{1cm} (3.39)
which may be reduced to

\[ C'_{i-1} + a_1 C_i + a_2 C'_{i+1} = b_i \]  

(3.40)

with

\[ a_1 = -2 \frac{\lambda a^2 (1 - Y) t + 1}{1 - \frac{\delta y}{1 - Y}}, \quad a_2 = \frac{1 - Y + \delta y}{1 - Y - \delta y} \]

\[ b_i = -C_{i+1} - 2 \left( \frac{\lambda a^2 (1 - Y) t + 1}{1 - \frac{\delta y}{1 - Y}} \right) C_i - a_2 C_{i-1} \]  

(3.41)

similar to the linear non-expanded case. A set of simultaneous equations is obtained but with an additional coefficient, \( a_2 \), to account for the grid expansion.

\[ C'_0 + a_1 C'_1 + a_2 C'_2 = b_1 \]

\[ \vdots \]

\[ C'_{i-1} + a_1 C'_i + a_2 C'_{i+1} = b_i \]

\[ \vdots \]

\[ C'_{n-1} + a_1 C'_n + a_2 C'_{n+1} = b_n \]  

(3.42)

that is reduced to a series in two variables as before

\[ C'_0 + a'_1 C'_1 = b'_1 \]

\[ \vdots \]

\[ C'_{i-1} + a'_1 C'_i = b'_i \]

\[ \vdots \]

\[ C'_{n-1} + a'_1 C'_n = b'_n \]  

(3.43)

with

\[ a'_n = a_1 n \]

\[ b'_n = b_n - a_2 n - C'_{n+1} \]  

(3.44)

and

\[ a'_{i-1} = a_1 i - a_2 i-1 \frac{a}{a'_i} \]
\[ b'_{i-1} = b_{i-1} - \frac{b_i a_{2i-1}}{a'_{i}} \] (3.45)

### 3.6.3 Spherical diffusion

To model spherical diffusion to the interface we use the diffusion equation

\[ \frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial R^2} + \frac{2}{R} \frac{\partial C}{\partial R} \right) \] (3.46)

Defining \( \lambda_R \), the radial term, as

\[ \lambda_R = \frac{\delta T D}{\delta R^2} \] (3.47)

and discretising equation (3.46) to give

\[ C'_i - C_i = \frac{\lambda_R}{2} (C_{i-1} - 2C_i + C_{i+1} + C'_{i-1} - 2C'_i + C'_{i+1}) \]
\[ + \frac{\lambda R \delta R}{2R} (C_{i+1} - C_{i-1} + C'_{i+1} - C'_{i-1}) \] (3.48)

collecting terms

\[ \left( -\frac{\lambda_R}{2} + \frac{\lambda_R \delta R}{2R} \right) C_{i-1} + (1 + \lambda_R)C'_i - \left( \frac{\lambda_R}{2} + \frac{\lambda_R \delta R}{2R} \right) C'_{i+1} \]
\[ = \left( \frac{\lambda_R}{2} - \frac{\lambda_R \delta R}{2R} \right) C_{i-1} + (1 - \lambda_R)C_i + \left( \frac{\lambda_R}{2} + \frac{\lambda_R \delta R}{2R} \right) C'_{i+1} \] (3.49)

We require an equation of the form,

\[ C'_{i-1} + a_1 C'_i + a_2 C'_{i+1} = b_i \] (3.50)

therefore divide by

\[ \left( -\frac{\lambda_R}{2} + \frac{\lambda_R \delta R}{2R} \right) \] (3.51)

to give

\[ C'_{i-1} + \frac{(1 + \lambda_R)}{2 \left( 1 - \frac{\delta R}{R} \right)} C'_i + \frac{1 + \frac{\delta R}{R}}{1 - \frac{\delta R}{R}} C'_{i+1} \]
\[ = -C_{i-1} + \frac{(1 - \lambda_R)}{2 \left( 1 - \frac{\delta R}{R} \right)} C_i - \frac{1 + \frac{\delta R}{R}}{1 - \frac{\delta R}{R}} C_{i+1} \] (3.52)
Thus

\[ a_{1i} = -2 \left(1 + \frac{\lambda R}{\lambda_R(1 - \frac{\delta R}{R})}\right) \]
\[ a_{2i} = \frac{1 + \frac{\delta R}{R}}{1 - \frac{\delta R}{R}} \]
\[ b_i = -C_{i-1} - 2 \left(1 - \frac{\lambda R}{\lambda_R(1 - \frac{\delta R}{r})}\right)C_i - a_{2i}C_{i+1} \quad (3.53) \]

All of the coefficients have a dependence on \( i \) where \( i \delta r \) is the radial distance from the axis. The term in parentheses is a common denominator of each expression and may be rewritten as

\[ \left(1 - \frac{\delta R}{i \delta R}\right) = \left(1 - \frac{1}{i}\right) \quad (3.54) \]

The C-N coefficients \( a_i', b_i' \) are obtained, and the concentration values calculated, in the same manner as the linear expanded case, as there are two 'a' coefficients (see equations (3.43) - (3.45)).

### 3.6.4 Spherical diffusion - expanded grid

As with the linear expanded expression the simultaneous equations are in three variables, with two 'a' coefficients, giving a general expression,

\[ C_{i-1}' + a_{1i}C_i' + a_{2i}C_{i+1}' = b_i \quad (3.55) \]

Substitution of the inverted grid expansion expression (3.19) and its derivatives into the general expanded form for spherical diffusion, equation (3.22) gives, for coefficients \( a_{1i}, a_{2i}, b_i, \)

\[ a_{1i} = -2 \frac{\frac{1}{\lambda \delta^2 (1 - V)^3} + 1}{1 - \frac{\delta V}{V}} , \quad a_{2i} = \frac{1 + \frac{\delta V}{V}}{1 - \frac{\delta V}{V}} \]
\[ b_i = -C_{i+1} - 2 \frac{\left(\frac{1}{\lambda \delta^2 (1 - V)^3} - 1\right)}{1 - \frac{\delta V}{V}}C_i - a_{2i}C_{i-1} \quad (3.56) \]

The C-N coefficients \( a_i', b_i' \) are obtained, and the concentration values calculated, in the same manner as the linear expanded case (see equations (3.43) - (3.45)).
An alternative expanded grid transformation uses an exponential function

\[ Y = 1 - \exp(-aR) \]  

(3.57)

and the inverse

\[ R = g(Y) = \frac{1}{a} \ln(1 - Y) \]  

(3.58)

As in the previous expansion, substitution of equation (3.58) and its derivatives into the general expanded form for spherical diffusion, equation (3.22) gives,

\[
\frac{\partial C}{\partial T} = \frac{D a^2 (1 - Y)}{2} \left[ (1 - Y) \frac{\partial^2 C}{\partial Y^2} - \left( 1 - \frac{2}{\ln(1 - Y)} \right) \frac{\partial C}{\partial Y} \right]
\]  

(3.59)

which discretises to

\[
C'_i - C_i = \lambda a^2 (1 - Y)^2 \left[ C_{i-1} - 2C_i + C_{i+1} + C'_{i-1} - 2C'_i + C'_{i+1} \right]
\]

\[
-\delta Y \lambda a^2 (1 - Y) \left[ \left( \frac{1}{2} - \frac{1}{\ln(1 - Y)} \right) \left( C_{i+1} - C_{i-1} + C'_{i+1} - C'_{i-1} \right) \right]
\]  

(3.60)

leading again to a series of simultaneous eqn in three variables of the form,

\[
C'_{i-1} + a_1 C'_i + a_2 C'_{i+1} = b_i
\]  

(3.61)

From equation (3.60) we obtain the coefficients \(a_1, a_2, b_i\), \n
\[
a_1 = -2 \frac{\left( \frac{1}{\alpha^2 (\lambda - (1 - Y))} + 1 \right)}{\frac{1}{1 - Y} \left( \frac{1}{2} - \frac{1}{\ln(1 - Y)} \right) + 1}
\]

\[
a_2 = \frac{1 - Y - \frac{\delta Y}{2} + \frac{\delta Y}{\ln(1 - Y)}}{1 - Y + \frac{\delta Y}{2} - \frac{\delta Y}{\ln(1 - Y)}}
\]  

(3.62)

\[
b_i = -C_{i-1} - 2 \left( \frac{1}{\alpha^2 (\lambda (1 - Y))} \right) - 1 \left( \frac{1}{\alpha^2 (\lambda (1 - Y))} \right)' \frac{\delta y}{C \lambda (1 - Y)} \left( \frac{1}{2} - \frac{1}{\ln(1 - Y)} \right) + 1 - a_2 C_{i-1}
\]

With solution for \(a'_i, b'_i\) and concentration values as above.
3.7 The spherical-linear simplification for diffusion to a pipette

3.7.1 Flux approximation

Consider the flux to an ultramicrodisc interface (fig.3–3). The area of a hemispherical interface is twice the area of a disc interface of the same radius. We make the assumption that the diffusion to the interface is to a hemisphere of radius \( r \), when it is actually to the interface, the 'disc'. We may then calculate the flux of species passing through the hemisphere, \( \tilde{j}_h \), that is, half the flux passing through the disc, \( \tilde{j}_d / 2 \).

\[
\frac{\tilde{j}_d}{2} = \tilde{j}_h = -\delta A \frac{\partial C}{\partial X}
\]  

(3.63)
3.7.2 Concentration approximation

The ratio of species concentrations at the interface is controlled by the Nernst or Butler-Volmer equations, modified due to area. The problem lies in deciding where this ratio of species concentrations is determined, and how to calculate the concentrations at those points, given that we may only work in spherical or linear diffusion geometries. Sensibly, the concentration ratio should be determined at the interface, but the diffusion regime and the resulting concentration profile in the area bounded by the imaginary hemisphere and the disc shaped interface are not uniform or tractable using a one-dimensional simulation. Species at the edge of the regime have no distance to travel from the edge of the sphere to edge of the disc, whereas species in the centre are at a distance \( r \) away from the interface. A possible solution is to determine the concentrations at the edge of the hemisphere and multiply by the hemispherical/disc area ratio, 2.

\[
i = 2 \frac{C_{A,1} - C_{A,0}}{\delta R_0} = \frac{C_{B,1} - C_{B,0}}{\delta R_0}
\]

where the \( A \) concentrations are determined at the hemispherical boundary and the \( B \) concentrations at the disc. It is necessary to determine the \( B \) concentrations at the disc interface as they are required for concentration profile calculations within an ultramicropipette.

3.7.3 Diffusion within an ultramicropipette

Figure 3–4 illustrates diffusion at an ultramicropipette. The diffusion regime outside the pipette is equivalent to that at an ultramicrodisc interface of the same radius. The interface is assumed to lie at the tip of the ultramicropipette. Within the pipette, diffusion is constrained by the internal walls and as the axial dimension is generally much greater than the radial dimension the diffusion can be approximated to a linear profile.
Figure 3-4: Diffusion at an ultramicro pipette
Applying the assumptions in the two sections above it can be seen that the total flux through the imagined hemisphere is equivalent to the total linear flux passing into the ultramicropipette. As the diffusion regimes inside and outside the ultramicropipette are different (linear and spherical respectively), differing space grid expansions may be required, with corresponding initial increments $\delta R_{0,L}$ and $\delta R_{0,S}$.

As with linear and spherical diffusion regimes alone we may obtain an expression to calculate the current at the interface,

$$i = \frac{1}{2} \frac{(C_{A,1} - C_{A,0})}{\delta R_{0,S}} = - \frac{(C_{B,1} - C_{B,0})}{\delta R_{0,L}}$$  \hspace{1cm} (3.65)

Using

$$\frac{C_{A,0}}{C_{B,0}} = \exp(-p)$$  \hspace{1cm} (3.66)

we obtain an expression in $C_1$ values

$$i = \frac{C_{A,1} - C_{B,1} \exp(-p)}{\delta R_{0,S}/2 + \delta R_{0,L} \exp(-p)}$$  \hspace{1cm} (3.67)
Chapter 3. The numerical method: Crank-Nicolson

3.8 Results

Implementing the above C-N methods in gives the following results for diffusion to both planar and spherical electrodes. These particular electrode geometries are chosen as analytical solutions are readily available.

3.8.1 Linear diffusion

Following the derivations detailed in this Chapter, the Crank-Nicolson algorithm was implemented as a FORTRAN\(^1\) program to model linear diffusion to and from the interface. The charge transfer was initially regarded as Nernstian (reversible). Variable 'experimental' parameters were \( \nu \) and \( \tau \), those associated with potential sweep rate and duration of the experiment, which in turn determine the potential range. Variable numerical parameters, those that affect the the accuracy and cpu time of the algorithm were \( n_x \), the number of space grid increments, \( n_t \), the number of time increments and \( \delta x \), the space grid size. For the expanded gridcase, the effect of \( a \), the grid expansion coefficient, was also considered.

The resulting current potential curves are compared with theoretical results obtained by Nicholson and Shain [65], Reinmuth [66,185] and Beyerlin [186].

A comparative measure of accuracy on variation of the parameters is given in tables 3-1 and 3-2, for variable \( \lambda \) and \( \delta x \) respectively. It can be seen that variation of \( \lambda \) has a marked effect on the accuracy of simulation, but holding \( \lambda \) constant over a range of CV sweep rates and varying \( \delta x \) gives a uniformly accurate simulation. This occurs because the duration of the experiment, \( \tau \), and the sweep rate, are dependent. It follows that, as \( \lambda \) is constant the value of \( \delta x \) remains a constant

\(^1\)see Appendix A
fraction of the diffusion layer, for all sweep rates. Calculating the peak current error for a wide range of \( \delta x \) and \( \delta t \) values gives the error 'contour map' depicted in figure 3–5. The data from tables 3–1 and 3–2 are indicated. The desired accuracy of simulation may be obtained by choosing the appropriate combination of \( \delta x \) and \( \delta t \) values. The combinations of \( \delta x \) and \( \delta t \) values that give errors of less than 0.5\% are highlighted. As the errors associated with the C-N method are of the order of \( \delta x^2 \), common to a central differences method, as \( \delta x \) tends to zero then the associated errors should vanish. An enthusiasm to reduce the space grid \( ad \ infinitum \) must be tempered by the following three considerations:

1. As \( \delta x \) decreases then \( \lambda \) increases. Although the C-N method can tolerate much higher values than a fully explicit algorithm, \( \lambda \) values greater than about \( 10^4 \) cause instability.

2. The simulation must 'go far enough into the solution'. If the simulation limit (\( x_{lim} \) or \( r_{lim} \) in the FORTRAN programs), is less than the Nernst diffusion layer \( \delta \), then accuracy will be lost as the limiting concentration value in the simulation will not agree with the assumed boundary condition of \( C_{n+1} = c^b \).

3. To obtain a 'readable' \( i - E - t \) response, a minimum number of simulation points should be calculated (given as \( nt \), the number of time steps).

Point 1 is illustrated in figure 3–5, by the rapid increase in error beyond \( \lambda = 1300 \). For points 2 and 3 table 3–3 gives the expected Nernst diffusion layer and a reasonable value for \( x_{lim} \), the spatial limit of the simulation. Once the number of time steps and the required accuracy have been decided, the appropriate \( \delta x \) may be read off figure 3–5. Examples are given in table 3–3 for \( nt = 1000 \) and an accuracy of 1\%. The total simulation time is proportional to \( nt \times nx \) (\( nx = x_{lim}/\delta x \)), so it is worth considering carefully how accurate a simulation is required. The calculation of \( \delta x \) in table 3–3 is such that as \( \tau \) increases \( \delta x^2 \) increases proportionately, keeping \( \lambda \) and the overall accuracy constant.
Chapter 3. The numerical method: Crank-Nicolson

<table>
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<tr>
<th>$\nu$</th>
<th>$\lambda$</th>
<th>$I_p$ (peak current)</th>
<th>$I_p$ (theoretical)</th>
<th>Error %</th>
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<td>13000</td>
<td>25.15</td>
<td>19.02</td>
<td>32.2</td>
</tr>
<tr>
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<td>38.04</td>
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</tr>
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<td>60.15</td>
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<td>6015</td>
<td>-15.1</td>
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</table>

$\delta x = 5.6 \times 10^{-5} \text{cm}$

potential range $= E_o \pm 0.5V$

$n_x = 1000$ (upper half of table), 500 (lower half of table)

**Table 3–1:** The effect of $\lambda$ on accuracy (CV at a planar electrode)
Chapter 3. The numerical method: Crank-Nicolson

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>$\delta x , (\mu m)$</th>
<th>$I_p , (\text{peak current})$</th>
<th>$I_p , (\text{theoretical})$</th>
<th>Error %</th>
</tr>
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<tr>
<td>0.001</td>
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</table>

$\lambda = 69$

potential range = $E_0 \pm 0.2V$

$nx = 1000$

Table 3–2: The effect of $\delta x$ on accuracy (CV at a planar electrode)
Figure 3-5: Error contour map for variable $\delta x$ and $\delta t$
Chapter 3. The numerical method: Crank-Nicolson

\[
\delta = \sqrt{\pi D \tau}, \quad D = 10^{-5} \text{cm}^2 \text{s}^{-1}
\]

\[
t = 1000, \quad nx = 3000, \quad \lambda = 28
\]

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<tr>
<th>(\tau)</th>
<th>(\delta t)</th>
<th>(\delta (\text{cm}))</th>
<th>(10\delta (\text{xlim}))</th>
<th>(\delta x (\mu\text{m}))</th>
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<td>0.18</td>
<td>0.613</td>
</tr>
<tr>
<td>5</td>
<td>0.005</td>
<td>0.013</td>
<td>0.13</td>
<td>0.424</td>
</tr>
<tr>
<td>2</td>
<td>0.002</td>
<td>0.0079</td>
<td>0.079</td>
<td>0.282</td>
</tr>
<tr>
<td>1</td>
<td>0.001</td>
<td>0.0056</td>
<td>0.056</td>
<td>0.188</td>
</tr>
<tr>
<td>0.5</td>
<td>0.0005</td>
<td>0.0040</td>
<td>0.040</td>
<td>0.134</td>
</tr>
<tr>
<td>0.2</td>
<td>0.0002</td>
<td>0.0025</td>
<td>0.025</td>
<td>0.0866</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0001</td>
<td>0.0018</td>
<td>0.018</td>
<td>0.0613</td>
</tr>
<tr>
<td>0.05</td>
<td>0.00005</td>
<td>0.0013</td>
<td>0.013</td>
<td>0.0424</td>
</tr>
</tbody>
</table>

Table 3-3: Nernst diffusion layer and \(\text{xlim}\) for a range of experimental parameters
Cyclic voltammograms calculated for a range of sweep rates are shown in figure 3-6 and their agreement with the Randles - Sevčik equation (eqn.(1.39)), as a plot of $i$ vs. $\nu^{1/2}$ is shown in figure 3-7.

A large reduction in simulation time may be achieved by using an expanded space grid. The expansion used is given above as equation (3.18), The expansion coefficient used throughout, $a = 0.2$, was found to be suitable for all experimental parameters.

A comparative measure of accuracy on variation of the parameters is given in table 3-4, on varying $\delta x$, whilst keeping lambda constant. The value of the initial space grid increment $\delta x_0$ is given for comparison with the non-expanded grid values (table 3-2)

It is notable that such large values of $\lambda_0$ ($1.17 \times 10^4$) are tolerated with the expanded grid method. This is due to the variable grid size allowing very small initial steps and therefore large $\lambda_0$ values at the interface. On an expanded grid the largest $\lambda$ is at the electrode, written as $\lambda_0$. The reduced initial value of $\delta x$ without reduction of the 'reach' of the simulation brings greater accuracy than the uniform grid method.

3.8.2 Spherical diffusion

The measurement of accuracy in the simulation of spherical CVs is more difficult as there does not exist a well defined peak in the current response. For the slower sweep rates, the CV exhibits steady state behaviour (see figure 3-8), with the plateau current eventually reaching a value given by

$$i = i_{planar} + \frac{nFAD_0c_0^b\phi(\sigma t)}{r_0}$$  \hspace{1cm} (3.68)

For more rapid sweep rates the enhanced diffusion profile to the ultramicrosphere is overcome and the CV begins to show a diffusion-limited peak (see figure 3-9). For extremely fast sweep rates, the diffusion layer $\delta$ becomes small compared to
Figure 3-6: Linear diffusion CVs - sweep rate dependence

\[ D = 10^{-5} \text{cm}^2\text{s}^{-1}. \]
Chapter 3. The numerical method: Crank-Nicolson

LINEAR - LINEAR DIFFUSION

Forward Peak Height

Figure 3-7: Peak height - root sweep rate dependence
### Table 3-4: The effect of $\delta x_0$ on accuracy (CV at a planar electrode)

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>$\delta x_0$ ((\mu)m)</th>
<th>Ip (peak current)</th>
<th>Ip (theoretical)</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.292</td>
<td>26.855</td>
<td>26.900</td>
<td>-0.17</td>
</tr>
<tr>
<td>0.002</td>
<td>0.207</td>
<td>37.979</td>
<td>38.042</td>
<td>-0.17</td>
</tr>
<tr>
<td>0.005</td>
<td>0.131</td>
<td>60.050</td>
<td>60.150</td>
<td>-0.17</td>
</tr>
<tr>
<td>0.01</td>
<td>0.0924</td>
<td>84.924</td>
<td>85.065</td>
<td>-0.17</td>
</tr>
<tr>
<td>0.02</td>
<td>0.0653</td>
<td>120.101</td>
<td>120.300</td>
<td>-0.17</td>
</tr>
<tr>
<td>0.05</td>
<td>0.0413</td>
<td>189.896</td>
<td>190.212</td>
<td>-0.17</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0292</td>
<td>268.55</td>
<td>269.000</td>
<td>-0.17</td>
</tr>
<tr>
<td>0.2</td>
<td>0.0207</td>
<td>379.79</td>
<td>380.423</td>
<td>-0.17</td>
</tr>
<tr>
<td>0.5</td>
<td>0.0131</td>
<td>600.50</td>
<td>601.502</td>
<td>-0.17</td>
</tr>
<tr>
<td>1.</td>
<td>0.00924</td>
<td>849.24</td>
<td>850.653</td>
<td>-0.17</td>
</tr>
<tr>
<td>2.</td>
<td>0.00653</td>
<td>1201.01</td>
<td>1203.00</td>
<td>-0.17</td>
</tr>
<tr>
<td>5.</td>
<td>0.00413</td>
<td>1898.96</td>
<td>1902.12</td>
<td>-0.17</td>
</tr>
<tr>
<td>10.</td>
<td>0.00292</td>
<td>2685.5</td>
<td>2690.00</td>
<td>-0.17</td>
</tr>
<tr>
<td>20.</td>
<td>0.00207</td>
<td>3797.9</td>
<td>3804.23</td>
<td>-0.17</td>
</tr>
<tr>
<td>50.</td>
<td>0.00131</td>
<td>6005.0</td>
<td>6015.02</td>
<td>-0.17</td>
</tr>
</tbody>
</table>

\[ \lambda_0 = 11,700 \]

potential range = $E_0 \pm 0.2V$

\[ nx = 1000, nt = 400 \]
Figure 3–8: Spherical diffusion - steady state CV \( D = 10^{-5} \text{cm}^2 \text{s}^{-1}, \ r = 5 \mu \text{m} \)
Chapter 3. The numerical method: Crank-Nicolson

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>$\delta x\ (\mu m)$</th>
<th>$\delta\ (\mu m)$</th>
<th>$\delta/r$</th>
<th>$I_p$ (peak current)</th>
<th>$I_p$ (theoretical)</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>1.34</td>
<td>396</td>
<td>79.3</td>
<td>1243</td>
<td>1550</td>
<td>-19.8</td>
</tr>
<tr>
<td>0.2</td>
<td>0.42</td>
<td>125</td>
<td>25.0</td>
<td>1691</td>
<td>1830</td>
<td>-7.6</td>
</tr>
<tr>
<td>2.0</td>
<td>0.134</td>
<td>39.6</td>
<td>7.93</td>
<td>2581</td>
<td>2653</td>
<td>-2.7</td>
</tr>
<tr>
<td>20.0</td>
<td>0.042</td>
<td>12.5</td>
<td>2.50</td>
<td>5183</td>
<td>5254</td>
<td>-1.6</td>
</tr>
<tr>
<td>0.02</td>
<td>1.34</td>
<td>396</td>
<td>7.93</td>
<td>258.1</td>
<td>265.3</td>
<td>-2.7</td>
</tr>
<tr>
<td>0.2</td>
<td>0.42</td>
<td>125</td>
<td>2.50</td>
<td>518.4</td>
<td>525.4</td>
<td>-1.6</td>
</tr>
<tr>
<td>2.0</td>
<td>0.134</td>
<td>39.6</td>
<td>0.793</td>
<td>1334.2</td>
<td>1348</td>
<td>-1.0</td>
</tr>
<tr>
<td>20.0</td>
<td>0.042</td>
<td>12.5</td>
<td>0.250</td>
<td>3911.8</td>
<td>3912</td>
<td>-0.005</td>
</tr>
</tbody>
</table>

$\lambda = 28$

potential range = $E_0 \pm 0.5V$

nr = 1000, radius = 5$\mu$m (upper half of table), 50 $\mu$m (lower half of table)

Table 3–5: The effect of $\delta r_0$ on accuracy (CV at spherical electrode)

the radius of the ultramicrosphere. The diffusion profile will then tend to the linear case.

An assessment of the errors for both uniform and expanded grids is given in tables 3–5 and 3–6. In the linear diffusion simulations above, $\lambda$ is the key variable that determines accuracy (i.e any combination of $\delta x$ and $\delta t$ that give the same $\lambda$ value will have equal accuracy). For the simulation of spherical diffusion the size of the diffusion layer compared to the radius of the ultramicrosphere, $r$, must also be taken into account. Parameters giving equivalent $\lambda$ values may not have the same accuracy. This can be seen in table 3–5. However, two electrode sizes with an equivalent ratio of diffusion layer thickness to interface radius and having equivalent lambda values will be equally accurate. For example a 5$\mu$m sphere with $\nu = 20\ V/s$ compared to a 50$\mu$m sphere with $\nu = 0.2\ V/s$. This occurs because the two systems 'look the same' in dimensionless parameters.

Accuracy is not solely dependent on the ratio of diffusion layer to the radius. The table contour map 3–10 shows the optimum combinations of this ratio and
Figure 3-9: Spherical diffusion CVs - sweep rate dependence $D = 10^{-5} \text{ cm}^2 \text{s}^{-1}$, $r = 5 \mu$.
the value of \( \lambda \) to reduce error. \( \lambda \) values for both expanded and uniform grids are indicated, the former giving a more efficient algorithm in both accuracy and computer time taken. The diffusion layer is defined as \( \delta = \sqrt{\pi D\tau} \).

The influence of the grid expansion parameter on accuracy in addition to the effects of \( \delta/r \) and \( \lambda_0 \) is shown in table 3-6 together with the variation in accuracy with potential. In contrast to the linear expanded case a grid expansion coefficient of \( a = 2.0 \) was chosen as the optimum value. The increased 'steepness' of this function and the greater density of points near the interface may be seen from equation 3.18 plotted in figure 3-11. The enhanced mass transfer due to a spherical (compared to linear) diffusion profile leads to a much steeper concentration gradient at the interface for a given set of experimental parameters. \( \lambda \) is given as \( \lambda_0 \), the value at the interface, as its value is variable, decreasing with increasing \( \delta/r \) increments moving away from the interface.

As listed in the three key considerations covered earlier on page 108, \( \lambda \) cannot be increased \textit{ad infinitum} by reducing \( nt \) and therefore increasing \( \delta t \), as a finite number of points are required to plot a complete \( i - E - t \) response. Also, for expanded grids, increasing the expansion coefficient \( a \) will give a large value for \( \lambda_0 \), but not the expected increase in accuracy as the density of simulation points at the electrode, relative to further into the solution, will be too great for the limiting values of the \( i - E - t \) response (such as the steady state and initial values for cyclic voltammetry where the concentration profile is relatively flat).
### Table 3-6: The effect of potential, $\delta r_o$ and expanded grid parameter $a$ on accuracy

<table>
<thead>
<tr>
<th>$E - E_0$</th>
<th>Ip (peak current)</th>
<th>Ip (theoretical)</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a = 0.2$</td>
<td>$a = 2.0$</td>
<td></td>
</tr>
<tr>
<td>-0.1</td>
<td>39.1</td>
<td>42.0</td>
<td>-6.9</td>
</tr>
<tr>
<td></td>
<td>43.0</td>
<td>42.0</td>
<td>2.4</td>
</tr>
<tr>
<td>0</td>
<td>949</td>
<td>1064</td>
<td>-10.8</td>
</tr>
<tr>
<td></td>
<td>1043</td>
<td>1064</td>
<td>-2.0</td>
</tr>
<tr>
<td>0.029</td>
<td>1404</td>
<td>1569</td>
<td>-10.5</td>
</tr>
<tr>
<td></td>
<td>1543</td>
<td>1569</td>
<td>-1.7</td>
</tr>
<tr>
<td>0.04</td>
<td>1523</td>
<td>1711</td>
<td>-11.0</td>
</tr>
<tr>
<td></td>
<td>1673</td>
<td>1711</td>
<td>-2.2</td>
</tr>
<tr>
<td>0.1</td>
<td>1758</td>
<td>1975</td>
<td>-11.0</td>
</tr>
<tr>
<td></td>
<td>1931</td>
<td>1975</td>
<td>-2.2</td>
</tr>
<tr>
<td>-0.1</td>
<td>90.3</td>
<td>89.5</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>91.4</td>
<td>89.5</td>
<td>2.1</td>
</tr>
<tr>
<td>0</td>
<td>1955</td>
<td>1976</td>
<td>-1.1</td>
</tr>
<tr>
<td></td>
<td>1977</td>
<td>1976</td>
<td>0.05</td>
</tr>
<tr>
<td>0.029</td>
<td>2619</td>
<td>2644</td>
<td>-1.0</td>
</tr>
<tr>
<td></td>
<td>2646</td>
<td>2644</td>
<td>0.08</td>
</tr>
<tr>
<td>0.04</td>
<td>2732</td>
<td>2768</td>
<td>-1.3</td>
</tr>
<tr>
<td></td>
<td>2759</td>
<td>2768</td>
<td>-0.3</td>
</tr>
<tr>
<td>0.1</td>
<td>2695</td>
<td>2732</td>
<td>-1.3</td>
</tr>
<tr>
<td></td>
<td>2720</td>
<td>2732</td>
<td>-0.4</td>
</tr>
</tbody>
</table>

$\lambda_0 = 139 \ (a=0.2), \ 4130 \ (a=2.0)$

$\delta r = 0.6 \ \mu m \ (a=0.2), \ 0.11 \ \mu m \ (a=2.0) \ \text{(upper half of table)}$

$\delta r = 0.06 \ \mu m \ (a=0.2), \ 0.011 \ \mu m \ (a=2.0) \ \text{(lower half of table)}$

potential range = $E_0 \pm 0.5V$

$nr = 1000, \ nt = 1000$
Figure 3-11: Space grid expansion, with $a = (1) \ 0.2, (2) \ 2.0$
Chapter 3. The numerical method: Crank-Nicolson

The coefficient chosen \((a = 2.0)\) gives a fairly uniform accuracy over a typical CV potential range (see figure 3–6). Reducing the initial step value, \(\delta r_0\), (and the neighbouring values) by increasing \(a\), or otherwise, will increase errors at the limiting potential values. This is to be avoided, especially when simulating CV with slow sweep rates or small interfaces, as the steady-state current is a key value to be simulated accurately. Optimum \(\lambda_0\) values for a given \(\delta/r\) ratio may be obtained from figure 3–10.

3.8.3 Limits of the spherical-linear simplification

This section suggests an approximation to cylindrical diffusion at an ultramicrodisc interface by means of a spherical approximation as discussed earlier in section 3.7. The approximation may also include diffusion into an ultramicropipette. Diffusion within of the pipette is here approximated to a linear profile (fig. 3–4).

It must be stressed that the results in this section have more qualitative than quantitative significance. The table below gives a measure of accuracy of the approximation for a range of simulation parameters. Table 3–7 shows that the spherical approximation model for a disc interface tends to that of a hemisphere. At higher values of potential, towards the end of the experiment, the diffusion zone around the disc is well established and almost hemispherical, thus all three right hand columns show good agreement with the spherical solution.

However, at low values of potential, or at the beginning of the simulation, all of the diffusion occurs near the disc interface and the approximation is not applicable. Correcting for the area difference between the imaginary hemisphere and the disc does increase accuracy, but does not lead to a general solution for a range of experimental parameters. The use of the same grid expansion coefficients as for linear and spherical diffusion gives the most accurate simulation, showing the self-consistency of the algorithm. Also, for the reverse potential sweep, where the diffusion is first linear, then spherical, (egress ion transfer from an ultrami-
### Table 3-7: The effect of potential, \( \delta r_0 \) and expanded grid parameter \( a \) on accuracy

<table>
<thead>
<tr>
<th>( E - E_0 )</th>
<th>Ip (peak current)</th>
<th>Ip (theoretical)</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( a = 0.2 )</td>
<td>( a = 2.0 )</td>
<td></td>
</tr>
<tr>
<td>-0.1</td>
<td>39.1</td>
<td>42.0</td>
<td>-6.9</td>
</tr>
<tr>
<td></td>
<td>43.0</td>
<td>42.0</td>
<td>2.4</td>
</tr>
<tr>
<td>0</td>
<td>949</td>
<td>1064</td>
<td>-10.8</td>
</tr>
<tr>
<td></td>
<td>1043</td>
<td>1064</td>
<td>-2.0</td>
</tr>
<tr>
<td>0.029</td>
<td>1404</td>
<td>1569</td>
<td>-10.5</td>
</tr>
<tr>
<td></td>
<td>1543</td>
<td>1569</td>
<td>-1.7</td>
</tr>
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<td>-11.0</td>
</tr>
<tr>
<td></td>
<td>1673</td>
<td>1711</td>
<td>-2.2</td>
</tr>
<tr>
<td>0.1</td>
<td>1758</td>
<td>1975</td>
<td>-11.0</td>
</tr>
<tr>
<td></td>
<td>1931</td>
<td>1975</td>
<td>-2.2</td>
</tr>
<tr>
<td>-0.1</td>
<td>90.3</td>
<td>89.5</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>91.4</td>
<td>89.5</td>
<td>2.1</td>
</tr>
<tr>
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<td>1955</td>
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</tr>
<tr>
<td></td>
<td>1977</td>
<td>1976</td>
<td>0.05</td>
</tr>
<tr>
<td>0.029</td>
<td>2619</td>
<td>2644</td>
<td>-1.0</td>
</tr>
<tr>
<td></td>
<td>2646</td>
<td>2644</td>
<td>0.08</td>
</tr>
<tr>
<td>0.04</td>
<td>2732</td>
<td>2768</td>
<td>-1.3</td>
</tr>
<tr>
<td></td>
<td>2759</td>
<td>2768</td>
<td>-0.3</td>
</tr>
<tr>
<td>0.1</td>
<td>2695</td>
<td>2732</td>
<td>-1.3</td>
</tr>
<tr>
<td></td>
<td>2720</td>
<td>2732</td>
<td>-0.4</td>
</tr>
</tbody>
</table>

\[ \lambda_0 = 139 \ (a=0.2), \ 4130 \ (a=2.0) \]

\[ \delta r = 0.6 \ \mu m \ (a=0.2), \ 0.11 \ \mu m \ (a=2.0) \ \text{(upper half of table)} \]

\[ \delta r = 0.06 \ \mu m \ (a=0.2), \ 0.011 \ \mu m \ (a=2.0) \ \text{(lower half of table)} \]

Potential range = \( E_0 \pm 0.5V \)

\( nr = 1000, \ nt = 1000 \ \text{‘Area corrected’ corrects for area of hemisphere being 2 x area of disc} \)

Table 3-7: The effect of potential, \( \delta r_0 \) and expanded grid parameter \( a \) on accuracy
cropipette) the current is peaked and tends to the linear diffusion model as the sweep rate or the interfacial dimensions increase (see figure 3-17).

The spherical-linear approximation to an ultramicrodisc or ultramicropipette has also been used by Stewart, Taylor, Girault and MacAlister to obtain a pseudo-analytical solution for linear sweep voltammetry [187]. Results from this work, compare qualitatively to figures 3-12, 3-13, 3-14, 3-15, 3-16, and 3-17 obtained using the approximate algorithm detailed in this section.

A graph of reverse peak height against maximum overpotential shows an approximately linear correlation (figure 3-17). This draws a comparison with stripping voltammetry where reverse peak height is proportional to the time the system is held at a certain overpotential.

### 3.9 Summary

The Crank-Nicolson method, combined with an expanded space grid provides an accurate, fast algorithm to model both linear and spherical diffusion in one-dimension for a wide range of experimental parameters. The accuracy of the algorithm may be determined in advance of the simulation by careful choice of simulation parameters.

None of the above approaches to model diffusion to an ultramicrodisc interface using a spherical-linear approximation are satisfactory. For any disc that has appreciable (i.e. finite) dimensions, an exact equivalence between diffusion to a disc and diffusion to a hemisphere cannot be made. Firstly, because of the broad assumptions made in Section 3.7. Secondly, current density is uniform across a sphere but varies constantly over the surface of an ultramicrodisc interface.

---

1Modelling of this variable current density is detailed further in Chapters 4 and 5
Figure 3-12: Egress transfer - linear-spherical diffusion approximation, $D = 10^{-5} \text{cm}^2 \text{s}^{-1}$, $r = 5 \mu\text{m}$.
Figure 3-13: Peak height - root sweep rate dependence, \( r = 5 \mu m \).
Figure 3-14: Steady state wave - $1/r$ dependence
Chapter 3. The numerical method: Crank-Nicolson

Reversible Sweep Rate Dependence

![Graph showing current density vs. overpotential](image)

**Figure 3-15:** Reverse peak height vs. $1/\nu^{1/3}$
Chapter 3. The numerical method: Crank-Nicolson

SPHERICAL - LINEAR DIFFUSION \( r = 5 \mu m \)

Reverse Peak Height \( D = 10^{-5} \text{cm}^2 \text{s}^{-1} \).

\[ V^* \quad \left( \text{V/s} \right)^6 \]

Figure 3-16: Reverse peak height vs. \( \nu^{\frac{1}{2}} \)
Figure 3-17: Reverse peak height vs. maximum overpotential
Chapter 3. The numerical method: Crank-Nicolson

The approximation is useful in that it allows a qualitative $i - E - t$ picture to be built of ultramicrodisc or ultramicropipette response by using a simple one-dimensional algorithm. This may then be used as a first approximation and compared with experimental results or a pseudo-analytical solution [187].

For an accurate simulation a two-dimensional algorithm is required. This is presented in the following chapters. Solutions are obtained for the complete $i - E - t$ response for an ultramicrodisc in Chapters 4 and 5 and for an ultramicropipette in Chapter 6.
Chapter 4

The 2-D numerical method: ADI

4.1 Introduction

Following the conclusions of Section 3.9 a more accurate model accounting for diffusion to a disc is required. The hemisphere/disc approximation outlined in Section 3.7 is inadequate, the major inaccuracy being that the current density remains constant over a sphere but is variable over a disc. This chapter presents an algorithm that allows modelling of variable current density over an ultramicrodisc interface.

The partial differential equation for cylindrical diffusion to a disc is

\[
\frac{\partial C}{\partial t} = D \left[ \frac{\partial^2 C}{\partial R^2} + \frac{1}{R} \frac{\partial C}{\partial R} + \frac{\partial^2 C}{\partial Z^2} + \frac{\partial^2 C}{\partial \theta^2} \right] \quad (4.1)
\]

The assumption is made that diffusion is symmetrical about the vertical axis of the disc in a \( \theta \) direction,

\[
\frac{\partial^2 C}{\partial \theta^2} = 0 \quad (4.2)
\]

The cylindrical diffusion equation may not be reduced to one dimension in the same manner as the spherical and linear cases. Its solution, in two dimensions,
Chapter 4. The 2-D numerical method: ADI

is slightly more complicated. The method used is an adaption of the method proposed by Peaceman and Rachford for the solution of a square point grid in two-dimensional cartesian coordinates. The diffusion equation

$$\frac{\partial C}{\partial T} = D \left[ \frac{\partial^2 C}{\partial R^2} + \frac{1}{R} \frac{\partial C}{\partial R} + \frac{\partial^2 C}{\partial Z^2} \right]$$

(4.3)

with

$$R = i\delta R, \quad Z = j\delta Z$$

(4.4)

discretises explicitly to

$$\frac{C'_{ij} - C_{ij}}{\delta T} = \lambda_R (C_{i-1,j} - 2C_{i,j} + C_{i+1,j}) + \frac{\lambda_R \delta R}{2R} (C_{i+1,j} - C_{i-1,j}) + \lambda_Z (C_{i,j-1} - 2C_{i,j} + C_{i,j+1})$$

(4.5)

with

$$\lambda_R = \frac{D\delta T}{\delta R^2}, \quad \lambda_Z = \frac{D\delta T}{\delta Z^2}$$

(4.6)

In the explicit case $\lambda_{R,Z}$ are constrained to be less than 0.25. This restriction prohibits accurate, rapid simulations, even with the use of an expanded grid. A method is required that allows semi-implicit calculation of concentration values, similar to the C-N method, but in two dimensions.

4.2 Dimensionless parameters

Transformation of variables into dimensionless parameters gives equations whose solutions are much more general than the specific solution of a dimensioned equation. Time becomes dimensionless by introducing $\tau$,

$$\tau = \frac{4Dt}{r_0^2}$$

(4.7)

Where $D$ is the diffusion coefficient, assumed equivalent for both species, $t$, the duration of the experiment and $r_0$, the interfacial radius. The spatial variables $z$
and $r$ become $Z$ and $R$, dividing by $\delta$ (the Nernst diffusion layer) and interfacial radius respectively.

$$\delta = \sqrt{\pi Dt} \quad (4.8)$$

Concentrations $c_A, c_B$ are rendered dimensionless $C_A, C_B$ by dividing by $c^b_A$ and $c^b_B$ the bulk concentrations of species A and B. The current is given as $\chi$, an expression of the total current density over the limiting current density for the steady-state, defined as [103],

$$I_d = \frac{4nFDc}{\pi r} \quad \frac{I}{I_d} = \chi \quad \chi_{ss} = 1 \quad (4.9)$$

### 4.3 The ADI Method

The method of Peaceman and Rachford used to solve diffusion equations in two dimensions is an Alternating Direction Implicit (ADI) method [155]. The concentration values are calculated as a set of points on a regular or expanded grid (figure 4-1).

#### Refined ADI method

Previous works by other authors have dealt with an ADI method that is alternately half-implicit in one direction and explicit in the other (page 75). A simpler and more accurate algorithm is to calculate the concentration values implicitly in one direction and explicitly in the other. The expression can be seen to be more mathematically symmetric than the previous ADI method. This is also apparent in the improved simulation results and error analysis (see Section 4.5.1).

Rows and columns of new concentration values are calculated alternately. First compute each ascending row, for $j = 0$ to $n_Z$, where $n_Z$ is the number of concentration points in the $Z$ direction, typically 100. The discretised partial differential
Figure 4-1: Space grid for two dimensional diffusion
equation, giving change in concentration with incremental time is expressed as implicit with respect to $R$ and explicit with respect to $Z$. For the next time increment, successive columns of new concentration values are calculated, for $i = 0$ to $n_R$, where $n_R$ is the number of concentration points in the $r$ direction, typically 200. The discretised partial differential equation is then expressed as explicit with respect to $r$ and implicit with respect to $Z$. This method, where the algorithm, calculates first implicitly along a line of concentration values and explicitly perpendicular and then on the succeeding time increment, calculates the concentrations conversely with respect to $R$ and $Z$, ensures stability for all values of $\lambda$ defined by equation (4.4) [177].

Order of computation

As we compute each ascending row, the calculation is carried out for all values of the radial increment $i$, for each value of the axial increment $j$. To avoid using new values from row $j$ when calculating values for the $j^{th}$ row a 'zipper' technique is used. Thus, for each $C_{i,j}$, compute $C'_{i,j}$, the concentration value after a time interval $t + \delta t$. Do not insert this new value as it would then be used in the consecutive row, but place in a holding file. Then once we have computed $C_{i,j+1}$ we may update $C_{i,j}$ to $C'_{i,j}$.

The refined ADI method is developed below for cylindrical coordinates with both uniform and expanded space grids.

4.3.1 C-N coefficients for cylindrical coordinates

For a cylindrical diffusion pattern we use the partial differential equation (4.3).

For the solution of concentrations radially.

Following the ADI method the diffusion equation discretises (rows implicitly and
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Columns explicitly) to

\[
\frac{C'_{i,j} - C_{i,j}}{\delta T} = \lambda_R (C'_{i-1,j} - 2C_{i,j} + C'_{i+1,j}) + \frac{\lambda_R \delta R}{2R} (C'_{i+1,j} - C'_{i-1,j})
\]

\[+ \lambda_Z (C_{i,j-1} - 2C_{i,j} + C_{i,j+1})\]  

(4.10)

Collecting terms gives

\[
\left( -\lambda_R + \frac{\lambda_R \delta R}{2R} \right) C'_{i-1,j} + (2\lambda_R + 1)C'_{i,j} + \left( -\lambda_R - \frac{\lambda_R \delta R}{2R} \right) C'_{i+1,j}
\]

\[= \lambda_Z C_{i,j-1} + (-2\lambda_Z + 1)C_{i,j} + \lambda_Z C_{i,j+1}\]  

(4.11)

This reduces to a general form

\[C'_{i-1,j} + a_2 C'_{i,j} + a_3 C'_{i+1,j} = b_4\]  

(4.12)

with C-N coefficients

\[a_2 = \frac{-1 + 2}{1 - \frac{\delta R}{2R}}, \quad a_3 = \frac{1 + \frac{\delta R}{2R}}{1 - \frac{\delta R}{2R}}\]  

(4.13)

and

\[b_4 = \frac{\lambda_Z}{\lambda_R \left( 1 - \frac{\delta R}{2R} \right)} (C_{i,j-1} + C_{i,j+1}) + \frac{1 - 2\lambda_Z}{\lambda_R \left( 1 - \frac{\delta R}{2R} \right)} C_{i,j}\]  

(4.14)

For the solution of concentrations axially

We obtain the discretised form of the partial differential equation (rows explicitly and columns implicitly),

\[
\frac{C'_{i,j} - C_{i,j}}{\delta T} = \lambda_R (C_{i-1,j} - 2C_{i,j} + C_{i+1,j}) + \frac{\lambda_R \delta R}{2R} (C_{i+1,j} - C_{i-1,j})
\]

\[+ \lambda_Z (C'_{i,j-1} - 2C'_{i,j} + C'_{i,j+1})\]  

(4.15)

Collecting terms,

\[\lambda_Z C'_{i,j-1} - (2\lambda_Z + 1)C'_{i,j} + \lambda_Z C'_{i,j+1} =
\]

\[
\left( -\lambda_R + \frac{\lambda_R \delta R}{2R} \right) C_{i-1,j} + (2\lambda_R - 1)C_{i,j} + \left( -\lambda_R - \frac{\lambda_R \delta R}{2R} \right) C_{i+1,j}\]  

(4.16)
to obtain the general form

\[ C'_{i,j-1} + a_{1,j} C'_{i,j} + C'_{i,j+1} = b_{3,j} \]  \hspace{1cm} (4.17)

with the C-N coefficients

\[ a_{1,j} = \frac{1 + 2\lambda_z}{\lambda_z} \]  \hspace{1cm} (4.18)

and

\[ b_{3,j} = -\frac{\lambda_R}{\lambda_z} \left( 1 - \frac{\delta R}{2R} \right) C_{i-1,j} + \frac{2\lambda_R - 1}{\lambda_z} C_{i,j} - \frac{\lambda_R}{\lambda_z} \left( 1 + \frac{\delta R}{2R} \right) C_{i+1,j} \]  \hspace{1cm} (4.19)

The solution of the simultaneous equations and their C-N coefficients is obtained by a Gaussian decomposition similar to that used in one dimension, following the order of computation given above. The following section discusses the derivation of appropriate boundary conditions used to solve the simultaneous equations.

### 4.3.2 Boundary conditions

The boundary conditions occur as one of two types, those relative to the geometry of the system which are constant throughout the simulation and independent of electrochemical technique

\[ c_{i, nr} = c_{nr, j} = c^b \]  \hspace{1cm} (4.20)

\[ \left( \frac{\partial C}{\partial R} \right)_{i=0,j} = 0 \]  \hspace{1cm} (4.21)

\[ \left( \frac{\partial C}{\partial Z} \right)_{i \geq n_{er}, j=0} = 0 \]  \hspace{1cm} (4.22)

(The area surrounding the interface is assumed to be infinite, coplanar and insulating)

\[ C'_{A, i, j} = 1 \ \forall \ i, j \ t = 0 \]  \hspace{1cm} (4.23)

\[ C'_{B, i, j} = 0 \ \forall \ i, j \ t = 0 \]  \hspace{1cm} (4.24)
and those that are variable and dependent on the electrochemical technique simulated. For example, for chronoamperometry,

\[ C'_{i,0} = 0 \quad i \leq n_{er} \quad (4.25) \]

or for Cyclic Voltammetry with Butler-Volmer kinetics

\[ \left( \frac{\partial C'}{\partial Z} \right)_{i,0} = k_f C_{A,i,0} - k_b C_{B,i,0} \quad i \leq n_{er} \quad (4.26) \]

For the forward and backward rate constants,

\[ k_f = k_s \exp \left[ -\frac{\alpha nF}{RT} (E - E'_0) \right] \quad (4.27) \]
\[ k_b = k_s \exp \left[ \frac{(1 - \alpha)nF}{RT} (E - E'_0) \right] \quad (4.28) \]

Where \( k_s \) is the heterogeneous rate constant, \( \alpha \) the charge transfer coefficient, \( n \) the charge transfer number and \( n_{er} \) the number of points on the electrode, typically between 40 and 70.

The discrete forms of equations (4.21) and (4.22) merit particular attention. Applying the boundary conditions

\[ \frac{C'_{i,1} - C'_{i,0}}{\delta Z} = 0 \quad (4.29) \]

beyond \( r = r_0 \), the edge of the interface and

\[ \frac{C'_{1,j} - C'_{0,j}}{\delta R} = 0 \quad (4.30) \]

leads to the equalities \( C'_{i,1} = C'_{i,0} \) and \( C'_{1,j} = C'_{0,j} \) respectively. The effects of these assumptions on the C-N coefficients derived below, and the relative accuracies of the different assumptions are outlined in Section 4.5.1.

The correct consideration of boundary conditions is of paramount importance in numerical simulation. An inadequate treatment will result in large and possibly compounding or exponentiating errors (Section 4.5.3). However, an overzealous
approach incurs large increases in computing time as the boundary value concentrations are not governed by the same diffusion equations and may need to be calculated independently of the bulk solution.

For the ADI method, boundary conditions may be determined by their own partial differential diffusion equations. The derivation of the discrete diffusion equations is identical to the approach used for the bulk solution, the discretised forms being modified to implicit and explicit respectively for the two variables \( i(r) \) and \( j(z) \), as in the previous section.

The calculation of C-N coefficients is as follows;

*At time \( t=0 \) (and successive even time steps) - calculate ascending rows*

For \( Z=0 \) only, implicit with respect to \( \delta R \), explicit with respect to \( \delta Z \). This is the calculation of the first row \( (j = 0, r > \text{radius}) \).

\[
C'_{i,0} - C_{i,0} = \lambda_R (C'_{i-1,0} - 2C'_{i,0} + C'_{i+1,0}) + \frac{\lambda_R \delta R}{2R} (C'_{i+1,0} - C'_{i-1,0})
+ \lambda_Z (C_{i,1} - C_{i,0})
\]

(4.31)

Thus

\[
\left(-\lambda_R + \frac{\lambda_R \delta R}{2R}\right) C'_{i-1,0} + (2\lambda_R + 1)C'_{i,0} + \left(-\lambda_R - \frac{\lambda_R \delta R}{2R}\right) C'_{i+1,0} = \lambda_Z C_{i,1} + (-\lambda_Z + 1) C_{i,0}
\]

(4.32)

Which reduces to the general form, a simultaneous equation in two variables.

\[
C'_{i-1,0} + a_{2i} C'_{i,0} + a_{3i} C'_{i+1,0} = b_{2i}
\]

(4.33)

with

\[
a_{2i} = -\frac{1}{\lambda_R} + \frac{2}{1 - \frac{\delta R}{2R}}, \quad a_{3i} = \frac{1 + \frac{\delta R}{2R}}{1 - \frac{\delta R}{2R}}
\]

(4.34)

and

\[
b_{2i} = -\frac{\lambda_Z}{\lambda_R \left(1 - \frac{\delta R}{2R}\right)} C_{i,1} + \frac{\lambda_Z - 1}{\lambda_R \left(1 - \frac{\delta R}{2R}\right)} C_{i,0}
\]

(4.35)
for the Crank-Nicholson coefficients as before.

At time $t + \delta t$ (and successive odd time steps) - calculate columns radially from centre

For $R=0$ only, explicit with respect to $\delta R$, implicit with respect to $\delta Z$. This is the calculation of column '0'. Using a Maclaurin expansion [188] which allows the partial differential equation to be re-expressed as

$$C_{0,j}' - C_{0,j} = 4\lambda_R (C_{1,j} - C_{0,j}) + \lambda_Z (C_{0,j-1}' - 2C_{0,j}' + C_{0,j+1}')$$  \hspace{1cm} (4.36)

Collecting terms as before,

$$-\lambda_Z C_{0,j-1}' + (2\lambda_Z + 1)C_{0,j}' - \lambda_Z C_{0,j+1}' = (-4\lambda_R + 1)C_{0,j} + 4\lambda_R C_{i+1,j}$$  \hspace{1cm} (4.37)

to obtain the general form

$$C_{0,j-1}' + a_{1,j}C_{0,j}' + C_{0,j+1}' = b_{1,j}$$  \hspace{1cm} (4.38)

with the C-N coefficients

$$a_{1,j} = \frac{1 + 2\lambda_Z}{\lambda_Z}$$  \hspace{1cm} (4.39)

and

$$b_{1,j} = \frac{4\lambda_R - 1}{\lambda_Z} C_{0,j} - \frac{4\lambda_R}{\lambda_Z} C_{i,j}$$  \hspace{1cm} (4.40)

Factor of 4 for diffusion into central point on disc is also discussed by Britz [133] and Flanagan and Marcoux [87].

From available analytical solutions an estimation of the accuracy of the algorithms may be determined. Qualitatively the results are excellent, see Section 4.5.1, but quantitatively appalling

This leads to the questions;

- Are the algorithms being used, correct?
• Is the method of simulation too coarse?

The second problem, appearing the more tractable, was approached first. The grid of concentration values may be expanded to give an increased density of points near the steepest concentration gradient, that is, near the circumference of the interface. Expanded grid parameters had already been calculated for linear and spherical diffusion. The same methodology may be extended to diffusion in two dimensions (Section 4.4).

The first question necessitates a complete revision of the ADI methods looked at above, giving an algorithm of increased complexity. This is explained briefly in Section 4.5.4 and detailed fully in Chapter 5.

4.4 The ADI method - Expanded Grid

Expansion of the space grid for cylindrical diffusion to a disc-shaped interface requires a more rigorous approach than for the simple one-dimensional cases of spherical and linear diffusion. The current density is no longer assumed uniform over interface and the concentration profile is symmetric in only one-dimension. Thus the choice of grid expansion must allow for a differing perturbation of the concentration profile axially and radially.

Size and direction of the grid expansion

Expansion parameters pertinent to each dimension must be chosen and the grid must give the highest density of points where the concentration profile changes most rapidly. Grid expansions in previous chapters have utilised an exponential or simple polynomial expansion for the function.
Joslin and Pletcher [135] first used a simple polynomial space grid expansion to model diffusion at a platinum microelectrode in one dimension (equation (3.18)).

Using the grid expansion from $R=0$ for the radial direction gives the highest density of points near the centre of the electrode (figure 4–2). Raising the whole polynomial to a power $n$ gives a higher density of points nearer to the edge of the electrode.
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Calculation of C-N coefficients

Equation (4.3) is expanded in the R direction, with

\[
Y = \frac{aR}{aR + 1} \quad (4.41)
\]

as in equation (3.18). This may then be substituted into the partial differential equation to give the discrete equation describing the concentration profile at a disc interface in expanded cylindrical coordinates.

For the solution of concentrations radially

Using the above approach we obtain

\[
\frac{C'_{i+1,j} - C_{i,j}}{\delta T} = a^2(1 - Y)^4 \lambda_Y \left[ (C'_{i-1,j} - 2C'_{i,j} + C'_{i+1,j}) + \frac{\delta Y(1 - 2Y)}{2Y(1 - Y)}(C'_{i+1,j} - C'_{i-1,j}) \right] \\
+ \lambda_Z (C_{i,j-1} - 2C_{i,j} + C_{i,j+1}) \quad (4.42)
\]

Collecting terms gives

\[
(-\lambda_Y \gamma_i(1 - \beta_i))C'_{i-1,j} + \gamma_i(2\lambda_Y + 1)C'_{i,j} - (-\lambda_Y \gamma_i(1 + \beta_i))C'_{i+1,j} \\
= -\frac{1}{\lambda_Y \gamma_i(1 - \beta_i)} \left( \lambda_Z C_{i,j-1} + (-2\lambda_Z + 1)C_{i,j} + \lambda_Z C_{i,j+1} \right) \quad (4.43)
\]

This reduces to a general form

\[
C'_{i-1,j} + a_2 C'_{i,j} + a_3 C'_{i+1,j} = b_4 \quad (4.44)
\]

with C-N coefficients

\[
a_2 = -\frac{1}{\lambda_Y \gamma_i} + 2, \quad a_3 = \frac{1 + \beta_i}{1 - \beta_i} \quad (4.45)
\]

and

\[
b_4 = -\frac{1}{\lambda_Y \gamma_i(1 - \beta_i)} \left( \lambda_Z C_{i,j-1} + (-2\lambda_Z + 1)C_{i,j} + \lambda_Z C_{i,j+1} \right) \quad (4.46)
\]

with \( \gamma_i \) and \( \beta_i \) defined as

\[
\gamma_i = a^2(1 - Y)^4, \quad \beta_i = \frac{\delta Y(1 - 2Y)}{2Y(1 - Y)} \quad (4.47)
\]
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For the solution of concentrations axially

We obtain the discretised form of the partial differential equation,

\[
\frac{C'_{i,j} - C_{i,j}}{\delta T} = a^2 (1 - Y)^4 \lambda_Y \left[ (C'_{i-1,j} - 2C'_{i,j} + C'_{i+1,j}) + \frac{\delta Y(1 - 2Y)}{2Y(1 - Y)} (C'_{i+1,j} - C'_{i-1,j}) \right] + \lambda_Z (C_{i,j-1} - 2C_{i,j} + C_{i,j+1})
\]

and the general form

\[
C'_{i,j-1} + a_{1j} C'_{i,j} + C'_{i,j+1} = b_{3j}
\]

with the C-N coefficients

\[
a_{1j} = \frac{-1 + 2\lambda_z}{\lambda_z}
\]

and

\[
b_{3j} = \frac{-a^2(1 - Y)^4}{\lambda_z} \lambda_Y \left[ (C'_{i-1,j} - 2C'_{i,j} + C'_{i+1,j}) + \frac{\delta Y(1 - 2Y)}{2Y(1 - Y)} (C'_{i+1,j} - C'_{i-1,j}) \right] - \frac{C_{i,j}}{\lambda_z}
\]

Expansion in both R and Z directions using the radial grid transformation given in equation (4.41) above and the axial grid expansion

\[
W = \frac{aZ}{aZ + 1}
\]

results in the partial differential equation

\[
\frac{\partial C}{\partial T} = Da^2 (1 - Y)^4 \left[ \frac{\partial^2 C}{\partial Y^2} + \frac{1 - 2Y}{Y(1 - Y)} \frac{\partial C}{\partial Y} \right] + Da^2 (1 - W)^4 \left[ \frac{\partial^2 C}{\partial W^2} - \frac{2}{1 - W} \frac{\partial C}{\partial W} \right]
\]

Discretisation and general forms are the same as the radial only expansion, given above, to obtain the C-N coefficients;

For the solution of concentrations radially

\[
a_{2i} = -\frac{1 + \beta_i}{1 - \beta_i}, \quad a_{3i} = \frac{1 + \beta_i}{1 - \beta_i}
\]
and

$$b_4 = \frac{-\lambda w \alpha_j}{\lambda y \gamma_i(1 - \beta_i)} \left[ C_{i,j+1} - 2C_{i,j} + C_{i,j+1} + \epsilon_j(C_{i+1,j} - C_{i-1,j}) \right]$$

$$- \frac{C_{i,j}}{\lambda y \gamma_i(1 - \beta_i)}$$

(4.55)

For the solution of concentrations axially

$$a_1 = -\frac{1 + 2\lambda w \alpha_j}{\lambda w(1 - \epsilon_j)}, \quad a_4 = \frac{1 + \epsilon_j}{1 - \epsilon_j}$$

(4.56)

and

$$b_3 = \frac{\lambda y \gamma_i}{\lambda w \alpha_j(1 - \epsilon_j)} \left[ C_{i,j-1} - 2C_{i,j} + C_{i+1,j} + \epsilon_j(C_{i+1,j} - C_{i-1,j}) \right]$$

$$- \frac{C_{i,j}}{\lambda w \alpha_j(1 - \epsilon_i)}$$

(4.57)

with $\gamma_i$ and $\beta_i$ as before and $\alpha_j$ and $\epsilon_j$ defined as

$$\alpha_j = a^2(1 - W)^4, \quad \epsilon_j = \frac{\delta W}{1 - W}$$

(4.58)

### 4.4.2 Other grid expansions

Simulations have been performed using a range of other grid expansions based on the polynomial expansion, equation (4.41), raised to the power $n, n \geq 2$ and expansions based on a 'Fermi-Dirac' type step function.

We obtain the general form of the partial differential equation

$$\frac{\partial C}{\partial T} = \gamma_i \left[ \frac{\partial^2 C}{\partial Y^2} + \beta_i \frac{\partial C}{\partial Y} \right] + \alpha_j \left[ \frac{\partial^2 C}{\partial W^2} + \epsilon_j \frac{\partial C}{\partial W} \right]$$

(4.59)

Values for the coefficients $\gamma_i, \beta_i, \alpha_j, \epsilon_j$ for for radial ($R$) calculations and axial ($Z$) calculations for each expansion are given in table 4-1. These expansions give a space grid of simulation points appropriate to the diffusion regime at an ultramicrodisc interface. The space grid for a two dimensional 'Fermi-Dirac' expansion is given in figure 4-3. Derivation of the coefficients for the 'Fermi-Dirac' expansion are detailed in Chapter 5.
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\[
\frac{a_R}{a_{R+1}}, \quad \left(\frac{a_R}{a_{R+1}}\right)^2, \quad \left(\frac{a_R}{a_{R+1}}\right)^4, \quad \left(\frac{a_R}{a_{R+1}}\right)^{10}, \quad \left(\frac{a_R}{a_{R+1}}\right)^n
\]

<table>
<thead>
<tr>
<th>(\gamma_i)</th>
<th>(a^2(1 - Y)^4)</th>
<th>(4a^2Y(1 - Y\frac{1}{4})^4)</th>
<th>(16a^2Y\frac{3}{2}(1 - Y\frac{1}{4})^4)</th>
<th>(100a^2Y^2(1 - Y\frac{1}{10})^4)</th>
<th>(na^2Y^{\frac{n-1}{2}}(1 - Y\frac{1}{n})^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\beta_i)</td>
<td>(\frac{8Y(1-2Y)}{2Y(1-Y)})</td>
<td>(\frac{8Y(2-3Y\frac{1}{4})}{4Y(1-Y\frac{1}{4})})</td>
<td>(\frac{8Y(4-5Y\frac{1}{4})}{8Y(1-Y\frac{1}{4})})</td>
<td>(\frac{8Y(10-11Y\frac{1}{10})}{20Y(1-Y\frac{1}{10})})</td>
<td>(\frac{8Y(n-(n+1)Y\frac{1}{n})}{2nY(1-Y\frac{1}{n})})</td>
</tr>
<tr>
<td>(\alpha_j)</td>
<td>(a^2(1 - W)^4)</td>
<td>(a^2(1 - W)^4)</td>
<td>(a^2(1 - W)^4)</td>
<td>(a^2(1 - W)^4)</td>
<td>(a^2(1 - W)^4)</td>
</tr>
<tr>
<td>(\epsilon_j)</td>
<td>(\frac{\delta W}{1-W})</td>
<td>(\frac{\delta W}{1-W})</td>
<td>(\frac{\delta W}{1-W})</td>
<td>(\frac{\delta W}{1-W})</td>
<td>(\frac{\delta W}{1-W})</td>
</tr>
</tbody>
</table>

**expansion =1 \(\lambda_W = \lambda_Z, \lambda_Y = \lambda_R\)**

\[
\gamma_i = \alpha_j = \epsilon_j = 1, \quad \beta_i = \frac{\delta R}{2R}
\]

**Table 4-1: C-N coefficients for 2-D grid expansion**
Figure 4-3: Grid for 2-D diffusion using 'Fermi-Dirac' expansion, number of points reduced for clarity. Values for simulation \( nz = 100 \), \( nr = 200 \), \( n_{cr} = 40-70 \).
4.4.3 Boundary conditions

As in the first ADI method described on page 135, the boundary conditions are determined by their own partial differential equations. The derivation follows exactly the same path with the discretised forms of the diffusion equation being modified to implicit and explicit respectively for the two variables, as in the previous section. The first example given below is for space grid expansion in the radial direction only using the grid expansion detailed in Section 4.4.1.

At time t - calculate ascending rows

For $Z=0$ only, implicit with respect to $\delta R$, explicit with respect to $\delta Z$. This is the calculation of the first row for $i > n_{cr}$.

\[
C_{i,0}' - C_{i,0} = a^2(1 - Y)^4 \lambda_Y \left( (C'_{i-1,0} - 2C'_{i,0} + C'_{i+1,0}) + \frac{\delta Y(1 - 2Y)}{2Y(1 - Y)} (C'_{i+1,0} - C'_{i-1,0}) \right) \\
+ \lambda_Z (C_{i-1} - C_{i,0})
\]

(4.60)

Which reduces to the general form, a simultaneous equation in three variables,

\[
C'_{i-1,0} + a_2 C'_{i,0} + a_3 C'_{i+1,0} = b_2 i
\]

(4.61)

with C-N coefficients

\[
a_2 = -\frac{1}{\lambda_Y \gamma_0} + 2, \quad a_3 = \frac{1 + \beta_0}{1 - \beta_0}
\]

(4.62)

and

\[
b_4 = \frac{-1}{\lambda_Y \gamma_i (1 - \beta_i)} \left( (-\lambda_Z + 1) C_{i,j} + \lambda_Z C_{i,j+1} \right)
\]

(4.63)

with $\gamma_0$ and $\beta_0$ again defined as

\[
\gamma_0 = a^2(1 - Y)^4, \quad \beta_0 = \frac{\delta Y(1 - 2Y)}{2Y(1 - Y)}
\]

(4.64)

At time $t + \delta t$ - Calculate columns radially from centre

For $R=0$ only, explicit with respect to $\delta R$, implicit with respect to $\delta Z$. This is the
calculation of the first column. Again using a Maclaurin expansion which allows
the discretised partial differential equation to be re-expressed as
\[
C'_{0,j} - C_{0,j} = 4\lambda \gamma_0 \left(C_{1,j} - C_{0,j}\right) + \lambda Z \left(C'_{0,j-1} - 2C'_{0,j} + C'_{0,j+1}\right)
\] (4.65)
Which may be reduced to the general form
\[
C'_{0,j-1} + a_{1,j}C'_{0,j} + a_{4,j}C'_{0,j+1} = b_{1,j}
\] (4.66)
With the Crank-Nicholson coefficients
\[
a_{1,j} = -\frac{1 + 2\lambda z}{\lambda Z}, \quad a_{4,j} = 1
\] (4.67)
and
\[
b_{1,j} = \frac{4\lambda \gamma_0 - 1}{\lambda Z} C_{0,j} - \frac{4\lambda \gamma_0}{\lambda Z} C_{1,j}
\] (4.68)
Boundary coefficients for other grid expansions, both axial and radial are cal-
culated in a similar manner.

The values given in table 4–1 may be used for the coefficients \(\gamma_0, \beta_0, \alpha_0, \epsilon_0\), replacing \(i\) and \(j\) with 0 as appropriate.

4.5 Results

The accuracy of the above methods when utilised to simulate the complete \((i - E - t)\) response of an interface to a constant potential (chronoamperometry) or a
variable potential (cyclic voltammetry) potential may not be determined directly,
or even implicitly. For chronoamperometry the current-time transient may be
compared to exact pseudo-analytical solutions in areas of the time domain where
solutions are available, that is, only for very short and very long times, although
approximate analytical solutions (error of 0.6 % compared to exact solutions) are
available over all time [100].
For cyclic voltammetry or linear sweep voltammetry the accuracy of the steady state value may be compared to analytical solutions. Full cyclic voltammograms have been calculated analytically [97] but only under the assumption that the diffusion to the interface is continuously steady state. Diffusion to the interface is not steady-state for fast sweep voltammetry at an ultramicrodisc or for cyclic voltammetry at any sweep rate at an ultramicropipette due to the asymmetric diffusion profile (see Chapter 6).

4.5.1 Uniform grid

The use of a uniform space grid with its simpler calculations, compared to the expanded grid, facilitates the detailed study of the effects of boundary condition assumptions on the overall accuracy of the simulation. Figure 4–4 illustrates simulation points typical of a uniform grid (number of points reduced for clarity). We apply the boundary conditions detailed in Section 4.3.2 to the \( r = 0 \) axis and the insulating surface surrounding the interface \( (z = 0 \text{ axis beyond } r = r_0) \).

The relative errors in dimensionless peak current and potential of half peak height obtained using the zero flux boundary conditions along both axes or the \( z \) axis alone are shown in table 4–2. Although the zero flux boundary condition will hold at all times at the \( r = 0 \) axis, due to the symmetry of the system (see eqn. 4.2), we must consider the distance \( \delta R \) between the points \( C'_{i,1} \) and \( C'_{i,0} \), due to the finite nature of the grid expansion. Looking at table 4–2 the most accurate results over a range of the parameter \( \rho \) are obtained when we do not assume \( C'_{i,1} = C'_{i,0} \), for \( i > n_{cr} \). One may deduce from these data that the simulation points for the boundary conditions are too far apart, when using a uniform grid, to apply the discrete approximation to the zero flux boundary condition. Using a uniform space grid with the discrete approximation to zero flux applied only to the \( r = 0 \) axis requires that the boundary value C-N coefficients for the \( r = 0 \) axis, given by
Figure 4-4: Discrete boundary concentration values on a uniform space grid
Table 4-2: Comparison of errors with various boundary conditions

<table>
<thead>
<tr>
<th>Method</th>
<th>( \rho )</th>
<th>( X_p )</th>
<th>( \text{err. vs } X_{p,th} )</th>
<th>( \xi_{p/2} )</th>
<th>( \text{err. vs } X_{p/2,th} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>zero flux boundary condition ( C_{1,j} = C_{0,j} )</td>
<td>4.41</td>
<td>2.00</td>
<td>-10.0%</td>
<td>-0.90</td>
<td>1.0%</td>
</tr>
<tr>
<td></td>
<td>6.98</td>
<td>2.79</td>
<td>-9.7%</td>
<td>-0.90</td>
<td>7.6%</td>
</tr>
<tr>
<td></td>
<td>14.0</td>
<td>4.88</td>
<td>-11.4%</td>
<td>-0.90</td>
<td>12.8%</td>
</tr>
<tr>
<td></td>
<td>44.1</td>
<td>11.88</td>
<td>-25.9%</td>
<td>-0.66</td>
<td>38.4%</td>
</tr>
<tr>
<td>zero flux boundary conditions on both axes ( C_{i,1} = C_{i,0} )</td>
<td>4.41</td>
<td>1.82</td>
<td>-18.0%</td>
<td>-0.97</td>
<td>-6.7%</td>
</tr>
<tr>
<td></td>
<td>6.98</td>
<td>2.66</td>
<td>-13.9%</td>
<td>-0.97</td>
<td>0.04%</td>
</tr>
<tr>
<td></td>
<td>14.0</td>
<td>4.81</td>
<td>-12.7%</td>
<td>-0.90</td>
<td>12.8%</td>
</tr>
<tr>
<td></td>
<td>44.1</td>
<td>11.87</td>
<td>-26.0%</td>
<td>-0.62</td>
<td>42.2%</td>
</tr>
</tbody>
</table>
Chapter 4. The 2-D numerical method: ADI

<table>
<thead>
<tr>
<th>$\lambda_R$, $\lambda_Y$</th>
<th>$\rho$</th>
<th>$\chi_p$</th>
<th>err. vs $\chi_{p,th}$</th>
<th>$\xi_{p/2}$</th>
<th>err. vs $\chi_{p/2,th}$</th>
<th>$\nu (V/s)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
<td>0.435</td>
<td>0.508</td>
<td>-52.4%</td>
<td>-0.47</td>
<td>-89.9%</td>
<td>0.2</td>
</tr>
<tr>
<td>72</td>
<td>0.698</td>
<td>0.560</td>
<td>-50.0%</td>
<td>-0.66</td>
<td>-77.4%</td>
<td>0.5</td>
</tr>
<tr>
<td>36</td>
<td>0.987</td>
<td>0.655</td>
<td>-52.9%</td>
<td>-0.74</td>
<td>-52.9%</td>
<td>1</td>
</tr>
<tr>
<td>18</td>
<td>1.40</td>
<td>0.797</td>
<td>-38.0%</td>
<td>-0.82</td>
<td>-35.5%</td>
<td>2</td>
</tr>
<tr>
<td>7.2</td>
<td>2.21</td>
<td>1.074</td>
<td>-44.0%</td>
<td>-0.90</td>
<td>-19.8%</td>
<td>5</td>
</tr>
<tr>
<td>3.6</td>
<td>3.12</td>
<td>1.383</td>
<td>-23.0%</td>
<td>-0.93</td>
<td>-10.7%</td>
<td>10</td>
</tr>
<tr>
<td>1.8</td>
<td>4.41</td>
<td>1.82</td>
<td>-18.0%</td>
<td>-0.97</td>
<td>-6.7%</td>
<td>20</td>
</tr>
<tr>
<td>0.72</td>
<td>6.98</td>
<td>2.66</td>
<td>-13.9%</td>
<td>-0.97</td>
<td>0.04%</td>
<td>50</td>
</tr>
<tr>
<td>0.72</td>
<td>14.0</td>
<td>4.81</td>
<td>-12.7%</td>
<td>-0.90</td>
<td>12.8%</td>
<td>2</td>
</tr>
<tr>
<td>0.072</td>
<td>44.1</td>
<td>11.87</td>
<td>-26.0%</td>
<td>-0.62</td>
<td>42.2%</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 4-3: CV parameters obtained using a uniform grid expansion

Equation 4.40 are re-expressed as

$$b_{1j} = \frac{-1}{\lambda_z} C_{0,j} \quad (4.69)$$

A set of cyclic voltammetry parameters for variable $\rho$ have been calculated using this method and are given in table 4-3. Cyclic voltammograms simulated with the same parameters are shown in figure 4-5. Variation of peak current and half-wave potential with $\lambda$ and may be seen in figure may be seen in table 4-3. The mid-range of $\lambda$ values from around 0.72 to 1.8 give the smallest errors. This is a limitation of using a uniform space grid in that only a small range of experimental parameters may be simulated with moderate accuracy.

4.5.2 Expanded Grid

Tables 4-2 and 4-3 show that, although careful consideration of discrete boundary conditions improves accuracy, the uniform grid algorithm is not consistently accurate over a range of experimental parameters. Accuracies to within 1% arise due to serendipitous error cancelling. To increase the accuracy of the simulation, as
Figure 4-5: Cyclic voltammetry at an ultramicrodisc using a non-expanded grid; variable $\nu$
Chapter 4. The 2-D numerical method: ADI

with the one-dimensional model in the previous chapter, we must use an expanded space grid.

This section details the results obtained from various grid expansions, their shape and the comparative accuracies of the expansions. The first direction in which we expand the space grid is the radial direction, as the concentration profile is expected to change more rapidly in this direction due to edge effects. There are a number of alternatives for grid expansions over the surface of an ultramicrodisc interface and the surrounding area.

1. A grid expansion from $r = 0$ (as detailed in Section 4.4.1) for the radial direction and taking all points, see figure 4-2

2. A grid having the same number of points on the electrode as the above

3. A grid expansion from $r = 0$ but with the greatest density of points near the edge of the electrode

Current density is greater towards the perimeter of the electrode due to edge effects. Therefore the second method detailed above would be expected to give a more accurate result than the first. The third approach is preferable as this will give the greatest number of simulation points where we have the most pronounced concentration gradient. As a general guide, the concentration should be mirrored by the grid transformation. We thus require a sigmoidal curve, with the point of inflexion on or near the boundary of the interface. Curves of this nature may be generated using the simple Joslin and Pletcher expansion raised to $n \geq 2$ with accompanying expanded grid C-N coefficients, as detailed in Section 4.4.1.

To reflect the sharp concentration gradient encountered at the edge of the electrode, a step function of the Fermi-Dirac (F-D) type is more suitable. It is also advisable to transform the space grid in the axial direction to give relatively more points near the surface of the electrode where the axial concentration is
Figure 4-6: Expanded space grid transformation with uniform spacing-across interface
Figure 4-7: Discrete boundary concentration values on an expanded space grid steeper. Details of the F-D expansion equations with illustrations of their shape are given in the next chapter. The following section presents results obtained with these suggested axial and radial grid expansions.

F-D expansion in radial direction plus expansion in axial direction

With an expanded space grid in both axial and radial directions we obtain a higher density of points near the surface of the ultramicrointerface and the surrounding insulating substrate (see figure 4-7). This leads to the increments $\delta R$ and $\delta Z$, associated with the discrete boundary conditions becoming much smaller. This
Table 4–4: CV parameters obtained with F-D expansion

allows us to reconsider the use of the zero flux boundary condition along the $z = 0$ axis ($C'_{i,1} = C'_{i,0}$).

Table 4–4 shows a comparison of the accuracies obtained by using the discrete forms of the zero flux boundary condition on both axes together with an axial and radial space grid expansion. The most accurate results over a range of the electrode parameter $\rho$ are obtained when we assume $C'_{i,1} = C'_{i,0}$ for $i > n_{er}$, in addition to $C'_{1,j} = C'_{0,j}$. This leads to the boundary value C-N coefficients in equations (4.35) and (4.40) being written as

\[
b_{2,i} = -\frac{1}{\lambda Y \gamma_i (1 - \beta_i)} C'_{i,0} \tag{4.70}\]

\[
b_{1,j} = \frac{-1}{\lambda Z} C_{0,j} \tag{4.71}\]
The data in table 4-4 also suggest that the value of $\lambda$ again constrains the accuracy of the simulation. Despite careful consideration of boundary conditions and selection of appropriate axial and radial space grid expansions, the level of accuracy is no better than $\pm 3\%$. To increase the accuracy of the simulation further, it is necessary to look more closely at the consistency, convergence and stability of the ADI method. This is discussed in the following section.

All of the simulation results presented here use the refined explicit/implicit ADI method (page 135), the stability of which has been shown to be superior to the earlier ADI method [133].

Further comments on ADI variations and other discrete boundary condition techniques, such as the half box method, are given in Section 2.4.2 in Chapter 2.

### 4.5.3 Consistency, convergence and stability

Although a number of papers have been published on the stability of the Crank-Nicholson method [154, 189-191], no work has been performed to look at the stability of the ADI method, particularly with independently determined boundary conditions (b.c.s calculated outwith the 'bulk solution' calculations). It is interesting to note that the axial boundary conditions are always calculated with an axial implicit, radial explicit algorithm and the radial boundary conditions conversely. The results imply that this approach reduces the overall stability of the complete method, despite the fact that the boundary conditions constitute only a small fraction of the total number of simulation points. This occurs because the b.c.s are used in the calculation of each row and column so any error will be transmitted when the appropriate set of simultaneous equations are solved. In certain cases, the stability criteria of a 2-D explicit method may apply, ($\lambda \leq 0.25$), greatly reducing the efficiency and accuracy of the algorithm.
Chapter 4. The 2-D numerical method: ADI

<table>
<thead>
<tr>
<th>Grid expansion</th>
<th>$\lambda_R$</th>
<th>$\lambda_R$</th>
<th>$i$ (1 sec)</th>
<th>$\chi$(1sec)</th>
<th>err. vs $\chi_{th}$</th>
<th>curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniform grid</td>
<td>180</td>
<td>180</td>
<td>1350</td>
<td>0.5497</td>
<td>-47%</td>
<td>a</td>
</tr>
<tr>
<td>Uniform grid</td>
<td>180</td>
<td>180</td>
<td>1450</td>
<td>0.5904</td>
<td>-43%</td>
<td>b</td>
</tr>
<tr>
<td>with 5-point flux calculation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-D expansion</td>
<td>50,000</td>
<td>100</td>
<td>2180</td>
<td>0.8876</td>
<td>-14%</td>
<td>c</td>
</tr>
<tr>
<td>F-D expansion</td>
<td>50,000</td>
<td>100</td>
<td>2975</td>
<td>1.211</td>
<td>18%</td>
<td>d</td>
</tr>
</tbody>
</table>

Boundary conditions on both axes; $C'_{i,1} = C'_{i,0}$ for $i > n_n \rightarrow C'_{1,j} = C'_{0,j}$, $\lambda = \lambda_0$ for expanded grids, $\delta t = 0.005s, i_{th}(1sec) = 2530\mu Acm^{-2}, \chi_{th} = 1.030$

Table 4-5: Chronoamperometry parameters obtained with various grid expansions

We resort to simple chronoamperometry to investigate the problem. A Cottrell plot may be used to illustrate the above and explain why some approaches do not exhibit consistency, convergence and stability [177].

Chronoamperometry

Table 4-5 and figure 4-8 show the inaccuracy and the instability of the algorithms detailed in the previous section even under the simple boundary conditions associated with chronoamperometry (see equation (4.25)). The oscillatory nature of the current-time plots is indicative of an irregularity in the calculation of the boundary values, as the oscillations occur at each time step when the concentrations are calculated, alternately along rows or up columns. Current-time plots for a number of different types and combination of grid expansion are given in figure 4-8.

The failure of the above algorithms to successfully model charge transfer at an ultramicrodisc interface leads to a closer inspection of the algorithm, partic-
Figure 4-8: Stability of the various methods with various grid expansions (see table 4-5).
ularly the determination of the boundary concentration values. Work performed on the stability of the one-dimensional Crank-Nicholson method [154] suggests that serious errors may occur when the new boundary concentration value \( C'_0 \) is not determined implicitly, in the same manner as the bulk concentrations. This appears to also hold for the two-dimensional ADI method.

### 4.5.4 Implicit determination of \( C'_0 \)

As detailed on page 161, close inspection of the separate algorithms used to determine the radial and axial boundary concentrations shows that they do not possess the alternating explicit-implicit calculation that gives stability to the ADI method, but are always fully explicit in \( j \) or \( i \) respectively. This leads to the instability of the above approaches. A solution requires that the boundary concentrations are calculated with the bulk concentrations as part of the ADI method.

An algorithm to implicitly calculate boundary concentration values as part of the bulk concentration calculation has been developed by Britz et al. for the C-N method [133,148]. It is extended here to two dimensions incorporating a two dimensional expanded grid of the F-D type and a 5-point determination of the interfacial current [148] for increased accuracy. As can be seen from figures 4–9 and 4–10 the increased accuracy and stability of the 'implicit \( C'_0 \)' method is immediately apparent in comparison to figure 4–8. The simulated results are compared with values obtained from pseudo-analytical expressions for short and long times by Oldham [68] and Osteryoung et al. [101] given respectively as equations (2.5) on page 40 and (2.12) on page 41.

Table 4–6 similar to table 2–2 in Chapter 2 shows the accuracy of the simulation over a range of \( \tau \) values \( (\tau = (Dt)^{1/3}/r_0) \) for a number of different radial grid expansion coefficients \( (a) \). As expected, different \( a \) values result in differing accuracies at various values of \( \tau \) - this reflects the fit of the grid expansion to the
Figure 4-9: Stability of the 'implicit $C_0'$ method - Short times ($\tau = 0.01$ sec)
Figure 4-10: Stability of the 'implicit $C_0$' method - Long times ($\tau = 1$ sec)

0.31% error at 1s
form of the concentration profile over the ultramicrointerface (see figure 5-2 in Chapter 5).

Using the same algorithm but changing the experimental conditions to simulate cyclic voltammetry we again obtain a simulation that is accurate across a wide range of experimental parameters. Simulation results for cyclic voltammetry (presented in the next chapter) agree closely with available pseudo-analytical solutions.

4.6 Summary

This chapter has outlined the derivation of the C-N coefficients from the discretised two-dimensional diffusion equation based on a uniform or expanded space grid. The resulting simultaneous equations possess similar general forms allowing the grid expansion to be easily altered without changing the underlying structure of the algorithm. Careful consideration of discrete boundary conditions is important and it is essential to include boundary concentration calculations within the main body of the ADI algorithm to ensure consistency, convergence and stability of the solution over a wide range of experimental parameters.

Chapter 5 fully develops the implicit $C_0'$ method in two dimensions with an expanded grid and 5-point polynomial to determine interfacial concentrations. Having proved the accuracy of the algorithm in modelling the reversible chronoamperometric response, results are presented for both reversible and kinetically controlled voltammetry.
### Table 4-6: Chronoamperometry parameters - variance with $\tau$

<table>
<thead>
<tr>
<th>$\tau$</th>
<th>Analytical (see eqn.)</th>
<th>Simulations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(2.87)x^{32}_{3x^2}$</td>
<td>$r$</td>
</tr>
<tr>
<td></td>
<td>(2.14)</td>
<td>$a=0.3$ $a=0.5$ $a=0.6$ $a=0.8$ $a=0.9$</td>
</tr>
<tr>
<td>0.01</td>
<td>48.368</td>
<td>45.50 48.94 51.04</td>
</tr>
<tr>
<td>0.02</td>
<td>24.434</td>
<td>22.61 22.74 23.06 23.46</td>
</tr>
<tr>
<td>0.03</td>
<td>17.259</td>
<td>17.83 18.20 18.30 18.34</td>
</tr>
<tr>
<td>0.04</td>
<td>12.481</td>
<td>11.63 11.73 11.85 11.86</td>
</tr>
<tr>
<td>0.06</td>
<td>8.667</td>
<td>8.319 8.322</td>
</tr>
<tr>
<td>0.07</td>
<td>7.241</td>
<td>6.990 6.994</td>
</tr>
<tr>
<td>0.08</td>
<td>6.293</td>
<td>6.105 6.113</td>
</tr>
<tr>
<td>0.09</td>
<td>5.821</td>
<td>5.665 5.675 5.685</td>
</tr>
<tr>
<td>0.10</td>
<td>5.237</td>
<td>5.221 5.234 5.243</td>
</tr>
<tr>
<td>0.11</td>
<td>4.879</td>
<td>4.780 4.798</td>
</tr>
<tr>
<td>0.13</td>
<td>4.411</td>
<td>4.340 4.355</td>
</tr>
<tr>
<td>0.14</td>
<td>3.945</td>
<td>3.901 3.911</td>
</tr>
<tr>
<td>0.17</td>
<td>3.482</td>
<td>3.465 3.473</td>
</tr>
<tr>
<td>0.20</td>
<td>3.024</td>
<td>3.421 3.427</td>
</tr>
<tr>
<td>0.25</td>
<td>2.573</td>
<td>2.603 2.609</td>
</tr>
<tr>
<td>0.33</td>
<td>2.133</td>
<td>2.181 2.185</td>
</tr>
<tr>
<td>0.5</td>
<td>1.714</td>
<td>1.770 1.773</td>
</tr>
<tr>
<td>1.0</td>
<td>1.330</td>
<td>1.374 1.368</td>
</tr>
<tr>
<td>1.1</td>
<td>1.295</td>
<td>1.335 1.337</td>
</tr>
<tr>
<td>1.4</td>
<td>1.226</td>
<td>1.259 1.257</td>
</tr>
</tbody>
</table>
Chapter 5

Diffusion to an ultramicrodisc interface

5.1 Introduction

Building on the learnings of the previous chapter, we now derive an efficient, accurate algorithm to simulate charge transfer at an ultramicrodisc interface. A novel space-grid expansion in two dimensions is presented, coupled with an ADI method allowing implicit determination of boundary concentrations and a 5-point polynomial fit to the concentration gradient for determination of boundary flux. This grid alleviates the need for recourse to a spline interpolation over areas of rapid concentration variation [143] and yields a simulation of comparable efficiency to that applying a conformal map [192].

These yield a fast and accurate algorithm applied to cyclic voltammetry and chronoamperometry for reversible, quasi-reversible and irreversible charge transfer at ultramicrodisc interfaces. This allows study of the effects of kinetic parameters $k, \Lambda, \alpha$ on current-potential-time response for ultramicrodisc interfaces of any size.
5.2 Space grid expansion

5.2.1 Axial expansion of space grid

To recap briefly on the benefits of grid expansion detailed in Chapters 3 and 4, if one considers the concentration profile over a distance of $10\delta$, a large proportion of the concentration values will be almost equivalent to the bulk concentration. The concentration values show a rapid increase with distance near to the electrode and a much less pronounced change with each spatial increment further out.

A sensible approach is to use increasing intervals on increasing distance from the electrode [135], retaining accuracy where the concentration change is rapid and saving computer time by eliminating unnecessarily small increments where the concentration changes very slowly, thereby reducing the total number of increments.

A suitable transformation mapping $w$ onto $z$ is an exponential expansion shown in figure 5-1. A constant step size in $w$ producing an increasing $z$ increment. A suitable form for the equation would be;

$$W = 0.5 - \frac{1}{\exp(Z/c) + 1} \quad (5.1)$$

With a typical value of $c$ lying between 0.01 and 0.2.

Defining the Grid Transformation Function in dimensionless parameters as

$$W = f(Z) \quad (5.2)$$

the inverse function

$$Z = g(W) = c \ln \left( \frac{0.5 + W}{0.5 - W} \right) \quad (5.3)$$

and the first derivative

$$g'(W) = \frac{c}{0.25 - W^2} \quad (5.4)$$
Figure 5-1: Axial space grid transformation

$C = 0.05, 0.1, 0.2, 0.5$. 
5.2.2 Radial expansion of space grid

The necessity for a two dimensional simulation over an ultramicrodisc interface arises from the variable current density as one proceeds from the centre to the edge of the electrode [68]. For optimum accuracy and speed of computation the radial space grid expansion should closely mirror the current density distribution and concentration gradient. The acknowledged distribution of current density across a disc is similar to that given in figure 5-2 which indicates that the local current density near the edge of the electrode is appreciably greater than at the centre.

The lowest curve is the steady-state value, obtained from the analytical solution given by equation (45) in reference [97]. This figure justifies an expanded space grid transformation which is suitable to take into account this effect. A 'Fermi-Dirac' step function was chosen (figure 5-3) as it closely follows the concentration profile at the edge of the electrode and the derivative follows the current density profile along the radius of the interface.

\[ Y = 1 - \frac{1}{\exp((R - b)/a) + 1} \]  \hspace{1cm} (5.6)

With a typical value of \( a \) lying between 0.1 and 2., \( b \) is calculated as the dimensionless equivalent of the electrode radius to ensure that the maximum density of simulation points occurs at the edge of the electrode.

As before, defining the grid transformation function as

\[ Y = f(R) \]  \hspace{1cm} (5.7)

the inverse function

\[ R = g(Y) = a \frac{Y}{1 - Y} + b \]  \hspace{1cm} (5.8)
Figure 5-2: Dimensionless current density as a function of radial distance $\tau = 0.0016, 0.016, 1.6, 16, 160$. 

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Chapter 5. Diffusion to an ultramicrodisc interface

Figure 5-3: Radial space grid transformation

\[ y = 1 - \frac{1}{1 + \exp(r - b/a)} \]

\(a = 0.1, 0.15, 0.2, 0.3, 0.5.\)
and the first derivative

\[ g'(Y) = \frac{a}{Y(1 - Y)} \quad (5.9) \]

also

\[ \frac{\partial}{\partial Y} \frac{1}{g'(Y)} = \frac{1 - 2y}{a} \quad (5.10) \]

Both grid transformation functions may be incorporated into the diffusion equation (equation (4.3)) via

\[ \frac{\partial C}{\partial R} = \frac{\partial Y}{\partial R} \frac{\partial C}{\partial Y} \quad \frac{\partial C}{\partial Z} = \frac{\partial W}{\partial Z} \frac{\partial C}{\partial W} \quad (5.11) \]

and re-expressing as

\[
\frac{\partial C}{\partial T} = \frac{1}{g'(Y)} \left[ \frac{1}{g'(Y)} \frac{\partial^2 C}{\partial Y^2} + \left( \frac{\partial}{\partial Y} \frac{1}{g'(Y)} + \frac{1}{g(Y)} \right) \frac{\partial C}{\partial Y} \right] \\
+ \frac{1}{g'(W)} \left[ \frac{1}{g'(W)} \frac{\partial^2 C}{\partial W^2} + \frac{\partial}{\partial W} \frac{1}{g'(W)} \frac{\partial C}{\partial W} \right] \quad (5.12)
\]

This leads to a simplified expression of the equation of conservation of mass given by

\[ \frac{\partial C}{\partial T} = \gamma_i \left[ \frac{\partial^2 C}{\partial Y^2} + \beta_i \frac{\partial C}{\partial Y} \right] + \alpha_j \left[ \frac{\partial^2 C}{\partial W^2} + \epsilon_j \frac{\partial C}{\partial W} \right] \quad (5.13) \]

via equations (5.4),(5.5) and (5.8-5.12). The coefficients in equation (5.13) are defined as

\[ \gamma_i = \frac{Y_i^2(1 - Y_i)^2}{a^2} \quad (5.14) \]

\[ \beta_i = \frac{1}{Y_i(1 - Y_i)} \left( 1 - 2Y_i + \frac{1}{\ln(Y_i/(1 - Y_i)) + b/a} \right) \quad (5.15) \]

\[ \alpha_j = \frac{(0.25 - W_j^2)^2}{c^2} \quad (5.16) \]

\[ \epsilon_j = \frac{-2W_j}{0.25 - W_j^2} \quad (5.17) \]
5.3 The ADI method

In the same manner as Chapter 4, page 135 the ADI method may be developed incorporating equations (5.14) - (5.17) into the discretised form of the cylindrical diffusion equation (5.13) to obtain the appropriate C-N coefficients.

5.3.1 C-N coefficients

The discretisation of the diffusion equation in an implicit fashion along the rows together with an explicit expression of the vertical diffusion reads as

\[
\frac{C'_{i,j} - C_{i,j}}{\delta T} = \frac{D \alpha_j}{\delta W^2} \left[ C_{i,j-1} - 2C_{i,j} + C_{i,j+1} + \frac{\delta W\epsilon_j}{2} (C_{i,j+1} - C_{i,j-1}) \right] \\
+ \frac{D \gamma_i}{\delta Y^2} \left[ C'_{i-1,j} - 2C'_{i,j} + C'_{i+1,j} + \frac{\delta Y \beta_i}{2} (C'_{i+1,j} - C'_{i-1,j}) \right]
\]

with

\[
\lambda_Y = \frac{D \delta T}{\delta Y^2} \quad \lambda_W = \frac{D \delta T}{\delta W^2}
\]

This reduces to a general form

\[
C'_{i-1,j} - a_3(i)C'_{i,j} + a_4(i)C'_{i+1,j} = b_{R,i,j}
\]

with Crank-Nicholson (C-N) coefficients

\[
a_3(i) = \frac{-(1/\lambda_Y \gamma_i + 2)}{1 - \delta Y \beta_i/2}, \quad a_4(i) = \frac{1 + \delta Y \beta_i/2}{1 - \delta Y \beta_i/2}
\]

and

\[
b_{R,i,j} = \frac{-\lambda_W \alpha_j}{\lambda_Y \gamma_i (1 - \delta Y \beta_i/2)} \left[ C_{i,j-1} - 2C_{i,j} + C_{i,j+1} + \frac{\delta W\epsilon_j}{2} (C_{i,j+1} - C_{i,j-1}) \right] \\
- \frac{C_{i,j}}{\lambda_Y \gamma_i (1 - \delta Y \beta_i/2)}
\]
Similarly, the discretisation of the diffusion equation in an implicit manner up
the columns and explicitly along the rows is given by

\[
\frac{C'_{i,j} - C_{i,j}}{\delta T} = \frac{D\alpha_j}{\delta W^2} \left[ C'_{i,j-1} - 2C'_{i,j} + C'_{i,j+1} + \frac{\delta W\epsilon_j}{2} (C'_{i,j+1} - C'_{i,j-1}) \right] + \frac{D\gamma_i}{\delta Y^2} \left[ C_{i-1,j} - 2C_{i,j} + C_{i+1,j} + \frac{\delta Y\beta_i}{2} (C_{i+1,j} - C_{i-1,j}) \right]
\] (5.23)

As before, we collect terms to give the general form

\[
C'_{i,j-1} - a1(j)C'_{i,j} + a2(j)C'_{i,j+1} = b_{A,i,j}
\] (5.24)

with the following C-N coefficients

\[
a1(j) = \frac{-(1/\lambda_W\alpha_j + 2)}{1 - \delta W\epsilon_j/2}, \quad a2(j) = \frac{1 + \delta W\epsilon_j/2}{1 - \delta W\epsilon_j/2}
\] (5.25)

\[
b_{A,i,j} = \frac{-\lambda_Y\gamma_i}{\lambda_W\alpha_j(1 - \delta W\epsilon_j/2)} \left[ C_{i-1,j} - 2C_{i,j} + C_{i+1,j} + \frac{\delta Y\beta_i}{2} (C_{i+1,j} - C_{i-1,j}) \right] - \frac{C'_{i,j}}{\lambda_W\alpha_j(1 - \delta W\epsilon_j/2)}
\] (5.26)

Where \(b_A\) denotes the axial coefficient and \(b_R\) the radial coefficient.

### 5.3.2 Evaluation of Crank-Nicholson coefficients

After establishing the initial and limiting boundary conditions it is important
to correctly determine the influence of the boundary conditions as they change
throughout the simulation. (See also Section 4.4.3).

The boundary concentration values after a time step \(\delta t\) are determined im-
plicitly via solution of a dual concentration, didiagonal C-N coefficient matrix, as
detailed by Britz et al. [153]. The extension of this matrix method to incorporate
the ADI method is detailed in Section 5.3.3. We require a dual concentration ma-
trix to allow implicit determination of the boundary conditions, as the five-point
polynomial fit uses an adaptation of the Butler-Volmer equation to obtain a value
for the interfacial concentration gradient.
Conditional statements are included in all the computer program subroutines to employ special Crank-Nicholson coefficients in the matrices when the spatial increment indices for the row \( j = 0 \) and the central column \( i = 0 \). These utilise either a Maclaurin expansion [188] of the diffusion equation (equation (4.3)) or the condition of zero concentration gradient at an insulating boundary (equation (3.13)).

Solution of ADI method by dual concentration matrix method, using the equivalence of flux, (as a polynomial expansion of the concentration profile) with the concentration gradient at the electrode determined by the Butler-Volmer equation, as in the previous chapter, section 4.3.2, to give

\[
\frac{1}{a_n \delta W} \sum_{j=0}^{n-1} b_{n,i,j} C'_{A,i,j} = k'_i C'_{A,i,0} - k'_b C'_{B,i,0} \tag{5.27}
\]

The combined flux equation for species \( A \) and \( B \) is given by

\[
\frac{1}{a_n \delta W} \sum_{j=0}^{n-1} b_{n,i,j} C'_{A,i,j} = \frac{d_B}{a_n \delta W} \sum_{j=0}^{n-1} b_{n,i,j} C'_{B,i,j} \tag{5.28}
\]

\( a_n \) is a scalar dependent on the order of polynomial, \( n \) and \( d_B \) is given as the ratio of diffusion coefficients in each phase, assumed equivalent for the simulations presented in this chapter

\[
d_B = \frac{D_B}{D_A} = 1 \tag{5.29}
\]

Using a five-point polynomial with the relevant coefficients [148] we obtain from equation (5.27)

\[
(-25 - 12\delta W k'_i)C'_{A,i,0} + 48C'_{A,i,1} - 36C'_{A,i,2} + 16C'_{A,i,3} - 3C'_{A,i,4} + d_B (-25C'_{A,i,0} + 48C'_{A,i,1} - 36C'_{A,i,2} + 16C'_{A,i,3} - 3C'_{A,i,4}) = 0 \tag{5.30}
\]

and from equation (5.28)

\[
-25C'_{A,i,0} + 48C'_{A,i,1} - 36C'_{A,i,2} + 16C'_{A,i,3} - 3C'_{A,i,4} + d_B (-25C'_{B,i,0} + 48C'_{B,i,1} - 36C'_{B,i,2} + 16C'_{B,i,3} - 3C'_{B,i,4}) = 0 \tag{5.31}
\]
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5.3.3 Matrix evaluation of C-N coefficients for an ultramicrodisc

The sets of concentration values are calculated for each time step using a matrix decomposition method detailed by Britz, Heinze and co-workers [153]. The bulk values for $C'_A$ and $C'_B$ are $C'_{A,k+1}$ and $C'_{B,k+1}$ where $k = nr, nz$. These are used to calculate the C-N coefficients $a'_{A,i,j}$ and $a'_{B,i,j}$ sequentially. The two additional flux equations at the top of each matrix are then required to solve the polynomial for the first five concentration points. On obtaining the new boundary value for the concentration, we may go down the column matrix to solve iteratively for all $C'_{i,j}$. All new concentration values are thus calculated during the same time increment and do not rely on using ‘old’ boundary concentration values.

For the radial solution of the concentration profile (along rows) using boundary condition equation (4.21) and the general form of the discretised diffusion equation, (eqn.(5.20)) we have,

\[
\begin{bmatrix}
-25 & 48 & -36 & 16 & -3 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & 0 & \cdots & -25 & 48 & -36 & 16 & -3 & \cdots \\
1 & a'_{A,1,j} & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots \\
\end{bmatrix}
\times
\begin{bmatrix}
C'_{A,0,j} \\
C'_{A,1,j} \\
C'_{A,2,j} \\
C'_{A,3,j} \\
C'_{A,4,j} \\
C'_{A,5,j} \\
C'_{A,6,j} \\
C'_{B,0,j} \\
C'_{B,1,j} \\
C'_{B,2,j} \\
C'_{B,3,j} \\
C'_{B,4,j} \\
\end{bmatrix}
=
\begin{bmatrix}
0 \\
0 \\
b'_{A,1,j} \\
b'_{A,2,j} \\
b'_{A,3,j} \\
b'_{A,4,j} \\
b'_{A,5,j} \\
b'_{B,1,j} \\
b'_{B,2,j} \\
b'_{B,3,j} \\
b'_{B,4,j} \\
\end{bmatrix}
\]
For axial solution of the concentration profile (up columns) where the boundary value for concentration lies on the electrode, \( r \leq r_0 \) using equations (5.30) and (5.31) and the general form (eqn.(5.24)), we have,

\[
\begin{align*}
-(&25 + 12hk') & 48 & -36 & 16 & -3 & \cdots & +12hk' & 0 & 0 & 0 & 0 & \cdots \\
-25 & 48 & -36 & 16 & -3 & \cdots & -25d & 48d & -36d & 16d & -3d & \cdots \\
1 & a_{A,i,1}' & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & 1 & a_{A,i,2}' & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 1 & a_{A,i,3}' & 0 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 1 & a_{A,i,4}' & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 0 & 0 & \cdots & 1 & a_{B,i,1}' & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & 0 & \cdots & 0 & 1 & a_{B,i,2}' & 0 & 0 & \cdots \\
0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 1 & a_{B,i,3}' & 0 & \cdots \\
0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 1 & a_{B,i,4}' & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots 
\end{align*}
\]

For axial solution of the concentration profile where the boundary value lies on the inert substrate, \( r > r_0 \) using boundary condition equation (4.22)
5.3.4 5-point current approximation with an expanded grid

The ultimate function of the algorithm is to yield a current in response to a fixed or variable applied potential. The importance of achieving a correct array of concentration values is paramount. To retain the accuracy of the concentration profile on the expanded grid a five-point polynomial is used to calculate the current. A higher order polynomial is not required as the errors associated with the method employed here, ≤ 0.1% are sufficiently small [148]. The expansion is taken into account by the following equations.

For the axial expansion, the grid equation

\[ W = f(Z) = 0.5 - \frac{1}{\exp(Z/c) + 1} \] (5.32)

\[
\left( \frac{\partial W}{\partial Z} \right)_{Z=0} = \frac{1}{4c} \] (5.33)

\[
\left( \frac{\partial C}{\partial Z} \right)_{Z=0} = \frac{1}{4c} \left( \frac{\partial C}{\partial W} \right)_{Z=0} \] (5.34)

and for the radial expansion

\[ Y = f(R) = 1 - \frac{1}{\exp((R - b)/a) + 1} \] (5.35)

\[
\left( \frac{\partial Y}{\partial R} \right)_{R=0} = \frac{1}{a} \frac{\exp(-b/a)}{\left( \exp(-b/a) + 1 \right)^2} \] (5.36)

\[
\left( \frac{\partial C}{\partial R} \right)_{R=0} = \frac{1}{a} \frac{\exp(-b/a)}{\left( \exp(-b/a) + 1 \right)^2} \left( \frac{\partial C}{\partial Y} \right)_{R=0} \] (5.37)

These simple coefficients transform the radial and axial fluxes on the expanded grid back to the uniform spatial coordinate system.
5.4 Results

5.4.1 Reversible Charge Transfer

Potential step chronoamperometry

Figure 5-4 shows the simulated chronoamperometric response compared to analytical solutions for short and long times. For the short time response, 1000 iterations yielded a maximum error of 0.9% at 0.3ms in comparison to the lower curve obtained from equation (40) reference [68]. For longer times the maximum error obtained is 0.03 % as compared to the analytical solution of Aoki and Osteryoung [90], later corrected by Shoup and Szabo [100], 1000 iterations were again used, $\delta t = 1ms$. The two curves are indistinguishable.

A more exact comparison of the chronoamperometric response is given in tables 2–2 and 2–22 in Chapters 2 and 5. Analytical solutions and numerical simulations carried out by previous workers are in agreement with the work presented in this paper.

In figure 5-5 the effect of differing electrode radius on chronoamperometric response may be observed. An almost steady-state response (less than 1.1 times steady-state current) is achieved extremely rapidly for the $i - t$ response with $4D/r^2 = 160$. Thus, considering rapid sensor design, a 5$\mu$m radius electrode would reach this state in less than 0.1 seconds, for a typical value of $D = 10^{-5} cms^{-1}$. The larger electrodes still exhibit a marked current decay even after 1 second has passed. The variation of current density with time may been seen in figure 5–2. The lowest curve is given by equation (45) in reference [97]. It may be seen that at $\theta = 16$, the current density profile has almost matched that of the analytical result for the steady-state. For the above electrode dimensions, this is again equivalent to 0.1 seconds.
Figure 5-4: Comparison of curves to short and long time analytical solutions. Short time upper curve simulation, lower curve analytical solution. Long time, analytical solution and simulation coincidental.
Figure 5–5: Variation of chronoamperometric response with time, $4D/r^2 = 160, 40, 10, 1.6, 0.4$
In addition, as $\tau$ tends to infinity, $X_0$, the local current density at the centre of the electrode tends to a value

$$\frac{X_0}{X_{ss}} = 0.5$$

as given by Oldham et al. $X_{ss}$ is defined in equation 5.40.

**Cyclic Voltammetry**

Figure 5–6 shows the cyclic voltammetric response for charge transfer approaching steady-state behaviour, $\rho = 0.099$, where

$$\rho = \left(\frac{nFv_0^2}{DRT}\right)^{1/2}$$

The current is given as $\chi$, an expression of the total current density over the limiting current density for the steady-state, defined as [103],

$$I_d = \frac{4nFD\xi}{\pi r} \frac{I}{I_d} = \chi \quad X_{ss} = 1$$

This cyclic voltammogram is compared to the steady-state curve for reversible charge transfer obtained by Bond and co-workers [97]. The two voltammograms are almost coincident. The maximum error occurs at $\xi = 3$ and is equivalent to 0.04%. $\xi$ is defined as [97]

$$\xi = \frac{nF}{RT}(E - E'_0)$$

For this data, 1000 iterations were taken for each of the forward and reverse scans.

For other values of $\rho$, the maximum value of $\chi$ is compared with an approximate expression given by equation (10) in the paper by Aoki et al. [103]

$$\chi_{p,th} = 0.34e^{-0.66\rho} + 0.66 - 0.13e^{(-11/\rho)} + 0.351\rho$$

A comparison of simulated and analytical results is given in table 5–1 together with the radial expansion coefficient used for each particular simulation (see equation (5.6)). The cyclic voltammograms simulated for the $\rho$ values in table 5–1 are
Figure 5-6: Near steady-state cyclic voltammetry of an ultramicrointerface, \( \rho = 0.099 \)
Table 5-1: Volumetric Response at an Ultramicroporous Interface

<table>
<thead>
<tr>
<th>( \xi_m )</th>
<th>( \xi_m )</th>
<th>( \Delta \xi_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Chapter 5: Diffusion to an Ultramicroporous Interface
Figure 5-7: Linear sweep voltammetry at an ultramicrodisc interface

$\rho$ values corresponding to table 5-1.
shown in figure 5-7. The $x_v$ values for these voltammograms are plotted against equation 5.42 in figure 5-8. Aoki et al. [103] also give an approximate expression for the dimensionless potential at half peak height, equation 13, reference [103]. This is plotted in figure 5-9 and compared with values from cyclic voltammetric curves having $\rho$ values as given in table 5-1. Heinze ?? gives peak separations (in mV) for varying values of $\sigma = 1/\rho$. These values, converted to dimensionless potential, via equation (5.41) are plotted in fig 5-10 along with peak separations simulated for various $\rho$ as above.

It should also be noted that the form of the simulation grid plays a large part in the final current summation. The optimum values of $a$ used in the radial grid expansion equation vary, as expected, as the form of the concentration profile differs with the timescale of the experiment. In addition the values of $a$, column 6 table 5-1, that correlate with the peak height values given by equation 5.42, are not the same as those which give rise to $\Delta \xi/2$ values in best agreement with the peak separation, table 1 in reference [143], and potential at half peak height, equation (13), reference [103]. The latter two sets of values of $a$ are underlined in table 5-1.

The absence of complete correlation between the solutions in table 5-1 implies more than a lack of accuracy in the analytical or digital simulation results. It indicates that solutions correct for one criterium, for example, peak height or half wave potential, are not suitable over the whole range of voltammetric criteria. Therefore, the digital simulation must incorporate variable space grid expansion parameters, as indicated in table 5-1. This ensures that the concentration and flux profiles may be followed accurately under the dynamic electrochemical conditions, giving a complete and faithful current-potential-time response.
Figure 5–8: Dimensionless current $\chi_p$ as a function of $\rho$.

$\rho$ values corresponding to table 5–1.
Figure 5-9: Dimensionless potential at half peak height as a function of $\rho$ $\rho$ values corresponding to table 5-1.
Figure 5–10: Dimensionless peak separation, variation with $\rho$

($\Box$), replotted from table 1 ref. [148]. ($\diamond$), values from table 5–1.
5.4.2 Quasi-reversible/Irreversible charge transfer

Cyclic voltammetry

The variation of cyclic voltammetric response with various kinetic parameters \((k, \Lambda, \alpha)\) is shown in figures 5-11-5-17. The dimensionless kinetic parameter \(\Lambda\) is defined as [95],

\[
\Lambda = \frac{k \tau_0}{D}
\]  

(5.43)

For typical values of \(\tau_0 = 5 \times 10^{-4}\text{ cm}, D = 10^{-5}\text{ cms}^{-1}\), almost steady-state voltammograms \((\rho = 0.099)\) are shown in figure 5–11, together with points obtained from the approximation [110] to the analytical solution first presented by Bond et al. The results show excellent agreement in the early sections of the voltammograms for all values of \(k\). The deviation observed after the transition from kinetic to diffusive control arises from the fact that the simulation is for \(\rho = 0.099\) and the analytical solution is for the steady-state \(\rho = 0\). A plot of \(\log\left\{i/(i_{d'} - i)\right\}\), figure 5–12, against \(\xi\) yields a gradient of 1.00, as expected, for the reversible case, \(k > 1.\text{ cms}^{-1} (\Lambda > 50)\). The maximum current is taken as the peak value \(i_{d'}\), not the diffusion limited current \(i_d\) as \(\rho \neq 0\). This unsteady-state also gives rise to the peaked behaviour in figure 5–12. For \(k \leq 0.01\) the shift in half-wave potential is measured as 118mV for each decade change of rate constant. This is in agreement with the expression of

\[
-\left[ \frac{59}{1 - \alpha} \right] \times \log(\Lambda) \equiv -118 \times \log\left(\frac{k \tau_0}{D}\right) \text{ mV}
\]  

(5.44)

by Aoki et al., where \(\alpha\) is the charge transfer coefficient. Progressively higher values of \(\rho\), typically, faster scan rates at a constant size electrode, are shown in figures 5–13 and 5–14. For the almost completely reversible peaks \(x, y\) the cyclic voltammograms appear very similar to those encountered under planar diffusion [106]. However, it is possible to discriminate between peaks \(x\) and \(y\) corresponding to 100 and 10 \text{ cms}^{-1}, emphasising the rapid response of the ultramicroelectrode.
Figure 5-11: Linear sweep voltammetry at ultramicrointerface, variable $k$. Reversible curves are 100, 10 cm$^{-1}$, $p=0.099$
Figure 5-12: Log plot of voltammograms from previous figure, reversible $k \geq 10$, irreversible $k \leq 0.1$. 
Figure 5-13: Fast CV at an ultramicrodisc interface
As figure 5-11, cyclic voltammetry, $\rho = 1.395$, $n=1$, $T=25^\circ C$, $c_0=10^{-6}$ mol cm$^{-3}$, $r_0=5 \times 10^{-4}$, $D=10^{-5}$. 
Figure 5–14: Very fast CV at an ultramicrodisc interface

As figure 5–13, \( p \approx 4.413 \),

\[
x \times 100 \\
y \times 10 \\
a \times 1 \\
b \times 0.1 \\
c \times 0.01 \\
d \times 0.001 \\
e \times 0.0001 \\
f \times 0.00001 \text{ cm}^{-1}
\]
The shift of half wave potential for irreversible kinetics is again 118mV/decade for both figures 5-13 and 5-14 illustrating that this effect is independent of scan rate. The steady-state is not a prerequisite.

Figure 5-15 shows the variation of voltammetric response with charge transfer coefficient for an irreversible reaction, $\Lambda \leq 0.2$ [95], under almost steady-state conditions ($\rho = 0.099$), comparison is made with the solution given by Bond et al.[97] and conclusions similar to the case of variable $k$ may be drawn. Figure 5-16 presents the response for $\rho = 1.395$. Once again the half-wave potential is seen to be independent of the steady state condition. A quantitative assessment of the shift imposed by the value of the charge transfer coefficient is given in figure 5-17. A plot of $\log\{i/(i_d' - i)\}$ yields straight lines of gradient dependent on $\alpha$

$$
\frac{d}{d\xi} \log \left( \frac{i}{i_d' - i} \right) = m\alpha
$$

(5.45)

Using a least squares method, for the results given in figure 5-17 $m = 0.99145$ with a standard deviation of 0.0094. This is comparable to a result of 0.94103 obtained by Bond et al. [97] by a best-fit to analytical $\log\{(i_d' - i)/i\}$ versus $\log(\pi k r_c/4D)$ data.

### 5.5 Summary

The technique presented provides a rapid accurate simulation of diffusive mass transport at an ultramicrointerface. Incorporation of an expanded grid that closely follows the concentration gradients at the interface greatly increases the speed and accuracy of the digital simulation. However a poorly chosen grid expansion may be counter productive and lead to large discretisation errors. The use of microelectrodes to elucidate kinetic parameters is of great importance, a complete analytical solution for the diffusion to a ultramicrointerface has not yet been found. Sets of
Figure 5–15: Cyclic voltammetry at ultramicrointerface, variable $\alpha$, $\rho=0.099$, $k=0.001\text{cm}^{-1}$
Figure 5-16: Cyclic voltammetry at ultramicrointerface, variable $\alpha$, $\rho = 1.395$
\[ \log \left( \frac{i}{(i_d - i)} \right) \]

**Figure 5-17:** Log plot of variable $\alpha$ CVs, $k = 0.001 \text{ cms}^{-1}$, gradient $= 0.99 \alpha$

Data from figure 5-15
working curves to derive kinetic parameters from steady-state cyclic voltammograms have been presented [110], but are unavailable for non steady-state cases. This chapter shows that numerical simulation is not constrained in this manner. Also, the relatively simple mathematical approach detailed here allows the algorithm to be adapted to more complex diffusion regimes such as ultramicropipettes, dealt with Chapter 6.
Chapter 6

Diffusion to an ultramicropipette

6.1 Introduction

Using the ADI method developed in the previous two chapters, it is possible to accurately simulate charge transfer at an ultramicropipette. A novel space grid expansion similar to that presented in the previous chapter is derived, with the grid adapted for the restricted diffusion regime encountered within the ultramicropipette.

The algorithm, developed along the same lines as in the previous chapter is fast and accurate over a wide range of experimental parameters when applied to chronoamperometry and cyclic voltammetry for reversible quasi-reversible and irreversible charge transfer. The algorithm may also be extended to model an ultramicrointerface within a tube which allows comparison with pseudo-analytical solutions and provides a measure of the 'wall' effects encountered within an ultramicropipette. Ultramicropipette simulations are compared with experimental results and show excellent correlation.
6.2 Space grid expansion

6.2.1 Axial Expansion of Space Grid

The axial expansion of the space grid used in the simulation of ultramicropipette response may be transported directly from the ultramicrodisc approach. The one change that is required in certain simulations is to use a differing axial grid expansions for species $A$ and $B$. If $B$ is the species within the ultramicropipette then the $B$ grid expansion will be more uniform than the $A$ grid expansion. This is due to the diffusion layer within the pipette approximating to the linear case compared to the cylindrical enhanced diffusion regime outside the pipette with its accompanying compact diffusion layer and steeper axial concentration gradient (see fig. 6-1).

6.2.2 Radial expansion of Space Grid

As with the ultramicrodisc interface, a two-dimensional grid expansion is required. This arises due to the variable current density as one proceeds from the centre to the edge of the interface. The radial grid expansion inside the pipette mirrors the expansion outside the pipette. This allows joint concentration value matrices for the solution of the C-N coefficients (see Section 6.3.3) and accounts for the increase in the concentration gradient near the walls of the ultramicropipette.

The simulation points within the ultramicropipette are, of course, limited to $i\delta r, r = 1,n_{er}$, where $n_{er}$ are the number of steps required to reach the edge of the electrode. The optimum values for the radial grid expansion coefficients and the axial grid expansion coefficient outside the pipette may be taken directly from tables 5-1 and 4-6 in chapters 5 and 4 respectively. To obtain the optimum grid expansion inside the pipette a more involved approach is required, through
Figure 6-1: Equiconcentration Lines for Charge Transfer in an Ultramicropipette
simulation of an ultramicro-interface in a semi-infinite tube. This approach and
the optimised grid expansion produced is detailed in Section 6.4.2.

6.3 The ADI method

In the same manner as detailed in Chapter 4, on page 135, the ADI method
may be developed incorporating equations (5.14) - (5.17) from Chapter 5 into
the discretised form of the equation of conservation of mass (5.13) to obtain the
appropriate C-N coefficients. The method is identical to that followed in Chapter
5.

6.3.1 Crank-Nicolson coefficients

Calculation of C-N coefficients for modelling diffusion at an ultramicropipette fol-

ows exactly the same method as detailed for the ultramicrodisc in Section 5.3 with
the addition of discrete boundary conditions appropriate to the ultramicropipette.
However, the numbering of the concentration values for the phase within the ul-
tramicropipette is expressed with respect to $n_{er}$.

The discretisation of the diffusion equation in an implicit fashion along the
rows together with an explicit expression of the vertical diffusion reads as

$$
\frac{C'_{ner-i,j} - C_{ner-i,j}}{\delta T} =
\frac{D_{er}}{\delta W^2} \left[ C_{ner-i,j-1} - 2C_{ner-i,j} + C_{ner-i,j+1} + \frac{\delta W_i}{2} (C_{ner-i,j+1} - C_{ner-i,j-1}) \right] +
\frac{D_{ner}}{\delta Y^2} \left[ C'_{ner-(i-1),j} - 2C'_{ner-i,j} + C'_{ner-(i+1),j} + \frac{\delta Y_{ner-i}}{2} (C'_{ner-(i+1),j} - C'_{ner-(i-1),j}) \right]
$$

(6.1)

with

$$
\lambda_Y = \frac{D\delta T}{\delta Y^2} \quad \lambda_W = \frac{D\delta T}{\delta W^2}
$$

(6.2)
Chapter 6. Diffusion to an ultramicropipette

This reduces to a general form

\[ C'_{\text{ner}-(i-1),j} - a_3(i)C'_{\text{ner}-(i),j} + a_4(i)C'_{\text{ner}-(i+1),j} = b_{R,i} \]  

(6.3)

with Crank-Nicholson (C-N) coefficients

\[ a_3(i) = \frac{-(1/\lambda_Y \gamma_{\text{ner}-i} + 2)}{1 - \delta Y \beta_{\text{ner}-i}/2}, \quad a_4(i) = \frac{1 + \delta Y \beta_{\text{ner}-i}/2}{1 - \delta Y \beta_{\text{ner}-i}/2} \]  

(6.4)

and

\[ b_{R,i} = \frac{-\lambda_W \alpha_j}{\lambda_Y \gamma_{\text{ner}-i}(1 - \delta Y \beta_{\text{ner}-i}/2)} \cdot \left[ C_{\text{ner}-(i),j-1} - 2C_{\text{ner}-(i),j} + C_{\text{ner}-(i),j+1} + \frac{\delta W \varepsilon_j}{2} \left( C_{\text{ner}-(i),j+1} - C_{\text{ner}-(i),j-1} \right) \right] \]  

(6.5)

Similarly, the discretisation of the diffusion equation in an implicit manner up the columns and explicitly along the rows is given by

\[ \frac{C'_{\text{ner}-(i),j} - C_{\text{ner}-(i),j}}{\delta T} = \frac{D \alpha_i}{\delta W^2} \left[ C'_{\text{ner}-(i-1),j} - 2C'_{\text{ner}-(i),j} + C'_{\text{ner}-(i+1),j} + \frac{\delta W \varepsilon_j}{2} \left( C'_{\text{ner}-(i),j+1} - C'_{\text{ner}-(i),j-1} \right) \right] \]  

(6.6)

\[ + \frac{D \gamma_{\text{ner}-i}}{\delta Y^2} \left[ C_{\text{ner}-(i-1),j} - 2C_{\text{ner}-(i),j} + C_{\text{ner}-(i+1),j} + \frac{\delta Y \beta_{\text{ner}-i}}{2} \left( C_{\text{ner}-(i+1),j} - C_{\text{ner}-(i-1),j} \right) \right]. \]

As before, we collect terms to give the general form

\[ C'_{\text{ner}-(i),j-1} - a_1(j)C'_{\text{ner}-(i),j} + a_2(j)C'_{\text{ner}-(i),j+1} = b_{A,j} \]  

(6.7)

with the following C-N coefficients

\[ a_1(j) = \frac{-(1/\lambda_W \alpha_j + 2)}{1 - \delta W \varepsilon_j/2}, \quad a_2(j) = \frac{1 + \delta W \varepsilon_j/2}{1 - \delta W \varepsilon_j/2} \]  

(6.8)

\[ b_{A,j} = \frac{-\lambda_Y \gamma_{\text{ner}-i}}{\lambda_W \alpha_j(1 - \delta W \varepsilon_j/2)}. \]  

(6.9)
Similarly, the discretisation of the diffusion equation

The discretisation of the diffusion equation in an implicit manner up the columns and explicitly along the rows, with special conditions for the pipette walls, is given by

\[
\frac{C'_{\text{ner},j} - C_{\text{ner},j}}{\delta T} = \frac{D \alpha_j}{\delta W^2} \left[ C'_{\text{ner},j-1} - 2C'_{\text{ner},j} + C'_{\text{ner},j+1} + \frac{\delta W \varepsilon_j}{2} (C'_{\text{ner},j+1} - C'_{\text{ner},j-1}) \right] \\
+ \frac{D \gamma_{\text{ner}}}{\delta Y^2} \left[ C_{\text{ner},j} - C_{\text{ner}-1,j} + \frac{\delta Y \beta_{\text{ner}}}{2} (C_{\text{ner},j} - C_{\text{ner}-1,j}) \right]
\]

(6.10)

As before, we collect terms to give the general form

\[
C'_{\text{ner},j-1} - a_1(j)C'_{\text{ner},j} + a_2(j)C'_{\text{ner},j+1} = b_{A,j}
\]

(6.11)

with the following C-N coefficients

\[
a_1(j) = \frac{-(1/\lambda_W \alpha_j + 2)}{1 - \delta W \varepsilon_j/2}, \quad a_2(j) = \frac{1 + \delta W \varepsilon_j/2}{1 - \delta W \varepsilon_j/2}
\]

(6.12)

\[
b_{A,\text{ner},j} = \frac{-\lambda_Y \gamma_{\text{ner}}}{\lambda_W \alpha_j (1 - \delta W \varepsilon_j/2)} \left[ C_{\text{ner},j} - C_{\text{ner}-1,j} + \frac{\delta Y \beta_{\text{ner}}}{2} (C_{\text{ner},j} - C_{\text{ner}-1,j}) \right] \\
- \frac{C_{\text{ner},j}}{\lambda_W \alpha_j (1 - \delta W \varepsilon_j/2)}
\]

(6.13)

6.3.2 Evaluation of Crank-Nicolson coefficients

For the concentration values outside the ultramicropipette the Crank-Nicolson coefficients are evaluated as detailed in Section 5.3.2. The additional boundary that applies in addition to those detailed in Chapter 4 is

\[
\left( \frac{\partial C}{\partial R} \right)_{R=\text{ner} \delta r_{j}=0} = 0
\]

(6.14)

This leads to the C-N coefficient equation (6.13) being re-expressed as

\[
b_{A,\text{ner},j} = \frac{-C_{\text{ner},j}}{\lambda_W \alpha_j (1 - \delta W \varepsilon_j/2)}
\]

(6.15)

The limiting discretised values of concentration, \( C_{B,\text{ner},j} \) where \( B \) indicates the phase within the pipette, are no longer defined. In this case, \( nr = n_{\text{cr}} \). and
these concentration values must be determined as part of the ADI scheme. This presents a problem as the $C_{B,j}$ values are normally also determined implicitly as part of the ADI scheme. A solution is obtained by calculating the central column of concentration values implicitly in an axial direction and using the values as the boundary conditions for a reversed ADI method with radial concentrations calculated implicitly first and the C-N coefficients numbered with respect to $n_{er}$. This will produce the smallest errors as the central concentration values are subject to only axial, not radial mass transport effects.

The solution of the ADI method then follows the method detailed in Section 5.3.2 using equations (5.27) - (5.31) and the C-N coefficients from Section 6.3.1.

### 6.3.3 Matrix evaluation of C-N coefficients for an ultramicropipette

As detailed in the previous section, for the phase within the pipette the C-N coefficients are numbered with respect to $n_{er}$ and calculated in a reverse order. For the radial solution of the concentration profile (along rows) using boundary condition equation (6.14) and the general form of the discretised diffusion equation, (eqn.(6.5)), the resulting matrices are

\[
\begin{bmatrix}
-25 & 48 & -36 & 16 & -3 & \ldots \\
1 & a_{B,n_{er}-1,j} & 0 & 0 & 0 & \ldots \\
0 & 0 & a_{B,n_{er}-2,j} & 0 & 0 & \ldots \\
0 & 0 & 0 & a_{B,n_{er}-3,j} & 0 & \ldots \\
0 & 0 & 0 & 1 & a_{B,n_{er}-4,j} & \ldots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\end{bmatrix}
\begin{bmatrix}
\vdots \cr C'_{B,n_{er},j} \cr C'_{B,n_{er}-1,j} \cr C'_{B,n_{er}-2,j} \cr C'_{B,n_{er}-3,j} \cr C'_{B,n_{er}-4,j} \\
\vdots \cr \vdots \\
\end{bmatrix}
= 
\begin{bmatrix}
0 \\
b'_{B,n_{er}-1,j} \\
b'_{B,n_{er}-2,j} \\
b'_{B,n_{er}-3,j} \\
b'_{B,n_{er}-4,j} \\
\vdots \\
b'_{B,1,j} \\
\end{bmatrix}
\]
Using boundary condition equation (4.21) and the general form of the discretised diffusion equation, (eqn.(5.20)) for the phase outside the pipette.

\[
\begin{bmatrix}
-25 & 48 & -36 & 16 & -3 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots \\
1 & a_{A,1j} & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & \cdots \\
0 & 1 & a_{A,2j} & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 1 & a_{A,3j} & 0 & \cdots & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 1 & a_{A,4j} & \cdots & 0 & 0 & 0 & 0 & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \ddots \\
\end{bmatrix}
\begin{bmatrix}
C_{A,0j} \\
C_{A,1j} \\
C_{A,2j} \\
C_{A,3j} \\
C_{A,4j} \\
\vdots \\
\end{bmatrix}
= 
\begin{bmatrix}
b'_{A,1j} \\
b'_{A,2j} \\
b'_{A,3j} \\
b'_{A,4j} \\
\vdots \\
\end{bmatrix}
\]

For axial solution of the concentration profile (up columns) where the boundary value for concentration lies on the electrode, \( r \leq r_0 \) and for axial solution of the concentration profile where the boundary value lies on the inert substrate, \( r > r_0 \) the matrices are equivalent to those given in Chapter 5 with the exception that the inert substrate matrix does not contain \( C_B \) values.

\[
\begin{bmatrix}
-25 + 12h_1^2 & 48 & -36 & 16 & -3 & \cdots & +12h_2^2 & 0 & 0 & 0 & 0 & \cdots \\
-25 & 48 & -36 & 16 & -3 & \cdots & -25d_4 & 48d_4 & -36d_4 & 16d_4 & -3d_4 & \cdots \\
1 & a'_{A,1j} & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & \cdots \\
0 & 1 & d'_{A,2j} & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 1 & d'_{A,3j} & 0 & \cdots & 0 & 0 & 0 & 0 & \cdots \\
0 & 0 & 0 & 1 & d'_{A,4j} & \cdots & 0 & 0 & 0 & 0 & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \ddots \\
\end{bmatrix}
\begin{bmatrix}
C_{A,0j} \\
C_{A,1j} \\
C_{A,2j} \\
C_{A,3j} \\
C_{A,4j} \\
\vdots \\
\end{bmatrix}
= 
\begin{bmatrix}
0 \\
0 \\
0 \\
0 \\
0 \\
\vdots \\
\end{bmatrix}
\]

5-point current approximation with an expanded grid

The transformation of the radial and axial fluxes from the expanded to the uniform space grid to give the true current value, is identical to that used for the ultamicrodisc model in the previous chapter.
6.4 Results - Reversible charge transfer

6.4.1 Ultramicropipette - ultramicrodisc equivalence as $\rho \to \infty$

Simulation results for an ultramicropipette may not be measured against any analytical solutions as no analytical solutions exist. What may be shown is the equivalence of the disc and pipette models under limiting conditions. This demonstrates that the approximations required to obtain a tractable ADI method for the ultramicropipette do not compromise the accuracy of the algorithm. Table 6–1 shows how the pipette solution approaches that of the disc as $\rho \to \infty$. $X_{df}$ is the forward peak current for the ultramicrodisc interface, $X_{pf}$ is the forward (ingress) peak current for the ultramicropipette and $X_{th}$ is the theoretical peak current derived from the pseudo-analytical solution, equation (2.25). The grid expansion parameters for both axial and radial space grids are optimised as detailed in Chapter 5 and are the same for both pipette and disc models. The lower diffusion-limited peak current for the ultramicropipette at lower values of $\rho$ arises due to the restricted diffusion away from the interface causing the electroactive species to ‘back-up’ af-

<table>
<thead>
<tr>
<th>$\rho$</th>
<th>$X_{th}$</th>
<th>$X_{df}$</th>
<th>$X_{pf}$</th>
<th>$X_{df}/X_{pf}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.791</td>
<td>1.6882</td>
<td>1.62043</td>
<td>1.59783</td>
<td>1.0141</td>
</tr>
<tr>
<td>8.372</td>
<td>3.5650</td>
<td>3.44496</td>
<td>3.39451</td>
<td>1.0149</td>
</tr>
<tr>
<td>13.95</td>
<td>5.4974</td>
<td>5.33056</td>
<td>5.29332</td>
<td>1.0070</td>
</tr>
<tr>
<td>27.91</td>
<td>10.369</td>
<td>10.1148</td>
<td>10.0718</td>
<td>1.0043</td>
</tr>
<tr>
<td>83.72</td>
<td>29.932</td>
<td>29.4144</td>
<td>29.3979</td>
<td>1.00056</td>
</tr>
<tr>
<td>139.5</td>
<td>49.504</td>
<td>48.7801</td>
<td>48.7720</td>
<td>1.00020</td>
</tr>
<tr>
<td>279.1</td>
<td>98.499</td>
<td>97.27130</td>
<td>97.26928</td>
<td>1.00002</td>
</tr>
</tbody>
</table>

**Table 6–1:** Ultramicropipette - ultramicrodisc equivalence as $\rho \to \infty$
ter it has crossed the interface. This results in a lower the interfacial concentration difference and a correspondingly lower interfacial current.

6.4.2 Ultramicrointerface in a cylinder - comparison to theory

To model diffusion within the ultramicropipette and particularly egress transfer from the ultramicropipette, it is equally important to develop a grid expansion that closely models the concentration profile within the pipette. No analytical solutions or pseudo-analytical solutions have been presented to date to simulate charge transfer at an ultramicropipette. It is not possible to directly determine the accuracy of the simulation or the quantity of error produced on variation of the grid expansion parameters.

A good estimate of the optimum radial and axial grid expansion parameters may be made by optimising the solution for diffusion at an ultramicro-interface within a very narrow, semi-infinite cylinder. Diffusion within a cylinder is considered to approximate to linear diffusion, neglecting the hydrodynamic effects of drag from the cylinder walls and only considering diffusion limited mass transport. As such, the simulation may be compared to the work of Nicolson and Shain [65] and the peak current produced due to diffusion limited mass transport and charge transfer at the interface may be calculated from the Randles-Sevčik equation

$$i_{\text{peak}} = (2.69 \times 10^3)n^{3/2}AD_0^{1/2}v^{1/2}c_0^b$$  \hspace{1cm} (6.16)

6.4.3 Ultramicropipette - optimisation of grid expansions

A number of simulations of charge transfer at an ultramicrointerface in a cylinder have been performed to optimise the grid expansion parameters and the results are presented in figures 6–2 and 6–3. As can be seen from figures 6–2 and 6–3 the accuracy of the simulation is affected primarily by the time and axial increments
Chapter 6. Diffusion to an ultramicropipette

Figure 6–2: Optimisation of $\delta z$ and $\delta t$
Figure 6-3: Optimisation of $\delta r$ and $\delta z$
Chapter 6. Diffusion to an ultramicropipette

<table>
<thead>
<tr>
<th>( \rho )</th>
<th>( \chi_{\text{linear}} )</th>
<th>( \chi_{\text{pipette}} )</th>
<th>( \chi_{\text{linear}}/\chi_{\text{pipette}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.632</td>
<td>0.2224</td>
<td>0.1085</td>
<td>2.050</td>
</tr>
<tr>
<td>0.885</td>
<td>0.4381</td>
<td>0.3686</td>
<td>1.189</td>
</tr>
<tr>
<td>1.14</td>
<td>0.5237</td>
<td>0.4603</td>
<td>1.138</td>
</tr>
<tr>
<td>3.6</td>
<td>1.3097</td>
<td>1.2668</td>
<td>1.034</td>
</tr>
<tr>
<td>11.4</td>
<td>4.0206</td>
<td>4.0035</td>
<td>1.004</td>
</tr>
<tr>
<td>113.7</td>
<td>39.687</td>
<td>39.665</td>
<td>1.0006</td>
</tr>
</tbody>
</table>

**Table 6-2**: Ultramicropipette - semi-infinite plane equivalence as \( \rho \to \infty \)

of the ADI method, \( \delta t \) and \( \delta z \). \( \delta r \) does not greatly affect the accuracy of the simulation so the optimisation of the radial grid expansion coefficient is secondary to the axial grid expansion coefficient for egress transfer. Using figure 6-2 after deciding appropriate experimental parameters \( \tau, \nu \) and simulation parameter \( nt \) to give the time increment \( \delta t \) we may determine the appropriate initial axial increment \( \delta z(0) \) that will give a space grid expansion that will models most closely the concentration gradient within the pipette. The lower axis of figure 6-2 gives the appropriate value for the axial space grid expansion parameter that may be entered into the simulation program along with the other simulation parameters.

For the simulation of an ultramicro-interface in a cylinder the radial grid expansion parameter may be arbitrarily set at the same value as the axial parameter. Due to the dimensionless calculation of the grid expansion parameters within the computer programme, a single grid expansion parameter will suffice for all interfacial radii.

Having obtained an expansion coefficient to optimise the space grid within the ultramicropipette, we may now consider the diffusion regime outside of the pipette. Egress transfer from an ultramicropipette tends towards semi-infinite linear diffusion as \( \rho \to \infty \) (see table 6-2). This shows the equivalence of the interface in a cylinder and the pipette models under limiting value conditions. The space grid expansion for the inside of the ultramicropipette may be transferred
Once the grid expansion coefficients have been obtained - from the disc model for outside the pipette and from the ultramicrointerface in a tube for inside the pipette we may vary the experimental parameters and observe the effect on the \( i - E - t \) response. The radial grid expansion for both phases is determined by the optimum grid expansion parameter for the phase outside the pipette. This is because we may optimise the radial grid expansion through the disc model and a differing radial increment has very little effect on the accuracy of the simulation of diffusion within the pipette.
6.4.4 Ultramicropipette - comparison to a pseudo-analytical approximation and experimental results

A pseudo-analytical approximation to diffusion at an ultramicropipette has been developed by Stewart et al [187]. The approximation is a development of the spherical-linear diffusion approximation detailed in Chapter 3. We may compare the results of this approximation and experimental results to the simulation of ultramicropipette behaviour detailed in the sections above.

Linear Sweep Voltammetry

Egress transfer cyclic voltammograms for a reversible reaction at an ultramicropipette are shown in figure 6-5. A plot of peak height versus root sweep rate (figure 6-6) shows that egress transfer from an ultramicropipette obeys the Randles-Sevčik equation. Figure 6-5 may also be compared with the pseudo-analytical solutions for egress transfer based on the spherical linear diffusion model outlined in Chapter 3 [187]. The numerical solution, allowing for cylindrical diffusion, provides a more accurate model of the charge transfer. This is supported by errors of less than 0.5% versus the R-S equation against errors of approximately 3% for the pseudo-analytical case.

Asymmetric Sweep Voltammetry

Due to the asymmetry of the diffusion field cyclic voltammetry is not a facile technique for the study of charge transfer at an ultramicropipette. As shown in figure 6-7 the reverse scan of a steady-state wave is not symmetrical, as found at a microdisc electrode, but a peak-shaped voltammogram. The shape of the voltammogram and position of peak potentials may not be expressed analytically as with the ultramicrodisc. (See Section 5.4). A cyclic voltammetric technique for ingress/egress transfer which may find analytical application is asymmetric
Figure 6-5: Cyclic voltammograms for egress transfer (experimental conditions of \( r_0 = 17\mu m \) and \( \nu = 0.02, 0.04, 0.08, 0.10, 0.14, 0.18 \) V/s, \( D = 7 \times 10^{-6} \text{ cm}^2 \text{s}^{-1} \)).
Figure 6–6: Plot of $\chi$ vs. $\sqrt{\nu}$ for figure 6–5
Figure 6-7: Cyclic voltammetry at an ultramicropipette ingress first, $\rho = 0.566$
sweep rate cyclic voltammetry (fig. 6-8). The forward sweep is carried out at a constant rate, and the reverse sweep rate is varied. The reverse peak height shows a linear dependence on the square root of the reverse sweep rate and the gradient of \( i \, \text{vs.} \, \nu^{\frac{1}{2}} \) is dependent on the forward sweep rate (fig. 6-9). The simulation results presented in figures 6-8 and 6-9 do not compare closely with the approximate pseudo-analytical solution presented in ref. [187]. The discrepancies between the simulation, the pseudo-analytical solution and the experimental results [187] may be attributed, respectively to

1. The spherical-linear approximation to cylindrical diffusion within the pipette is not accounted for. Diffusion within the pipette will always be modelled as linear. This is acceptable at high sweep rates or large electrode sizes (\( \rho \) is large) but for low sweep rates and small interfaces (\( \nu = 0.049V/s, \, r_0 = 9\mu m \) as in fig. 6-8) the approximation is not accurate.

2. The finite pipette wall thickness produces a larger experimental current than expected. As the interface is not set in a semi-infinite insulating plane, electroactive species may diffuse to the interface from below the level of the plane further enhancing the mass transport to the ultramicrointerface.

6.5 Results - Quasi-reversible/Irreversible charge transfer

Cyclic voltammetry

The variation of cyclic voltammetric response with various kinetic parameters \((k, \Lambda, a)\) is shown in figures 6-10 and 6-11. Cyclic voltammograms with higher value of \( \rho \), are shown in figure 6-11. For the almost completely reversible peak the cyclic voltammograms again appear very similar to those encountered under
Figure 6-8: Asymmetric sweep voltammograms (experimental conditions of $r_0 = 9 \mu m$, $v_f = 0.049 V/s$ and $v_r = 0.009, 0.016, 0.025, 0.036, 0.049, 0.064, 0.081, 0.100, 0.121, 0.144 V/s$, $D = 7 \times 10^{-6} cm^2 s^{-1}$).
Figure 6-9: Plot of $\chi$ vs. $\nu^{1/2}$ for the previous figure with $\nu_f = 0.025(\circ), 0.049(\Box), 0.081(\times) V/\text{s}$. 
Figure 6-10: Linear sweep voltammetry at an ultramicropipette, variable $k$. $\rho=0.099$
Figure 6-11: Fast CV at an ultramicropipette interface

As figure 6-10, cyclic voltammetry, $\rho = 1.395$, $n = 1$, $T = 25^\circ C$, $c_b = 10^{-6}$ mol cm$^{-3}$, $r_0 = 5 \times 10^{-4}$, $D = 10^{-5}$. 
planar diffusion [106] the egress peak showing more 'linear character' as expected. The shift of half wave potential for irreversible kinetics is again 118mV/decade for figure 6–11 illustrating that this effect is independent of scan rate. The steady-state is not a prerequisite in either the ultramicrodisc or the ultramicropipette.

6.6 Summary

The technique presented provides a rapid accurate simulation of diffusive mass transport at an ultramicropipette. Incorporation of an expanded grid that closely follows the differing concentration gradients on either side of the interface greatly increases the speed and accuracy of the digital simulation. Simplification of the model to an ultramicrointerface in a tube allows optimisation of the ‘inside’ grid expansion against available solutions for linear diffusion. The ‘outside’ grid expansion may be transported directly from the ultramicrodisc algorithm.

Kinetically controlled cyclic voltammetry at an ultramicropipette may be easily simulated using this model. For ingress transfer on the forward scan the results compare closely with those found for an ultramicrodisc, as expected. Kinetics effects on the reverse scan are much more marked in the case of the ultramicropipette due to better defined current peaks resulting from the asymmetric diffusion profile. Simulation over a range of kinetic parameters and comparison to experimental results would provide an easy and accurate measure of charge transfer kinetics at an ultramicropipette.
Chapter 7

Conclusions

This work presents a novel algorithm for the simulation of charge transfer at ultramicrointerfaces. The Alternating Direction Implicit (ADI) method is extended to include expansion of the space grid in two dimensions, a n-point current calculation and implicit determination of boundary conditions. The algorithm is fast, stable and accurate over a wide range of experimental parameters and is easily adapted to different electrode geometries and experimental techniques including cyclic voltammetry and chronoamperometry at macro, ultramicrodisc and ultramicropipette electrodes, including asymmetric sweep voltammetry at ultramicropipette electrodes. Results are easily obtained for both reversible and quasi-reversible charge transfer and the effects of sweep rate, electrode radius, charge transfer coefficient and rate of charge transfer may be studied.

However, careful consideration is required of; simulation point separation, choice of grid expansion equation, boundary conditions and the relative number of points on the interface and in solution. Also, diffusion geometry, time increment, and the stability of algorithm must be considered in detail. In comparison to the various methods currently available to model electrochemical response at ultramicrointerfaces the above approach gives a high degree of accuracy, and has the advantage that it is not limited to a range of experimental parameters or requires the assumption of limiting behaviour (e.g. steady-state).
Appendix A

Computing

The programs modelling the charge transfer processes are written in FORTRAN and run on the Edinburgh Multi-Access System (EMAS) on a NAS EX/40 machine. The programs were compiled using an Amdahl FORTRAN 77 compiler version 2.2 using source level optimisation within each program. As a guide to the time and computer resources required to perform the numerical simulations each iteration within the programs consumes approximately 0.43 cpu seconds. Source codes of all programs are available on request.

The example given below is for cyclic voltammetry at an ultramicropipette with ingress then egress charge transfer. The program allows for differing grid expansion coefficients inside and outside the pipette.

```fortran
program dcinasymnu2

C-------------------------------------------------------------------
C WRITTEN BY GORDON TAYLOR
C
C Asymmetric sweep rate (introduce NFACTOR)
C```

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c NR,Nz fixed at 200,100, dt,delta,lr,lz all variable
C
C AFD to allow for optimisation of radial grid
C CFD to allow for optimisation of axial grid in pipette.

C Quasi-reversible cyclic voltammetry by the ADI method.
c This program models CYLINDRICAL diffusion
c on both sides of the interface. Restricted diffusion for
c species B.
c
C Implicit calculation of all concentration points
c including boundary values.
c
C ASSUMPTION: Diffusion at interface is controlled by
C Butler-Volmer equation only, no radial diffusion
C on the interface.

IMPLICIT DOUBLE PRECISION(A-H,L,O-Z)
DOUBLE PRECISION NU,NFACTOR,KS,KF,KB

DIMENSION R(0:200),DR(200)
COMMON/BLK0in/A1in(100),A2in(100)
COMMON/BLK0out/A1out(100),A2out(100)
COMMON/BLK1/CST1in(100),CST1out(100),CST2
COMMON/BLK2/A3(200),A4(200)
COMMON/BLK3/CST6,CST7(200)
COMMON/BLK5in/CST3in(200,100),CST4in(200,100),CST5in(200,100)
Appendix A. Computing

COMMON/BLK6in/CST8in(200,100),CST11in(200,100),CST12in(200,100)
COMMON/BLK5out/CST3out(200,100),CST4out(200,100),CST5out(200,100)
COMMON/BLK6out/CST8out(200,100),
CST11out(200,100),CST12out(200,100)
COMMON/BLK8/CA(0:201,0:101),CANEW(0:201,0:101)
COMMON/BLK9/CB(0:201,0:101),CBNEW(0:201,0:101)
COMMON/BLK10/CST9in(100),CST9out(100),CST10(100)

CHARACTER*6 FNAME
CHARACTER*2 NUMFIL

DO 1 I=0,201
   DO 2 J=0,101
      CA(I,J)=1.0DO
      CANEW(I,J)=1.0DO
      CB(I,J)=0.0DO
      CBNEW(I,J)=0.0DO
   2 CONTINUE
   1 CONTINUE

NUM=10
alpha=.5
FNAME='CVIN'
BEYOND=0.
PI=4.*ATAN(1.)
F=96485.0D0
DIFCO=0.00001DO
OPEN(12,FILE=FNAME, 
   @ ACCESS='SEQUENTIAL',FORM='FORMATTED')

C

C READ IN EXPERIMENTAL PARAMETERS.
C

3 READ(5,*) AFD,CFD,NU,NUFACTOR,TAU,NT,RADIUS,KS

C

C GRID EXPANSION PARAMETERS
C

A=AFD*RADIUS
B=RADIUS
Cin=CFD*RADIUS
Cout=AFD*RADIUS
print*, 'a', a, 'cin,cout', cin, cout

prange= nu*tau
dt=tau/nt
p= -prange/2.
 pstep = nu*dt
 do 40 icycl=1,2
  if(icycl.eq.2) then
   nu=nu*nufactor
   tau=tau/nufactor
   dt=tau/nt
   pstep=-nu*dt
  endif

C

C CALCULATION OF DISTANCE INCREMENT.
NR=200
NZ=100

C Axial Expansion

DELTA=SQRT(DIFCO*TAU)
ZLIM=10.*DELTA

C Expansion for inside the pipette

IF(ZLIM/Cin.GT.174) THEN
   WLIM=0.5
ELSE
   WLIM=0.5-1./(EXP(ZLIM/Cin)+1)
ENDIF
NW=100
DWin=WLIM/NW
DZ0in=Cin*LOG((0.5+DWin)/(0.5-DWin))

C Expansion for outside the pipette

IF(ZLIM/Cout.GT.174) THEN
   WLIM=0.5
ELSE
   WLIM=0.5-1./(EXP(ZLIM/Cout)+1)
ENDIF
NW=100
Appendix A. Computing

\[
DW_{\text{out}} = \frac{W_{\text{lim}}}{N_W}
\]

\[
DZ_{0\text{out}} = C_{\text{out}} \times \log\left(\frac{0.5 + DW_{\text{out}}}{0.5 - DW_{\text{out}}}\right)
\]

print*,' zlim',zlim,' dz0in,dz0out',dz0in,dz0out

C

C Radial Expansion

C

\[
RL_{\text{lim}} = 10 \times R_{\text{ADIUS}}
\]

\[
YL_{\text{lim}} = \frac{1}{\exp((RL_{\text{lim}} - B)/A) + 1.}
\]

\[
Y_0 = \frac{1}{\exp(-B/A) + 1.}
\]

\[
Y_{\text{RANGE}} = Y_{\text{LIM}} - Y_0
\]

NY = 200

DY = Y_{\text{RANGE}} / NY

\[
Y_{\text{RADIUS}} = 0.5 ! \text{Point of inflection, smallest}
\]

NER = (Y_{\text{RADIUS}} - Y_0) / DY ! grid spacing.

PRINT* , NER, 'POINTS ON ELECTRODE'

YY = Y_{\text{RADIUS}} + DY

\[
D_{\text{RO}} = A \times \log\left(YY/(1.-YY)\right)
\]

PRINT*,'FIRST INCREMENT BEYOND ELECTRODE',DRO,' CM'

\[
L_{\text{R}} = DIFCO \times DT/D_{\text{RO}}^{*2}.
\]

\[
L_{\text{Zin}} = DIFCO \times DT/DZ_{0\text{in}}^{*2}.
\]

\[
L_{\text{Zout}} = DIFCO \times DT/DZ_{0\text{out}}^{*2}.
\]

\[
L_{\text{Y}} = DIFCO \times DT/DY^{*2}.
\]

\[
L_{\text{Win}} = DIFCO \times DT/DW_{\text{in}}^{*2}.
\]

\[
L_{\text{Wout}} = DIFCO \times DT/DW_{\text{out}}^{*2}.
\]

C CALCULATION OF CONVERSION FACTORS

C FOR POLYNOMIAL CURRENT EXPANSION

C (Current is calculated in expanded grid coordinates)
that are regularly spaced, then converted back to standard coordinates and multiplied by the conversion factor."

```
CFAXIALin = 1./(4.* Cin)  !corrected 30/1/90
CFAXIALout = 1./(4.* Cout) !corrected 30/1/90
CFRADIAL= 1./A * (EXP(-B/A))/(EXP(-B/A)+1)**2.
```

C CALCULATION OF RADIAL STEPS ACROSS ELECTRODE SURFACE

```
Y=YO
R(0)=0.
DO 33 I=1,nr
  Y=Y+DY
  R(I)=A*LOG(Y/(1.-Y))+B
33 CONTINUE
  DO 34 I=1,NER+1
    DR(I)=R(I)-R(I-1)
34 CONTINUE

AREA=PI*RADIUS**2
PRINT 6000, NT,LR,LZin,LZout,DR0,DZ0in,DZ0out,NR,NZ
PRINT*,RADIUS,' CM RADIUS ELECTRODE.'
PRINT 6010
```

C

C CALCULATION OF C-N COEFFICIENTS.

C
Appendix A. Computing

CST2 = 0.0D0
CST6 = 0.0D0

WIN = 0.0D0
WOUT = 0.0D0
DO 7 J = 1, NZ
    Y = Y0
    WIN = WIN + DWIN
    WOUT = WOUT + DWOUT
DO 7 I = 1, NR
    Y = Y + DY

BETA = (1. - 2. * Y + 1. / (LOG(Y/(1. - Y)) + (B/A)))/Y/(1.-Y)
EPSILONIN = -2.*WIN/(0.25-WIN*WIN)
EPSILONOUT = -2.*WOUT/(0.25-WOUT*WOUT)

TERM = 1.-DY*BETA/2.
TERM2IN = 1.-DWIN*EPSILONIN/2.
TERM2OUT = 1.-DWOUT*EPSILONOUT/2.
FACTOR = LY*(Y*(1.-Y)/A)**2.
FACTOR2IN = LWIN*((0.25-WIN*WIN)/CIN)*((0.25-WIN*WIN)/CIN)
FACTOR2OUT = LWOUT*((0.25-WOUT*WOUT)/COUT)*((0.25-WOUT*WOUT)/COUT)

C Inside pipette C-N CSTants
CST3IN(I,J) = -FACTOR*TERM/FACTOR2IN/TERM2IN
CST4IN(I,J) = (FACTOR*2.-1.)/FACTOR2IN/TERM2IN
CST5IN(I,J) = -FACTOR*(1.+DY*BETA/2.)/FACTOR2IN/TERM2IN
CST8IN(I,J) = (2.*FACTOR2IN-1.)/FACTOR/TERM
CST11IN(I,J) = -FACTOR2IN*(1.+DWIN*EPSILONIN/2.)/FACTOR/TERM
Appendix A. Computing

CST12in(I,J) = -FACTOR2in*TERM2in/FACTOR/TERM

C Outside pipette C-N CSTants
CST3out(I,J) = -FACTOR*TERM/FACTOR2out/TERM2out
CST4out(I,J) = (FACTOR*2. -1.)/FACTOR2out/TERM2out
CST5out(I,J) = -FACTOR*(1.+DY*BETA/2.)/FACTOR2out/TERM2out
CST8out(I,J) = (2.*FACTOR2out-1.)/FACTOR/TERM
CST11out(I,J) = -FACTOR2out*(1.+DWout*EPSILONout/2.)/FACTOR/TERM
CST12out(I,J) = -FACTOR2out*TERM2out/FACTOR/TERM

IF(J.EQ.1) THEN
CST7(I) = -1./FACTOR/TERM
A3(I) = -(2.+1./FACTOR)/TERM
A4(I) = (1.+DY*BETA/2.)/TERM
ENDIF

IF(I.EQ.NER) THEN

C Inside pipette C-N CSTants
A1in(J) = -(2.+1./FACTOR2in)/TERM2in
A2in(J) = (1.+DWin*EPSILONin/2.)/TERM2in
CST1in(J) = -1./FACTOR2in/TERM2in
CST9in(J) = -1./FACTOR2in/TERM2in

C Outside pipette C-N CSTants
A1out(J) = -(2.+1./FACTOR2out)/TERM2out
A2out(J) = (1.+DWout*EPSILONout/2.)/TERM2out
CST1out(J) = -1./FACTOR2out/TERM2out
CST9out(J) = -1./FACTOR2out/TERM2out
CSS10(J)=0.0d0

ENDIF
7 CONTINUE

C
C DENOMINATOR DETERMINES NUMBER OF POINTS FOR CYCLIC VOLTAMMOGRAM.
C
NINT=NT/10
K=1
INTV=0
C
C CALCULATION OF CONCENTRATION PROFILES AND RESULTING CV
C OVER NT POTENTIAL STEPS.
C
DO 40 IT1,nt
   CURRTOT=0.0
   P=P+PSTEP
   KF=KS*EXP(P*ALPHA*F/8.314/298.)
   KB=KS*EXP(-(1.-ALPHA)*P*F/8.314/298.)
C
C THIS SECTION ALTERNATES BETWEEN ROW AND COLUMN
C CONCENTRATION CALCULATIONS.
C
K=1-K
   IF(K .EQ. 0) THEN
      DO 15 II=0,NR
         IFLAG=II
         ..
CALL CNSOLZ(IFLAG,NZ,NER,KF,KB)
IF (CANEW(II,NZ).LT.0.995) BEYOND=1.
15 CONTINUE
16 ELSE

IFLAG=0
CALL CNSOLZ(IFLAG,NZ,NER,KF,KB)
DO 20 J=0,NZ
   JFLAG=J
   CALL CNSOLR(JFLAG,NR,NER)
   IF(CA(NR,J).LT.0.995) BEYOND=1.
20 CONTINUE
21 ENDIF

C
C SET CONCENTRATIONS TO NEW VALUES.
C

DO 30 I=0,NR
   DO 30 J=0,NZ
      CA(I,J)=CANEW(I,J)
      IF(I.LE.NER) CB(I,J)=CBNEW(I,J)
30 CONTINUE

INTV=INTV+1
IF(K.EQ.0) THEN
   IF(INTV.LT.NINT) GOTO 38
   INTV=0
C
Appendix A. Computing

C Current calculation dependent on sweep direction
C

38 if(icycl.eq.1) then

DO 35 I=1,NER

ANNULUS=(R(I)+DR(I+1)/2.)**2.-(R(I)-DR(I)/2.)**2.
IF(I.EQ.NER) ANNULUS=2.*R(I)*DR(I)/2.-0.25*DR(I)**2.
CC=(-25.*CA(I,0)+48.*CA(I,1)-36.*CA(I,2)+16.*CA(I,3)-3.*CA(I,4))
CURRC=CC*F*PI*ANNULUS*DIFCO/DWout/12.
CURRTOT=CURRTOT+CURRC

35 CONTINUE

CC=(-25.*CA(0,0)+48.*CA(0,1)-36.*CA(0,2)+16.*CA(0,3)-3.*CA(0,4))
CURRC=CC*PI*DR0*DR0*F*DIFCO/DWout/48.
CURRTOT=CURRTOT+CURRC

C Transformation from expanded grid space back to real space.
CURRTOT=CURRTOT*CFAXIALout

ELSE

DO 45 I=1,NER

ANNULUS=(R(I)+DR(I+1)/2.)**2.-(R(I)-DR(I)/2.)**2.
IF(I.EQ.NER) ANNULUS=2.*R(I)*DR(I)/2.-0.25*DR(I)**2.
CC=(-25.*CB(I,0)+48.*CB(I,1)-36.*CB(I,2)+16.*CB(I,3)-3.*CB(I,4))
CURRC=CC*F*PI*ANNULUS*DIFCO/DWin/12.
CURRTOT=CURRTOT+CURRC

45 CONTINUE

CC=(-25.*CB(0,0)+48.*CB(0,1)-36.*CB(0,2)+16.*CB(0,3)-3.*CB(0,4))
CURRC=CC*PI*DR0*DR0*F*DIFCO/DWin/48.
CURRTOT = CURRTOT + CURRc

C Transformation from expanded grid space back to real space.
CURRTOT = CURRTOT * CFAXIALin

ENDIF

C Transformation of current into experimental variable
C independent units chi & xi

T = IT * DT
chi = CURRTOT / (4. * F * DIFCO * RADIUS)
xi = P * F / 8.314 / 298
PRINT(6020), IT, T, xi, chi
WRITE (12, *) (xi, chi)
ENDIF

40 CONTINUE
CLOSE (UNIT = 12)

PRINT*, 'Reduced accuracy for x/ylim.'
PRINT*, 'Overrun set at 0.995 before warning.'
IF (BEYOND.GT.0.5) PRINT*, 'WARNING -DIFFUSION BEYOND 10*RADIUS'
STOP

6000 FORMAT ('1 Cyclic Voltammetry by C-N'//
@ ' NT/T = ', I8/, ' LAMBDA R,Zin,Zout= ' 3E10.2/, 
@ ' DRO,DZ0in,DZ0out = ' 3E10.2/, ' NR,NZ = ', 2I8/) 
6010 FORMAT(4X,'IT',5X,'T',7X,'nF(E'-Eo)/RT',3x,'i/4rnFDc',//) 
6020 FORMAT(I6,f11.5,4X,2F11.5) 
6030 FORMAT(I2)
SUBROUTINE CNSOLR(JJ, N, NER)

IMPLICIT DOUBLE PRECISION (A-H,O-Z)

COMMON/BLK2/A3(200),A4(200)
COMMON/BLK3/CST6,CST7(200)
COMMON/BLK6in/CST8in(200,100),CST11in(200,100),CST12in(200,100)
COMMON/BLK6out/CST8out(200,100),
  CST11out(200,100),CST12out(200,100)
COMMON/BLK8/CA(0:201,0:101),CANEW(0:201,0:101)
COMMON/BLK9/CB(0:201,0:101),CBNEW(0:201,0:101)

DIMENSION AAD(200),ABD(200),ABTERM(200)
DIMENSION BAD(200),BBD(200),BBTERM(200)

CADN=CANEW(N+1,JJ)

DO 10 I=1,N
   C2=CA(I,JJ)
   C1=CA(I,JJ+1)
   IF(JJ.EQ.0) THEN
      ABTERM(I)=CST6*C1+CST7(I)*C2
   ELSE
      C3=CA(I,JJ-1)
Appendix A. Computing

\[ \text{ABTERM}(I) = \text{CST11out}(I,JJ) \times C1 + \text{CST8out}(I,JJ) \times C2 + \text{CST12out}(I,JJ) \times C3 \]

ENDIF

10 CONTINUE

\[ \text{AAD}(N) = \text{A3}(N) \]
\[ \text{ABD}(N) = \text{ABTERM}(N) - \text{CADN} \times \text{A4}(N) \]

DO 20 K = N-1, 1, -1
\[ \text{AAD}(K) = \text{A3}(K) - \text{A4}(K) / \text{AAD}(K+1) \]
\[ \text{ABD}(K) = \text{ABTERM}(K) - \text{A4}(K) \times \text{ABD}(K+1) / \text{AAD}(K+1) \]

20 CONTINUE

C IMPLICIT CO' CALCULATION - 5 POINT METHOD.

\[ \text{AU1} = \text{ABD}(1) / \text{AAD}(1) \]
\[ \text{AV1} = -1 / \text{AAD}(1) \]
\[ \text{AU2} = (\text{ABD}(2) - \text{AU1}) / \text{AAD}(2) \]
\[ \text{AV2} = -\text{AV1} / \text{AAD}(2) \]
\[ \text{AU3} = (\text{ABD}(3) - \text{AU2}) / \text{AAD}(3) \]
\[ \text{AV3} = -\text{AV2} / \text{AAD}(3) \]
\[ \text{AU4} = (\text{ABD}(4) - \text{AU3}) / \text{AAD}(4) \]
\[ \text{AV4} = -\text{AV3} / \text{AAD}(4) \]
\[ \text{AP} = 48 \times \text{AU1} - 36 \times \text{AU2} + 16 \times \text{AU3} - 3 \times \text{AU4} \]
\[ \text{AQ} = -25 + 48 \times \text{AV1} - 36 \times \text{AV2} + 16 \times \text{AV3} - 3 \times \text{AV4} \]
\[ \text{AGAH} = 0.0 \]
\[ \text{CANEW}(0, JJ) = (\text{AGAH} - \text{AP}) / \text{AQ} \]

DO 30 I = 1, N
\[ \text{IF}(JJ \text{EQ} 0 \text{AND} I \text{LE} \text{NER}) \text{THEN} \]


Appendix A. Computing

\[
\text{CANEW}(I,JJ) = \text{CANEW}(I-1,JJ) \quad \text{ELSE} \\
\text{CANEW}(I,JJ) = \frac{(ABD(I) - \text{CANEW}(I-1,JJ))}{AAD(I)} \\
\text{ENDIF}
\]

30 CONTINUE

C Calculation of concentration values within pipette

\[
\text{DO 40 } I = 1, \text{NER}-1 \\
\quad \text{C2 = CB}(I,JJ) \\
\quad \text{C1 = CB}(I,JJ+1) \\
\quad \text{IF} (JJ \cdot \text{EQ}. 0 \text{ THEN} \\
\quad \quad \text{BBTERM}(I) = \text{CST6} \times \text{C1} + \text{CST7}(I) \times \text{C2} \\
\quad \quad \text{ELSE} \\
\quad \quad \quad \text{C3 = CB}(I,JJ-1) \\
\quad \quad \quad \text{BBTERM}(I) = \text{CST11in}(I,JJ) \times \text{C1} + \text{CST8in}(I,JJ) \times \text{C2} + \text{CST12in}(I,JJ) \times \text{C3} \\
\quad \text{ENDIF}
\]

40 CONTINUE

\[
\text{BAD}(1) = A3(1) \\
\text{BBD}(1) = \text{BBTERM}(1) - \text{CBNEW}(0,JJ) \times A4(1) \\
\text{DO 50 } K = 2, \text{NER}-1 \\
\quad \text{BAD}(K) = A3(K) - A4(K) / \text{BAD}(K-1) \\
\quad \text{BBD}(K) = \text{BBTERM}(K) - A4(K) \times \text{BBD}(K-1) / \text{BAD}(K-1)
\]

50 CONTINUE

C IMPLICIT Cner' CALCULATION - 5 POINT METHOD.
Appendix A. Computing

BUNER1 = BBD(NER-1)/BAD(NER-1)
BVNER1 = -1./BAD(NER-1)
BUNER2 = (BBD(NER-2)-BUNER1)/BAD(NER-2)
BVNER2 = -BVNER1/BAD(NER-2)
BUNER3 = (BBD(NER-3)-BUNER2)/BAD(NER-3)
BVNER3 = -BVNER2/BAD(NER-3)
BUNER4 = (BBD(NER-4)-BUNER3)/BAD(NER-4)
BVNER4 = -BVNER3/BAD(NER-4)
BP = 48.*BUNER1-36.*BUNER2+16.*BUNER3-3.*BUNER4
BQ = -25.+48.*BVNER1-36.*BVNER2+16.*BVNER3-3.*BVNER4
BGAH = 0.D0
CBNEW(NER, JJ) = (BGAH-BP)/BQ

DO 60 I=NER-1,1,-1
   CBNEW(I, JJ) = (BBD(I)-CBNEW(I+1, JJ))/BAD(I)
60 CONTINUE
RETURN
END

SUBROUTINE cnso1z(II,N,NER,KF,KB)
C
C SOLVES THE I-DEPENDENT CRANK-NICOLSON SYSTEM.
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DOUBLE PRECISION KF,KB
Appendix A. Computing

COMMON/BLK0in/A1in(100),A2in(100)
COMMON/BLK0out/A1out(100),A2out(100)
COMMON/BLK1/CST1in(100),CST1out(100),CST2
COMMON/BLK5in/CST3in(200,100),CST4in(200,100),CST5in(200,100)
COMMON/BLK5out/CST3out(200,100),CST4out(200,100),CST5out(200,100)
COMMON/BLK8/CA(0:201,0:101),CANEW(0:201,0:101)
COMMON/BLK9/CB(0:201,0:101),CBNEW(0:201,0:101)
COMMON/BLK10/CST9in(100),CST9out(100),CST10(100)

DIMENSION AADD(100),ABDD(100),ABTERMM(100)
DIMENSION BADD(100),BBDD(100),BBTERMM(100)

CADN=CANEW(II,N+1)
DO 10 JJ=1,N
   C2=CA(II,JJ)
   C3=CA(II+1,JJ)
   IF (II.EQ.0) THEN
      ABTERMM(JJ)=CST1out(JJ)*C2-CST2*C3
   ELSE
      C1=CA(II-1,JJ)
      ABTERMM(JJ)=CST3out(II,JJ)*C1+CST4out(II,JJ)*C2+CST5out(II,JJ)*C3
   ENDIF
10 CONTINUE

AADD(N)=A1out(N)
ABDD(N)=ABTERMM(N)-CADN*A2out(N)
DO 20 K=N-1,1,-1
   AADD(K)=A1out(K)-A2out(K)/AADD(K+1)
\[ ABDD(K) = ABTERM(K) - A2out(K) \times ABDD(K+1) / AADD(K+1) \]

\[ \text{CONTINUE} \]

C \text{ IMPLICIT CO' CALCULATION - 5 POINT METHOD.}

\[ \text{AU1} = ABDD(1) / AADD(1) \]
\[ \text{AV1} = -1. / AADD(1) \]
\[ \text{AU2} = (ABDD(2) - AU1) / AADD(2) \]
\[ \text{AV2} = -AV1 / AADD(2) \]
\[ \text{AU3} = (ABDD(3) - AU2) / AADD(3) \]
\[ \text{AV3} = -AV2 / AADD(3) \]
\[ \text{AU4} = (ABDD(4) - AU3) / AADD(4) \]
\[ \text{AV4} = -AV3 / AADD(4) \]
\[ \text{AP} = 48. \times \text{AU1} - 36. \times \text{AU2} + 16. \times \text{AU3} - 3. \times \text{AU4} \]
\[ \text{AQ} = -25. + 48. \times \text{AV1} - 36. \times \text{AV2} + 16. \times \text{AV3} - 3. \times \text{AV4} \]

IF(II.GT.NER) GOTO 60

DO 40 JJ=1,N

CBDN=CBNEW(II,N+1)
C2=CB(II,JJ)
IF (II.EQ.0) THEN
C3=CB(II+1,JJ)
BBTERM(JJ)= CST1in(JJ) \times C2 - CST2 \times C3
ELSEIF(II.EQ.NER) THEN
C1=CB(II-1,JJ)
BBTERM(JJ)= CST1in(JJ) \times C2 - CST2 \times C1
ELSE
C1=CB(II-1,JJ)
C3=CB(II+1,JJ)
Appendix A. Computing

$BBTERM(JJ)= CST3in(II,JJ)\cdot C1+CST4in(II,JJ)\cdot C2+CST5in(II,JJ)\cdot C3$

ENDIF

40 CONTINUE

BADD(N)=A1in(N)
BBDD(N)=BBTERM(N)-CBDN*A2in(N)
DO 50 K=N-1,1,-1
   BADD(K)=A1in(K)-A2in(K)/BADD(K+1)
   BBDD(K)=BBTERM(K)-A2in(K)*BBDD(K+1)/BADD(K+1)
50 CONTINUE

C IMPLICIT CO' CALCULATION - 5 POINT METHOD.

BU1 = BBDD(1)/BADD(1)
BV1 = -1./BADD(1)
BU2 = (BBDD(2)-BU1)/BADD(2)
BV2 = -BV1/BADD(2)
BU3 = (BBDD(3)-BU2)/BADD(3)
BV3 = -BV2/BADD(3)
BU4 = (BBDD(4)-BU3)/BADD(4)
BV4 = -BV3/BADD(4)
BP = 48.*BU1-36.*BU2+16.*BU3-3.*BU4
BQ = -25.+48.*BV1-36.*BV2+16.*BV3-3.*BV4

60 GAH= 0.DO

IF(II.GT.NER) THEN
   CANEW(II,0)=(GAH-AP)/AQ
ELSE
   CANEW(II,0)= (-BQ*AP+KB*(AP+BP))/(BQ*(AQ-KF)-KB*AQ)
   CBNEW(II,0)= (-AP-(AQ-KF)*CANEW(II,0))/KB
ENDIF

DO 30 J=1,N
  CANEW(II,J) = (ABDD(J) - CANEW(II, J-1))/AADD(J)
  IF(II.LE.NER) CBNEW(II,J) = (BBDD(J) - CBNEW(II,J-1))/BADD(J)
30 CONTINUE

RETURN

END
Bibliography


Bibliography


Bibliography


Bibliography


Courses and Lectures Attended 1986/87

Physical Chemistry Departmental Seminars

20/11 Two Photon Excitation
      Kinetics of Combustion
5/3 Computer control of Mass Spectroscopy
      Molecular Beam ToF MS
7/5 Silica Solubility
      Free Radical Reactions

Electrochemistry Group Meetings

9/10 Cyclic Voltammetry
13/10 Rotating Disc Voltammetry
27/10 ChemFETs
3/11 Electron Transfer
4/2 Laplace Transforms
4/3 Manufacture of MIAEs
15/5 MIAE/Computer simulations
22/5 AC, Convolution & SW Voltammetry
25/5 Microelectrodes/Ion Transfer
1/6 IGFET/ChemFET
4/6 Uranium Electrochemistry

Undergraduate Lecture Courses

1st term Chem4 Techniques
      Electroanalytical Methods
2nd term Electrode Reactions

Postgraduate Lecture Courses

1st term German Translation
      Mass Spectroscopy
2nd term Cell Biology
3rd term Signal Processing
      Electrochemistry

Guest Speaker Lectures

Prof Ertl Polygold Adsorption onto Electrodes
J. Smeulders Effect of Functional Groups on Eo
M. Archer Photochemical aspects of Direct Solar Energy Conversion

External Seminars

Strathclyde Prof Albery; New Chemical Sensors
Ross Priory 4th Discussion meeting on Electrochemical Sensors

Pharmacology/Biochemistry Seminars

1st term Calcium Dependent Outward Current
1st term Antibodies and Antigens at the Molecular level