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Mathematical modelling of corrosion measurements

Ahmed Ali El-Feki

University of Wollongong

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Mathematical Modelling of Corrosion Measurements

A thesis submitted in fulfillment of the requirements for the award of the degree of

Doctor of Philosophy

from

The University of Wollongong

by

Ahmed Ali El-Feki, B.E.(Honours), B.Sc., UNSW

School of Mathematics and Applied Statistics

1999
This thesis is submitted to the University of Wollongong, and has not been submitted for a degree to any other University or Institution.

Ahmed Ali El-Feki

March, 1999
In the Name of God, Most Gracious, Most Merciful

Dedicated to my parents
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Abstract

The ability to predict the corrosion rate of a metal in a given environment is of great importance to BHP and to the metal industry in general. Because of the electrochemical nature of almost all corrosion reactions, electrochemical methods are commonly used to measure corrosion rates in the laboratory or in the field. The basic approach used in these techniques is to perturb the corrosive system from a known steady state value, and subsequently record its relaxation to a new steady state value. Experimental data are then fitted to a mathematical model in order to calculate the kinetic parameters of the reaction.

Most of the currently used methods for corrosion rate measurements are based on a kinetic equation, which was derived by Wagner and Traud in 1938. One of the most important simplifying assumptions used in the derivation of this equation is that the charge-transfer (or kinetic) processes at the electrode/solution interface are rate determining, and thus dominate the rate of reaction. Transport of reactants towards, and products away from the electrode surface is assumed to proceed at a much higher rate compared to the kinetic processes, and thus has a negligible effect on the overall reaction rate. This assumption has been shown to produce significant errors in the calculated corrosion rates for many practical situations, e.g. zinc, zinc coatings and steel in near neutral solutions, where the transport processes proceed at a lower or comparable rate relative to the charge-transfer processes. In these
cases, mathematical models based on mixed charge-transfer and mass transport control should be used for corrosion rate measurements, for closer approximation of experimental conditions and greater accuracy of calculation.

The central concern of this project is to modify existing and/or find new improved, electrochemical corrosion rate measurement methods, based on mixed transport (diffusion in a finite layer) and charge-transfer control of all reactions, so that corrosion rates can be calculated with more accuracy and efficiency under a greater range of experimental conditions. This is achieved by developing and solving appropriate mathematical models representing different electrochemical techniques, which simultaneously account for kinetic (charge-transfer) and transport processes.

We derive a new steady state polarization equation, and show that neglecting the effects of metal-ion build up and diffusion away from the electrode can produce significant errors in the measured corrosion rate. We also present new analytical and approximate solutions to a number of boundary value problems representing transient electrochemical methods. It is shown that compared to the full numerical solutions, the approximate solutions produce very good results, when the applied perturbation is small in magnitude. It is also shown that these can be used for nondestructive corrosion testing, with acceptable levels of accuracy. The existence of these exact and approximate solutions makes possible the calculation of corrosion parameters by merely fitting an elementary class of functions to transient experimental data. This leads to greater accuracy and efficiency compared to currently used steady state methods.

Finally, we develop a numerical scheme for the simulation of electrochemical
diffusion-migration transport processes, involving multiple electrochemical reactions and nonlinear boundary conditions. This is in contrast to the currently available algorithms in the literature, which are limited in their application or make restrictive simplifying assumptions. Using this algorithm, we examine the effects of migration on metallic corrosion, and show that this leads to a lower rate of metal dissolution compared to that obtained when diffusion is the sole mechanism for transport.
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Chapter 1

Introduction

1.1 Background

Corrosion is defined as the destruction or deterioration of a (metallic) material, due to reaction with its environment. Corrosion wastes resources and represents great economic losses. It has been reported earlier [102], that in the industrialised countries of the west, the cost of corrosion can range from two to three percent of the gross domestic product, a quarter of which could be saved through the application of well understood principles of corrosion and corrosion prevention. Some examples of the cost of corrosion experienced by various industries include [30]:

- according to the Wall Street Journal (Sept. 11, 1981), the annual cost to oil and gas producers is approximately $2 billion,

- corrosion of bridges costs approximately $500 million annually,

- the paper industry estimates that corrosion increases the price of paper by
Chapter 1. Introduction

$6-7\text{ per tonne,}$

- the petroleum industry estimates that corrosion protection of underground pipelines costs $1\text{ million per day.}$

One of the most comprehensive studies into the annual cost of metallic corrosion in the United States, was conducted in 1980 by the National Bureau of Standards and the Battelle Memorial Institute. In the first report of a seven part series [30], it was estimated that corrosion costs incurred in 1975 alone, were $70\text{ billion.}$ The report further indicated that approximately $10\text{ billion could be saved if reliable methods were used to combat corrosion.}$ Of course, corrosion being inevitable, its costs cannot be completely eliminated, but rather reduced.

Corrosion reactions can be classified in a variety of ways, for example, low-temperature and high-temperature corrosion, and wet and dry corrosion. Wet corrosion occurs when a metal is in contact with a liquid, usually an aqueous solution or an electrolyte. A common example of this is the corrosion of steel or zinc in water. Dry corrosion, on the other hand, occurs in the absence of a liquid phase, where vapours and gases are the oxidising agents (usually at high temperatures).

This thesis is restricted to wet corrosion occurring at low (i.e. room) temperatures. In particular, this thesis treats only uniform corrosion, which is one of the most commonly encountered forms of corrosion [30, 102]. This is typically characterized by an electrochemical reaction proceeding uniformly over the entire surface of the metal. For example, a piece of steel or zinc, which is immersed in an acidic solution would normally corrode at a uniform rate over its entire surface, at least when viewed over scales larger than the micron scale of typical surface imperfec-
tions. It is also assumed that there are no coupled chemical reactions, such that only electrochemical reactions are considered.

1.2 Corrosion Measurements

In order to compare various metals in a given environment on the basis of their corrosion resistance, the rate of corrosion must be expressed quantitatively. To achieve this, use is made of the fact that corrosion reactions involve the transfer of charge, and hence produce an electrical current (referred to as the corrosion current). By using Faraday’s law, the corrosion current can be converted into weight loss measurements, according to the equation

\[
\frac{d\Delta M}{dt} = \frac{W I_k}{nF},
\]

where \(\Delta M\) is the weight loss (in grams), \(W\) is the atomic weight of metal, \(I_k\) is the instantaneous corrosion current, \(n\) is number of electrons involved in the corrosion reaction, and \(F\) is Faraday’s constant. Alternatively, Equation (1.1) can be rearranged to obtain the rate of penetration (i.e. rate at which the thickness of the metal decreases), which is more familiar to the corrosion engineer, as

\[
\frac{d\Delta P}{dt} = \frac{W i_k}{n\rho F},
\]

where \(\Delta P\) is the penetration depth, \(i_k\) is the instantaneous corrosion current density, and \(\rho\) is the density of the metal. Common units for the penetration rate, are \(\mu m\) or \(mm\) per year, or in severe cases, per day or month.

Corrosion is a steady state process, which occurs when a steady potential difference exists between the metal and its environment (taken to be a solution containing
a species with a more “noble” equilibrium potential than the metal's equilibrium potential). This steady potential difference is commonly known as the corrosion potential, $E_k$. When such conditions exist, the rate of metal oxidisation (dissolution) is equal in magnitude, and opposite in direction to the rate of reduction of the oxidising agent (e.g. hydrogen or oxygen). Therefore, one cannot simply attach an ammeter to a naturally corroding metal to measure the equivalent (i.e. average) or instantaneous corrosion current, because this current is internally shorted (i.e. net current is zero). It is for this reason that special techniques must be resorted to, in order to measure the corrosion current density, $i_k$.

Because of the electrochemical nature of almost all corrosion reactions [7, 60], electrochemical techniques, which were originally developed for the study of single electrochemical reactions [6, 22, 25, 49, 62, 94], are very attractive and may be used to study corrosion reactions in the laboratory or in the field [23, 60]. The basic approach used in these techniques, is to perturb the corrosive system from a known equilibrium or steady state value, and subsequently record its relaxation to a new steady state value. Experimental data are then fitted to a mathematical model (i.e. solutions obtained for the appropriate mathematical model), in order to calculate the kinetic parameters (reaction rate and Tafel slopes) of the reaction. Electrochemical techniques are generally classified as either DC (where the perturbation is a direct input) or AC (where the perturbation is a sinusoidal input) techniques. In this thesis, we only consider DC electrochemical techniques. These can further be divided into steady state or transient techniques. In steady state methods, only the final steady state response to an input perturbation is recorded, from which a steady
state polarization (current/potential) curve is constructed. In contrast, transient methods make use of the transient response (current/time or potential/time) to an input perturbation.

In 1938, Wagner and Traud [95] published a paper where they postulated that corrosion reactions can be represented by the superposition of two or more electrochemical reactions. They further demonstrated that the rate of corrosion reactions may be calculated using electrochemical techniques. Today, this paper is regarded as the classic work on mixed potential theory. They considered a simple corrosion reaction consisting of two electrochemical reactions, of the form

\[ M \rightarrow M^{n+} + ne^-, \quad (1.3) \]

\[ 2H^+ + 2e^- \rightarrow H_2, \quad (1.4) \]

where \( M \) is the corroding metal, and the oxidising agent is taken here to be the hydrogen ions (i.e. metal is corroding in an acidic solution). Equation (1.3) represents the metal dissolution (anodic) reaction and Equation (1.4) represents the hydrogen evolution (cathodic) reaction. For the corrosion reaction given above, Wagner and Traud proposed the following kinetic relationship relating the steady state current density, \( i \), to the applied metal electrode potential, \( E \),

\[ i = i_k \left( e^{(E-E_k)/b_a} - e^{-(E-E_k)/b_c} \right), \quad (1.5) \]

where \( E_k \) is the initial steady state (corrosion) potential, \( E - E_k \) is known as the electrode polarization, and \( b_a \) and \( b_c \) are known as the anodic and cathodic Tafel slopes, respectively. The derivation of this polarization equation was based on a number of simplifying assumptions. One of the main assumptions, is that the cor-
rosion potential, $E_k$, is far removed from the equilibrium potential of the metal and hydrogen ions, $E_{e,M}$ and $E_{e,H}$, respectively. In such cases, it can be assumed that the back reactions, i.e. reactions given by Equations (1.3) and (1.4) proceeding to the left (cathodic metal-ion deposition and anodic dissolution of hydrogen gas), are negligible. The second important assumption is that the charge-transfer (or kinetic) processes at the electrode/solution interface are rate determining, and thus dominate the rate of reaction. Transport of reactants towards, and products away from the electrode surface is assumed to proceed at a much higher rate compared to the kinetic processes, and thus has a negligible effect on the overall reaction rate.

In 1951, Bonhoeffer and Jena [96] introduced the concept of polarization resistance, defined as the slope of the above polarization equation, Equation (1.5), at the corrosion potential, $E_k$. In 1957, Stern and Geary [88] derived an equation relating this slope at $E_k$, to the corrosion rate and Tafel slopes, given by

$$i_k = \frac{B}{R_p}, \quad B = \left( \frac{1}{b_{a,M}} + \frac{1}{b_{c,H}} \right)^{-1},$$

(1.6)

where $R_p$ is the polarization resistance. This equation is now known as the Stern-Geary linear polarization resistance equation. The introduction of this (linear polarization resistance) method for determining corrosion rates from steady state low polarization data, led to a significant improvement compared to weight loss measurements. Special linear polarization resistance industrial instruments have been manufactured, and have found extensive application in the prediction of corrosion rates of industrial process equipment. However, since the introduction of this important technique, several possible sources of measurement error have been suggested, most importantly of which, is the assumption of pure charge-transfer control. Un-
under these (i.e. charge-transfer only) conditions, an equivalent circuit (see Figure 2.2) representing charge-transfer processes at the electrode/solution interface can be used to calculate the response to an input perturbation (current or potential). Experimentally, the steady state responses, to several input perturbations, are read at time $t_{ss} \approx 4 \tau_{ss}$, where $\tau_{ss} = R_p C_d$, is the time constant of the equivalent circuit, and $C_d$ is the double layer capacitance. In this fashion, a steady state polarization curve (of current versus potential) can be constructed, which is then used to calculate the corrosion parameters. For typical values of $R_p \left( 1 \times 10^4 \Omega \text{cm}^2 \right)$ and $C_d \left( 20 \mu \text{Fcm}^{-2} \right)$, the time to steady state, $t_{ss} \approx 200 \text{ms}$. However, Walter [96, 98, 99, 100] has found that for zinc, zinc coatings and steel in slightly acidic, stagnant solutions, attainment of steady state values can take up to several minutes. He found that for the galvanostatic (current step) method, the potential response was made up of slow rise (diffusion) portion superimposed on a fast rise (charge-transfer) portion. This slow approach to steady state was believed to be due to mass transport of reactants to, and products away from the electrode surface, which could contribute to the overall rate of the corrosion reaction. Therefore, Walter considered that the polarization curve cannot be described completely by Equation (1.5), and hence the Stern-Geary linear polarization resistance equation cannot be used for accurate corrosion measurements under these experimental conditions. Because a steady state polarization equation based on charge-transfer and diffusion control did not then exist, Walter eliminated the diffusion portion of the response from the charge-transfer portion. The corrosion current could then be calculated using the Stern-Geary polarization resistance method. Other sources of error, which are discussed in Section 2.2.2, were
also considered in [2, 3, 24, 43, 50, 51, 52, 55, 61, 68, 75, 97, 100].

Following the introduction of the Linear Polarization Resistance method, other improved methods have been suggested for determining the corrosion parameters, from low polarization (steady state) data. Examples are the 3-point method of Barnartt [8, 9, 10], the graphical method of Oldham and Mansfeld [67], the curve fitting method of Mansfeld [53], and the CORFIT [54] and POLFIT [82] programs. The latter use non-linear least squares analysis techniques to fit low polarization data to the steady state polarization curve equation [54, 82]. Numerous other methods, utilising a range of algorithms, have also been suggested [29, 41, 42, 74, 77, 78, 79, 80, 87, 105]. However, all of these methods are based on Equation (1.5), where diffusion effects are not considered, and thus can lead to significant measurement errors in practical situations where diffusion becomes important compared to charge-transfer processes.

So far, all the different methods considered above have been pseudo steady state methods, these being the most commonly used for corrosion measurements. Transient methods, on the other hand, are rarely used for the study of corrosion reactions. For corrosion reactions which are controlled by mixed kinetic and mass transport, the time taken to reach a steady state following a perturbation can be too long for experimental needs or compared to the physicochemical fluctuations of the system. In such cases, transient techniques are more attractive, providing quick measurements of the corrosion rate either in the laboratory or in the field. The transient response of a corroding system to a perturbation is usually calculated from an equivalent electric circuit representation [43, 92]. These circuits however, fail to predict transient
behaviour observed experimentally when the corrosion reaction is not under kinetic control, for the reasons discussed above.

To overcome these problems, and to predict transient behaviour more accurately, mathematical models based on classical semi-infinite diffusion were used instead of the equivalent circuit approach. These models however were derived for a single electrochemical reaction where initially equilibrium conditions exist [6, 22, 25, 49, 62, 94]. It was stressed by Nagy et al. [63] that the initial and boundary conditions for a corrosion reaction are not the same as those for a single electrochemical reaction, and that a corroding system can only approach steady state, rather than chemical equilibrium conditions. This is due to the fact that there is a net electrochemical reaction occurring at all times in a corroding system (anodic metal dissolution and cathodic reactions such as hydrogen evolution or oxygen reduction).

A modified finite diffusion model was introduced [63], which included a Nernst (finite) diffusion layer, inside of which the concentrations of species vary and outside of which, the mixing effects of natural convection maintain the concentrations constant at their bulk values (see Figure 2.3 for a schematic diagram). The finite model is more appropriate than the semi-infinite model for the study of corrosion reactions for a number of reasons. Firstly, because the semi-infinite model in theory, never reaches a steady state. Secondly, corrosion is a steady state reaction which takes place over long periods of time, and it cannot be assumed that natural convection effects are negligible.
1.3 Overview

This is an industrial mathematics thesis, where known mathematical techniques are applied to a real industrial problem. The practical aim of this project is to modify existing and find new improved, electrochemical corrosion rate measurement methods (both steady state and transient), based on mixed transport (diffusion in a finite layer) and charge-transfer control of all reactions, so that corrosion rates can be calculated with greater accuracy and efficiency under a wider range of conditions. This is achieved by developing and solving more rigorous mathematical models representing different electrochemical techniques, which account for kinetic and transport processes. These solutions can then be integrated into currently used corrosion software, such as those mentioned above in Section 1.2, instead of the currently used models.

Throughout this thesis, solutions are derived for well known fundamental electrochemical kinetic-diffusion problems that are challenging mathematical boundary value problems, for which few antecedent approximate analytical solutions are known. In many cases, analytical or approximate analytical methods are used as well as numerical methods. Numerical methods are of dubious accuracy when they cannot be compared to exact “bench-test” models. However, when two vastly different solution methods have close predictions, this not only gives us added confidence in both methods, but it suggests an approximate magnitude of error for the less accurate method.

After a general introduction to electrochemical kinetics, mixed potential theory and kinetic-diffusion models in Chapter 2, the derivation of an accurate polariza-
tion equation, under conditions of mixed charge-transfer and diffusion control of all reactions, is considered in Chapter 3. These conditions occur in some practical situations, and a number of modified polarization equations have been presented [17, 27, 39, 56, 57]. All of these equations were either limited in their application, or required the determination of additional parameters, which may be difficult to obtain experimentally. The most general polarization equation that incorporates the effect of mass transport was derived by Nagy and Thomas in 1986 [64]. However, in deriving this equation, Nagy and Thomas assumed that the back reactions were negligible, in which case diffusion of metal-ions away from the electrode into the bulk solution was not considered, since metal dissolution is independent of the metal-ion concentration (which is not thermodynamically true).

While in most practical situations, the corrosion potential is far removed from the equilibrium potential of the cathodic reaction (e.g. \( \text{O}_2 \) reduction or \( \text{H}_2 \) evolution in the presence of a very active metal), which validates neglecting the corresponding back reaction, it is not necessarily true for the anodic reaction (especially the dissolution of zinc). In this case, the effects of the metal-ion deposition partial reaction need to be considered [55]. In other practical cases, Walter [99] has shown that even if the equilibrium potential of the metal is far from the corrosion potential, the build-up of metal-ions at the electrode surface (due to metal dissolution) causes the back reaction to have a more significant effect.

To investigate this problem, we present a new polarization equation, based on mixed charge-transfer and diffusion control, and including the metal-ion deposition partial reaction. Unlike earlier modifications, this equation is derived by including
concentration terms in the kinetic equations, and solving the steady state Fick’s diffusion equation for the steady state concentration response to a potential step, $\Delta E$. An error analysis is also presented, which investigates the errors in calculating corrosion parameters using the polarization equation in [64]. It is shown that these errors can be significantly larger than the corresponding values under charge-transfer controlled kinetics, even for values of $E_k$ well removed from $E_{e,M}$ (e.g. at $E_k - E_{e,M} = 64\text{mV}$, errors were $-65\%$ compared to $5\%$ under complete charge-transfer control). It is also shown that, for high corrosion rates, the build up of metal-ions at the metal surface increases these errors further. Because of the slow mass transport of metal-ions away from the metal surface, the back reaction has a more significant effect, hence errors due to neglect of the back reaction increase. This new equation can easily be incorporated into the existing corrosion software available to analyse polarization curves. These, of course, are based on fitting polarization data to the conventional polarization equation (Equation (1.5)), which assumes complete charge-transfer control of all reactions. From experience, this can produce values for the corrosion rate and Tafel slopes which contain large errors. Therefore, we believe that including our modified equation would produce greater accuracy and reliability of the corrosion rates and Tafel slopes calculated for a wide range of experimental conditions.

In the first part of Chapter 4, we consider the potentiostatic electrochemical method, where a constant potential step is applied to the electrode and the current transient response is recorded. Exact analytical solutions have been obtained for the current transients. A numerical solution has previously been published [63], but it is
believed that this is the first time an analytical solution has been presented. These solutions can be used to analyse the kinetics of corrosion reactions by simply curve-fitting experimentally obtained results to the analytical solution (which consists of elementary functions). This has a number of advantages, compared to steady state methods, some of which are:

- Kinetic parameters can be predicted from the current transients, thus greatly reducing measurement times involved, especially for reactions with large times to steady state.

- No assumptions about the system reaching a steady state would be required, since the actual current transients would be used for the analysis.

- Because measurements are carried out in short intervals of time, coupled chemical reactions (e.g. \(\text{Zn}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Zn(OH)}_2\), and passivating film formation on metallic surfaces) would have minimal effects.

In the second part of Chapter 4, we consider the potentiodynamic experiment, which is another commonly used technique. In this experiment, the electrode potential is varied linearly with time according to \(E = E_k + vt\), where \(v\) is the scan rate. The current produced is then recorded against the applied potential. The currently used method of analysing curves produced by such an experiment are based on a steady state polarization equation, i.e. the curve is treated as a steady state polarization curve, relating steady state current to potential. If steady state information is not obtained, due for example, to the scan rate being too large, this leads to a degree of uncertainty in the calculated corrosion rates. Walter [100] has previously
examined this problem and showed that, for pure zinc in aerated and deaerated 0.1M NaCl solutions, the polarization resistance, $R_p$ (which is inversely proportional to the corrosion current density) generally decreased with faster scan rates (larger values of $v$). That is, corrosion rates calculated from such polarization curves were dependent on the scan rate used. A number of authors [43, 76, 92] have proposed methods of obtaining the maximum scan rate, such that steady state polarization data may be obtained. These however, were based on analysing equivalent circuit representations, which assume pure charge-transfer control.

For mixed diffusion and charge-transfer control, determining the maximum allowable scan rate for steady state conditions would be much more complicated. Instead, we take a different approach, where we solve the diffusion equation with the appropriate boundary conditions, which would eventually lead to an expression for the current density as a function of time and the applied scan rate, $v$. Once this expression is obtained, one can then fit the resulting experimental current/potential polarization data to it, without making any assumptions about steady state at all. However, due to the nature of the resulting boundary conditions, it was not possible to obtain exact analytical solutions. Instead, a perturbation analysis is utilised (where the scan rate $v$ is assumed to be small in magnitude), to obtain some approximate solutions, which have not previously been presented. Given that it is common to use scan rates as low as 0.1 mV/sec in laboratory experimentation to prevent destruction of the working sample (i.e. nondestructive corrosion testing), these approximate solutions can be used with confidence to represent the physical processes during such experiments. Furthermore, these solutions should produce
greater accuracy than the conventional procedure of using a steady state polarization equation.

In Chapter 5, the galvanostatic experiment is examined, where a constant current is applied across the electrode/solution interface, and the resulting potential transients are recorded. The resulting boundary value problems representing such conditions applied to a corrosion reaction consist of highly nonlinear, coupled boundary conditions. To the knowledge of the author, no solutions, either numerical or analytical, have been presented for this model. As well as presenting a numerical solution, a perturbation analysis is also performed to obtain approximate solutions when the applied current step is small in magnitude. This experiment is very similar, in principle, to the potentiostatic experiment, and can also be used as part of a curve-fitting routine where potential transients are analysed to evaluate the corrosion rate. However, it is recommended that this experiment be used only for nondestructive testing (i.e. small applied currents) since in this case the approximate solutions may be used for the curve-fitting instead of the full numerical solutions. This would significantly reduce the number of computations required for the curve-fitting, thus increasing the overall efficiency of the measurement process.

Finally, in Chapter 6, the more complicated problem of electrochemical transport due to diffusion and migration (i.e. transport of charged ions under the influence of an electric field) is considered. Migration effects can be important in practical situations because, for example, most natural waters are of low conductivity, where excess of supporting electrolyte is absent and consequently transport processes due to diffusion and migration need to be considered. Here, the governing equations
constitute a system of coupled nonlinear partial differential equations, along with nonlinear boundary conditions. To the knowledge of the author, the only analytical solution that exists for the transient model, is that derived by Choi and Chan in 1991 [19] for a binary inert electrolyte. In general, one must resort to numerical methods for the solution of transient electrochemical processes. In 1992, Choi and Chan [20] proposed a fractional step (or operator splitting) algorithm for the numerical simulation of diffusion-migration transport processes, using finite difference methods. However, their algorithm was limited to transport of inert ions, i.e. zero flux boundary conditions. Furthermore, their algorithm exhibited only first order spatial and temporal accuracy. Using a splitting algorithm similar to that in [20], Kwok and Wu [45] developed a finite difference numerical scheme for modelling diffusion-migration processes with reactions at the electrodes (their model was set up for a two electrode model where metal dissolution occurs at the anode and metal-ion deposition occurs at the cathode). Their algorithm was more accurate, exhibiting second order spatial and temporal accuracy. However, the algorithm was limited for a number of reasons. Firstly, it was assumed that only one ion took part in an electrochemical reaction at each of the electrodes (i.e. only one reactive ion). Secondly, it was assumed that the concentrations of the inert ions were much larger than that of the reactive ion. This allowed them to expand the concentrations of ions and the potential as a perturbation series, where to the zeroth-order, only inert ions were present in the electrolytic solution. This led to decoupling the leading order equations governing the concentration evolution of inert and reactive ions and simplifying the boundary conditions. Finally, they only consider linearized reaction kinetics, which is valid at
low current densities only.

In Section 6.4, we develop a general finite difference scheme, with second-order spatial and temporal accuracy, for examining the transient physical behaviour of electrolytes containing any number of reacting and inert ions, without making any simplifying assumptions about their relative concentrations. Furthermore, we present an alternative way of linearizing the reaction kinetics which, we believe, is more accurate and reliable than the conventional linearization found in the literature. Finally, the effect of migration on metallic corrosion is discussed and it is shown that this leads to a lower rate of metal dissolution compared to that obtained when diffusion is the sole mechanism for transport.

It is believed that the aim of this project has been substantially achieved, and that this will provide BHP with more accurate models, which will not only lead to more reliable corrosion rate measurements, but also increase the efficiency of the measurement process. In particular, the existence of exact analytical solutions for some transient electrochemical methods means that these methods can be readily used for rapid corrosion rate measurements, instead of the much slower steady state methods (which are presently the standard methods used at BHP Research Laboratories and elsewhere). Also, extensive use can be made of the approximate analytical solutions, especially when conducting nondestructive tests, where the magnitude of a given perturbation is relatively small.
Chapter 2

Electrochemical Reactions and Butler-Volmer Kinetics

2.1 Electrochemical Kinetics

In this section a general introduction to electrochemical kinetics and the theory of mixed potentials is presented. The reader is referred to [6, 12, 94] for a more detailed study.

2.1.1 Single electrochemical reactions

Consider the electrochemical reaction occurring at an electrode surface, given by

$$ R \rightleftharpoons O + ne^{-}, \quad (2.1) $$

where $O$ and $R$ are the oxidised and reduced species respectively, and $n$ is the number of electrons involved in the reaction. In the absence of a potential difference across the electrode/solution interface (double layer), the rate of the above reaction
is given by

$$v = v_a - v_c,$$  \hspace{1cm} (2.2)

where $v_a$ is the rate of the anodic partial reaction (proceeding to the right), and $v_c$ is the rate of the cathodic partial reaction (proceeding to the left). These rates are given by

$$v_a = K_a C_R(0,t),$$  \hspace{1cm} (2.3)

$$v_c = K_c C_O(0,t),$$  \hspace{1cm} (2.4)

where $C_R(0,t)$ and $C_O(0,t)$ are the surface concentrations of species $R$ and $O$ respectively, and $K_a$ and $K_c$ are the anodic and cathodic rate constants respectively. The rate constants may be regarded as the typical frequency with which an ion successfully “jumps” the energy barrier (activation energy) in order to take part in the reaction, and are given by the Boltzmann distribution law,

$$K_i = \frac{kT}{h} e^{-\Delta G_i / RT},$$  \hspace{1cm} (2.5)

where $k$, $h$, $R$, $T$, $\Delta G_i$, $i = a$, or $c$, are Boltzmann’s constant, Planck’s constant, the universal gas constant, absolute temperature, and the anodic and cathodic chemical free energies of activation respectively. Note that since there is assumed to be no potential difference across the double layer, the reaction rates are functions of the chemical free energy, $\Delta G_i$.

If a potential difference exists at the electrode/solution interface (which is the case when charge-transfer occurs across the interface), then this will affect the reaction rates, $v_a$ and $v_c$, by altering the activation energy of the partial reactions. The direction of this potential difference will either assist or impede a given partial
reaction, depending on its sign. In this case the anodic and cathodic activation
ergies are given by the electrochemical free energy,

\[ \Delta G^*_a = \Delta G_a - (1 - \alpha)nFE, \]  
\[ \Delta G^*_c = \Delta G_c + \alpha nFE, \]

where \(\Delta G^*_a, F, E, \) and \(\alpha\) are the electrochemical free energy, Faraday’s constant, potential difference across the double layer and the symmetry factor, respectively.

The presence of this symmetry factor is due to the fact that in considering the contribution of the electrostatic work to the activation energy of either partial reaction, only part of the potential difference, \(E\), is of importance [11] (i.e. the part of the electrostatic work which assists a given ion to the summit of the energy barrier).

Note that if \(E > 0\), i.e. the electrode is positive with respect to the solution, then this will assist the anodic partial reaction (where a positive ion moves away from the electrode surface), by reducing the activation energy required for the anodic partial reaction to proceed. In contrast, this will impede the cathodic partial reaction (where a positive ion moves towards the electrode surface), by increasing the activation energy required for the cathodic reaction to proceed. If, however, \(E < 0\), then this will have the opposite effect on the partial reactions. Therefore, the electrochemical reaction rates are given by

\[ v^*_a = K_a e^{(1-\alpha)nFE/RT} C_R(0, t), \]  
\[ v^*_c = K_c e^{-\alpha nFE/RT} C_O(0, t). \]

We define the equilibrium potential difference, \(E_0\), across the double layer as the potential when the total rate of reaction is zero. At this potential, there is no net
reaction occurring, and thus the surface concentrations of the reactive ions are equal to their bulk values (i.e. concentration profiles are uniform), and

\[ v_a^* = v_c^* = v_0, \quad \text{at} \ E = E_0, \]  

(2.10)

where \( v_0 \) is the rate of the anodic and cathodic partial reactions at equilibrium. Substituting Equations (2.8) and (2.9) into Equation (2.10), yields

\[ K_a = v_0 e^{-(1-a)nFE_0/RT} \frac{1}{C_R^b}, \]  

(2.11)

\[ K_c = v_0 e^{anFPE_0/RT} \frac{1}{C_O^b}, \]  

(2.12)

where \( C_R^b \) and \( C_O^b \) are the bulk concentrations. Substituting Equations (2.11) and (2.12) into Equations (2.8) and (2.9), the net electrochemical reaction rate is given by

\[ v^* = v_0 \left( \frac{C_R(0,t)}{C_R^b} e^{(E-E_0)/b_a} - \frac{C_O(0,t)}{C_O^b} e^{-(E-E_0)/b_c} \right), \]  

(2.13)

where \( b_a = RT/(1-a)nF \), and \( b_c = RT/anF \), are the so called anodic and cathodic Tafel slopes respectively, and \( E-E_0 \) is known as the electrode overpotential. Finally the total current density, \( i \), produced by reaction (2.1), at a potential \( E \), is given by

\[ i = nFv^*, \]  

(2.14)

therefore we have,

\[ i = i_0 \left( \frac{C_R(0,t)}{C_R^b} e^{(E-E_0)/b_a} - \frac{C_O(0,t)}{C_O^b} e^{-(E-E_0)/b_c} \right), \]  

(2.15)

where \( i_0 = nFv_0 \), is known as the exchange current density for reaction (2.1), and represents the rates of oxidation (anodic) and reduction (cathodic) at equilibrium. Equation (2.15) above is usually referred to as the Butler-Volmer equation [6, 12, 94],
and it represents a relationship between the current density, $i$, the electrode overpotential, $E - E_0$, and the surface concentrations of the reactive ions, $C_R(0, t)$ and $C_O(0, t)$. It can be seen from Equation (2.15) that if the electrode overpotential is positive, i.e. $E - E_0 > 0$, then the first exponential term will be greater than the second term, and hence there is a net anodic (oxidisation) partial reaction produced by reaction (2.1). Furthermore, if $E - E_0 \gg 0$, then the anodic partial reaction dominates and Equation (2.15) can be approximated by the first term only. Similarly, if $E - E_0 \ll 0$, then the cathodic partial reaction becomes the dominating reaction, and Equation (2.15) can be represented by the second term only. Therefore, we can approximate Equation (2.15) by

$$i = i_0 \frac{C_R(0, t)}{C_R^b} e^{(E - E_0)/b_a}, \quad E - E_0 \gg 0,$$

(2.16)

$$i = -i_0 \frac{C_O(0, t)}{C_O^b} e^{-(E - E_0)/b_c}, \quad E - E_0 \ll 0.$$

(2.17)

Finally using Equation (2.15), it is straightforward to derive the Nernst equation, which expresses the equilibrium potential across the electrode/solution interface in terms of the surface concentrations of the reactive ions [6, 12, 94],

$$E_0 = E_0^\circ + \frac{RT}{nF} \ln \left( \frac{C_O(0, t)}{C_R(0, t)} \right),$$

(2.18)

where $E_0^\circ$, is the standard equilibrium potential, defined as the equilibrium potential at unit concentration of the reactive ions (i.e. $C_R^b = C_O^b = 1$).
2.1.2 Mixed potential theory

Although the concepts utilized in the mixed potential theory were known before 1900, the first formal presentation of this theory is usually attributed to the classic work of Wagner and Traud [95]. A general review and a theoretical analysis of mixed potentials was presented in [35]. The mixed potential theory consists of two hypotheses. First, any electrochemical reaction can be divided into two or more anodic or cathodic partial reactions, which occur simultaneously at the metal/electrolyte interface. This has been demonstrated experimentally. The second hypothesis states that there can be no net accumulation of electric charge during an electrochemical reaction. This is a statement of the law of conservation of charge.

To illustrate the above hypotheses, consider a metal electrode immersed in an acidic solution, which contains some metal-ions. Under these conditions, the metal is corroded by the acid, and the electrochemical reactions occurring at the electrode surface are represented by Figure 2.1, and are given by

\[ M \rightleftharpoons M^{n+} + ne^-, \quad (2.19) \]

\[ H_2 \rightleftharpoons 2H^+ + 2e^- . \quad (2.20) \]

Let \( i_0_j \) and \( E_0_j, j = 1, 2 \) denote the exchange current density and equilibrium potential of reactions (2.19) and (2.20), respectively. If one of these reactions has a high exchange current density relative to the other reaction(s), then it will dominate and the electrode will measure the equilibrium potential of that reaction, which is calculated by the Nernst equation. Under these conditions, the electrode is referred to as a reversible electrode. However, if the exchange current densities are of comparable magnitude, then the electrode cannot remain at either of the equilibrium
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Figure 2.1: Schematic representation of the kinetic behaviour of a metal electrode immersed in an acidic solution. Here, $E_{01}$, $E_{02}$, and $i_{01}$, $i_{02}$ are the equilibrium potentials and exchange current densities of the metal and hydrogen reactions (reactions (2.19) and (2.20)) respectively. $E_k$ is the corrosion (steady state) electrode potential, and $i_k$ is the corrosion current density.
potentials, but must lie somewhere between the equilibrium potentials. This potential is achieved when the second hypothesis is satisfied, that is the sum of all anodic currents is equal in magnitude (and opposite in sign) to the sum of all cathodic currents, such that the net current is zero. This potential is known as a mixed potential, or corrosion potential, $E_k$, when corrosion reactions are considered. In other words, for the reactions considered above, at $E_k$, there is an anodic current produced by reaction (2.19) (i.e. net metal dissolution) and a net cathodic current produced by reaction (2.20) (i.e. net hydrogen evolution). These net anodic and cathodic currents are coupled as they must proceed at the same rate (steady state conditions), which is referred to as the corrosion current density, $i_k$.

From Figure 2.1, it can be seen that at $E_k$, the overpotential of reaction (2.19) is positive, i.e. $E_k - E_{01} > 0$. Therefore, the anodic partial reaction of (2.19) is greater than the cathodic partial reaction, and there is a net metal dissolution occurring. Similarly, since $E_k - E_{02} < 0$, then the cathodic partial reaction (2.20) is greater than the anodic partial reaction, and there is a net hydrogen evolution. For simplicity, let us assume that the corrosion potential $E_k$ is far removed from either of the equilibrium potentials $E_{01} \text{ and } E_{02}$ (as is commonly assumed in the literature), such that $E_k - E_{01} \gg 0$ and $E_k - E_{02} \ll 0$. In this case, reactions (2.19) and (2.20) can be represented as

$$M \rightarrow M^{n+} + ne^{-}, \quad (2.21)$$

$$2H^+ + 2e^{-} \rightarrow H_2, \quad (2.22)$$

and thus the current density produced by each reaction, at a potential $E$, is given
by

\[ i_1 = i_0_1 e^{(E - E_0_1)/b_a}, \quad (2.23) \]

\[ i_2 = -i_0_2 \frac{C_2(0, t)}{C_2^b} e^{-(E - E_0_2)/b_c}, \quad (2.24) \]

where \( i_1 \) and \( i_2 \) are the partial current densities produced by anodic metal dissolution and cathodic hydrogen evolution respectively, \( C_2 \) is the concentration of the hydrogen ions, and the total current density produced is given by the sum of all the partial current densities. Note that the concentration of the metal \( M \), is taken to be unity. Now by definition, we have

\[ i_1 = |i_2| = i_k, \text{ at } E = E_k, \quad (2.25) \]

where \( i_k \) is the corrosion current density. Using Equation (2.25), the current densities, \( i_1 \) and \( i_2 \), can be expressed in terms of important physical parameters for corrosion testing, namely \( E_k, i_k \), and the Tafel slopes \( b_a \) and \( b_c \). It should be noted that unlike \( E_k \), values of \( i_k \) cannot be measured directly since the net current density at \( E_k \) is zero. Therefore, we have

\[ i_0_1 e^{(E_k - E_0_1)/b_a} = i_0_2 \frac{C_2(0, 0)}{C_2^b} e^{-(E_k - E_0_2)/b_c} = i_k, \quad (2.26) \]

where \( C_2(0, 0) \), is the surface concentration of the \( H^+ \) ions at \( E = E_k \), which is taken to be at time \( t = 0 \). Using Equation (2.26), the exchange current densities \( i_0_1 \) and \( i_0_2 \) can be expressed in terms of \( i_k \). Substituting this into Equations (2.23) and (2.24) and summing, the total current density is given by

\[ i = i_k \left( e^{(E - E_k)/b_a} - \frac{C_2(0, t)}{C_2^b(0, 0)} e^{-(E - E_k)/b_c} \right), \quad (2.27) \]

where \( E - E_k \) is known as the electrode polarization.
2.1.3 Charge-transfer Control

Consider the corrosion reaction given by Equations (2.21) and (2.22), where the charge-transfer (kinetic) processes at the electrode surface proceed at a lower rate compared to the transport of products away from and reactants towards the electrode surface. In this case, the kinetic processes largely determine the reaction rate, and the reaction is said to be under complete kinetic or charge-transfer control. In other words, the surface concentrations of the reactive ions are assumed to remain constant. Therefore the current density is given by

\[ i = i_k \left( e^{\Delta E/b_{\text{an}}} - e^{-\Delta E/b_{\text{cat}}} \right), \]

(2.28)

where \( \Delta E = E - E_k \), is the electrode polarization. Equation (2.28) was first presented by Wagner and Traud in 1938 [95], and is only valid under conditions of pure kinetic control and when \( E_k \) is far removed from either of the equilibrium potentials, such that metal-ion deposition and hydrogen oxidation partial reactions (back reactions) are neglected. This Equation is commonly used in the corrosion literature to investigate corrosion reactions, and to measure the corrosion current density, \( i_k \).

In some practical situations however, where the reactions are under mixed kinetic and mass transport control, or if the back reactions are not negligible, Equation (2.28) can introduce large errors in the calculated values of \( i_k \). Errors due to neglecting mass transport have been examined by several authors [17, 39, 61, 64, 96, 98, 99] and this will be examined in more detail in the remaining chapters. Errors due to neglecting the back reactions under complete kinetic control have also been considered [51, 52, 55]. In particular, it has been demonstrated experimentally [99] that the metal-ion deposition reaction can have significant effects on the corrosion rate.
This will be considered in detail in Chapter 3.

2.2 Electrochemical Methods

2.2.1 Introduction

The ability to predict the corrosion rate of a metal in a given environment is of great importance to the metal industry. Because of the electrochemical nature of almost all corrosion reactions [7, 60], electrochemical techniques, which were originally developed for the study of single electrochemical reactions [6, 22, 25, 49, 62, 94], provide a valuable and convenient way of predicting the kinetic parameters (Tafel slopes and corrosion rate) of a corrosion reaction, in the laboratory or in the field [23, 60]. The basic principle behind these methods is to perturb (by an excitation) the corrosive system from a known equilibrium or steady state value, and subsequently record its relaxation to a new steady state. Important kinetic parameters of the reactions are then estimated by fitting a mathematical model to experimental results. Methods of excitation are generally divided into DC and AC methods. In this thesis we consider only DC methods, such as the potentiostatic (potential step), the galvanostatic (current step), and the potentiodynamic (potential scan) methods.

2.2.2 Steady state methods

Steady state electrochemical techniques involve the analysis of the final steady state response to an excitation. A polarization (steady state) equation, similar to Equation (2.28), relating steady state current and potential, is then fitted to steady
state current/potential experimental data (commonly known as polarization data), in order to predict the kinetic parameters of the reaction(s). Most electrochemical methods used to analyse and calculate the rate of corrosion reactions are based on steady state methods [23, 42, 60, 100]. Almost all of these methods are based on a polarization equation which was derived by Wagner and Traud [95], for conditions of kinetic control only, and neglecting the back reactions (i.e. Equation (2.28)).

The Polarization Resistance method is one of the simplest and most commonly used method for corrosion rate measurements. In their classic work on mixed potential theory, Wagner and Traud showed that, under certain conditions, it is possible to calculate the rate of corrosion reactions using electrochemical techniques. In 1951 Bonhoeffer and Jena [96] introduced the concept of polarization resistance, defined as the slope of the polarization curve (steady state current density vs electrode polarization) at the corrosion potential. They demonstrated that the corrosion rate decreased as the polarization resistance increased, for a series of 11 steel alloys in sulphuric acid solution. In 1957, Stern and Geary [88] derived an equation relating the slope of the polarization curve to the corrosion rate and Tafel slopes. This equation was based on the kinetics of electrochemical reactions and mixed potential theory as presented by Wagner and Traud (i.e. Equation (2.28)). The slope of the polarization curve (Equation (2.28)) is given by

\[
\left( \frac{di}{dE} \right)_{E=0} = \frac{1}{R_p} = i_k \left( \frac{1}{b_{a_1}} + \frac{1}{b_{c_2}} \right), \tag{2.29}
\]

where \( R_p \) is the polarization resistance. Rearranging the above equation yields,

\[
i_k = \frac{B}{R_p}, \quad B = \left( \frac{1}{b_{a_1}} + \frac{1}{b_{c_2}} \right)^{-1}. \tag{2.30}
\]
This equation is now known as the Stern-Geary linear polarization equation. The introduction of this (linear polarization resistance) method for determining corrosion rates from steady state low polarization data, led to a significant improvement compared to weight loss measurements. Termed the 'Linear Polarization Resistance Method', it provided a simple, sensitive, relatively non-destructive and repeatable test, which could build up the corrosion history of a sample immersed in solution. Special linear polarization resistance industrial instruments have been manufactured, and have found extensive application in the prediction of corrosion rates of industrial process equipment.

However, the technique was not without its shortcomings. Prior to the advent of non-linear least squares corrosion analysis routines, the low polarization data simply provided a calculation of 'linear polarization resistance', being the slope of the potential, $E$, versus current density, $i$, curve at the corrosion potential, $E_k$. Conversion to corrosion rate (or corrosion current density, $i_k$) required the assumption of fixed anodic metal, $b_{a_1}$, and cathodic hydrogen, $b_{c_2}$, Tafel slope values. Stern and Geary provided a partial solution to this by observing that the lumped Tafel constant, $B$, in Equation (2.30), relating corrosion current density, $i_k$, to the inverse of the linear polarization resistance, $R_p$, rarely varied more than a factor of 2 (within 200% error) for most practical possibilities of $b_{a_1}$ and $b_{c_2}$. An average value of $B$, equal to 0.025V is usually taken. Some commercial linear polarization resistance industrial instruments are still based on this principle.

Since the introduction of this important technique, several possible sources of measurement error have been suggested. The effect of curvature in polarization
curves close to the corrosion potential, $E_k$, was one source of error [52, 68, 98, 100] causing problems with linearization in order to obtain the linear polarization resistance slope. Oldham and Mansfeld [68] pointed out that polarization resistance was the more general name, being the slope of the polarization curve at $E_k$. The word ‘linear’ was superfluous, and a linear range near $E_k$ was not essential for use of the technique. They argued that for the polarization curve to be linear at $E_k$, the second derivative of Equation (2.27), given by

$$\left( \frac{d^2 i}{d\Delta E^2} \right)_{\Delta E=0} = i_k \left( \frac{1}{b_{a_1}} - \frac{1}{b_{c_2}} \right), \quad (2.31)$$

must be equal to zero, which occurs only if the anodic and cathodic Tafel slopes are equal. Other sources of error include $IR$ voltage drops due to resistance of surface films and/or poorly conductive solutions [50, 97]; presence of anodic processes other than metal dissolution [75]; unknown or inappropriate Tafel slopes obtained from high polarization data which may not be applicable at the corrosion potential [100]; non-uniform corrosion [75]; and neglect of back reactions when corrosion potentials are close to equilibrium potentials [55]. An excellent review of the polarization resistance technique has been presented by Mansfeld [51].

Another problem in calculating corrosion rates from low polarization data is the slow attainment of a steady state situation (slow response) following polarization. This can show up in the commonly used potentiodynamic polarization curve method as being scan rate dependent, as well as in the potentiostatic and galvanostatic step methods, and can occur from two quite separate causes. Firstly, for very low corrosion rates, the charging of the double layer capacitance, $C_d$, via a parallel polarization resistance, $R_p$, following a perturbation can be quite lengthy,
because the value of $R_p$ is high [43, 100]. Secondly, other effects can cause the slow attainment of a steady state response following polarization. For a galvanostatic (or potentiostatic) polarization step, the potential (or current) response is made up of a slow rise (diffusion) portion superimposed on a fast rise (charge-transfer) portion. This has been reported for zinc coatings [100] and steel [2, 3, 99, 100] in near neutral solutions. Explanations for the slow response to steady state following a perturbation have been varied. Azzerri [2, 3] considered that hindered surfaces (the dissolving metal surface covered by corrosion product layers or films) give rise to a large pseudo-capacitance which causes the corrosion potential to change during polarization. The effect of a changing corrosion potential during polarization has also been noted by Defrancq [24] for cast iron in 1N H$_2$SO$_4$. Walter [97, 98, 99, 100] considered that, in near neutral solutions, the transport of reactants ($H^+$ ions or O$_2$) to, or products ($M^{n+}$ ions) away from the electrode surface, generally known as diffusion or mass transfer, proceeds more sluggishly than charge-transfer controlled reactions, and so can contribute in the overall rate of the corrosion reaction. Corrosion rate measurements under conditions of mixed charge-transfer and diffusion control will be considered in detail in Chapter 3, where a modified polarization equation will be derived.

Some of the other well known methods for calculating corrosion rates from low polarization data are, the Tafel plot extrapolation method [95], Barnartt's three-point method [8, 9, 10] and Mansfeld's curve fitting method [53]. These methods are all based on pure charge-transfer control and will be discussed in the next chapter.
2.2.3 Transient methods

For corrosion reactions which are controlled by mixed kinetic and mass transport, the time taken to reach a steady state can be too long for experimental needs or compared to the physicochemical fluctuations of the system. In such cases, transient techniques are more attractive, providing quick measurements of the corrosion rate either in the laboratory or in the field.

The transient response of a corroding system to a perturbation is usually calculated from an equivalent electric circuit representing the kinetics of the reaction at the electrode surface (see for example [34], [43] and [92]). The electric circuit consists of a resistor (the polarization resistance, $R_p$) and a capacitor ($C_d$, due to the double layer across the electrode surface) in parallel (see Figure 2.2).

These circuits however, fail to predict transient behaviour observed experimentally when the corrosion reaction is not under pure kinetic control. For example, the potential response of the circuit given by Figure 2.2, to a current step $\Delta i$, is given by

$$E(t) = \Delta i R_p \left(1 - e^{-t/R_p C_d}\right). \quad (2.32)$$

The steady state response is read at time $t_{ss}$, corresponding to $E(t)$ effectively reaching a steady state value, where $t_{ss} \approx 4 R_p C_d$. For typical values of $C_d = 20 \mu F cm^{-2}$ and $R_p = 1 \times 10^4 \Omega cm^2$, $t_{ss} \approx 200 ms$. However, Walter [96, 98, 99, 100] has found that for zinc, zinc coatings and steel in slightly acidic solutions, attainment of steady state values can take up to several minutes. He found that for the galvanostatic (current step) method, the potential response was made up of slow rise (diffusion) portion superimposed on a fast rise (charge-transfer) portion.
This slow approach to steady state was believed to be due to mass transport of reactants to, and products away from the electrode surface, which can contribute to the overall rate of the corrosion reaction.

![Equivalent circuit](image)

Figure 2.2: Equivalent circuit representing kinetic processes at the electrode/solution interface. Here $R_p$ is the polarization resistance and $C_d$ is the double layer capacitance.

To overcome these problems, and to predict transient behaviour more accurately, mathematical models based on classical semi-infinite diffusion were used instead of the equivalent circuit approach. These models however were derived for a single electrochemical reaction (given by Equation (2.1)) where initially equilibrium conditions exist [6, 22, 25, 49, 62, 94]. It was stressed by Nagy et al. [63] that the initial and boundary conditions for a corrosion reaction are not the same as those for a single electrochemical reaction, and that a corroding system can only approach steady state, rather than chemical equilibrium conditions. This is, of course, due to the fact that there is a net electrochemical reaction occurring at all times in a corroding system (anodic metal dissolution and cathodic reactions such as hydrogen evolution or oxygen reduction). A modified finite diffusion model was introduced, which in-
cluded a Nernst diffusion (finite diffusion) layer, inside of which the concentrations of species vary and outside of which, the mixing effects of natural convection maintain the concentrations constant at their bulk values (see Figure 2.3 for a schematic diagram). The finite model is more appropriate than the semi-infinite model for the study of corrosion reactions for a number of reasons. Firstly, because the semi-infinite model in theory, never reaches a steady state. Secondly, corrosion is a steady state reaction which takes place over long periods of time, and it cannot be assumed that natural convection effects are negligible. Finally, the diffusion layer model can be used to explain in a qualitative sense, the limiting current phenomenon. This limiting value for the current occurs when the surface concentration of a reacting ion becomes zero, such that the current produced by the corresponding reaction becomes potential independent. Furthermore, Nagy et al. investigated the errors produced in using classical semi-infinite diffusion models for calculating corrosion parameters, instead of the finite diffusion model. They found that, for the potentiostatic experiment, the relaxation curves (current transients) calculated using the finite diffusion model can be considerably different from those calculated using the classical model, and thus corrosion rates calculated using these classical models were not accurate. In this thesis, the finite diffusion model is used to represent corrosion reactions.

2.3 Mathematical Model

A simple electrochemical model is considered, where a metal electrode corrodes in an acidic electrolyte, consisting of a mixture of charged ions. For a relatively large
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Figure 2.3: Schematic diagrams of steady state concentration profiles for the classical semi-infinite (top) and Nernstian diffusion layer (bottom) models.
electrode compared to the diffusion layer thickness, it is possible to neglect transport in the lateral directions and hence the transport (diffusion) equation becomes one-dimensional. The metal-ions and the oxidising ions (taken to be $H^+$ ions) are reactive at the electrode surface, while all other ions are inert (i.e. do not react). The presence of inert ions is primarily to improve the electrical conductivity of the electrolyte. In a stagnant solution, transport of these charged ions will be due to diffusion and migration (due to electric potential in solution). The governing equations describing such transport constitute a set of coupled nonlinear differential equations, which in general must be solved numerically [20, 45, 72]. However, it is commonly assumed that there exists an excess of inert ions in the electrolyte (i.e. concentrations of inert species are much higher than those of the reactive ions) [81, 91]. In these cases, the concentrations of the inert species and the solution potential are assumed to be constant throughout the solution. Thus the transport of the reactive species is due to diffusion only and the governing equations for ionic transport reduce to the diffusion equation. These simplified models are physically realistic and are widely used in the electrochemical literature [49, 65, 66, 81, 91, 94]. Electrochemical models involving transport due to diffusion and migration (driven by an electric field) will be considered in Chapter 6.

The finite diffusion model representing the corrosion reaction, given by Equations (2.19) and (2.20), is described by a set of two partial differential equations, one for each of the reacting species, along with the appropriate initial and boundary conditions.

$$\frac{\partial C_j}{\partial t} = D_j \frac{\partial^2 C_j}{\partial x^2}, \quad \text{(2.33)}$$
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\[ C_j(x, 0) = C_j(0, 0) + \left( \frac{C_j^b - C_j(0, 0)}{\delta} \right) x, \]  
\[ C_j(\delta, t) = C_j^b, \]  
\[ \frac{\partial C_j(0, t)}{\partial x} = -\frac{i_j}{n_j F D_j}, \]  

where \( j = 1, 2 \) denotes the metal and hydrogen ions respectively, \( \delta \) is the diffusion layer thickness, \( D_j \) is the diffusivity of species \( j \), and \( C_j(0, 0) \) refers to the surface concentrations of ionic species \( j \), at the corrosion potential, \( E_k \). Note that this is taken to be the initial surface concentration of species \( j \), i.e. we set \( E = E_k \) at \( t = 0 \).

Equation (2.33) is the one-dimensional diffusion equation for ion transport governed by Fick’s law. Equation (2.34) is the linear concentration profile that represents an initial unperturbed steady state in a finite diffusion layer. The boundary condition (2.35) states that at a distance \( \delta \) (the diffusion layer thickness) away from the electrode surface, the concentration of species \( j \) is constant and equal to its bulk concentration, \( C_j^b \). The boundary condition (2.36) states that the flux of ions at the electrode is proportional to the corresponding partial current density, given by the nonlinear Equations (2.23) and (2.24) (if the back reactions are neglected). It will be shown in subsequent chapters, that even under these simplified conditions, where mass transport is due to diffusion only, the nonlinear boundary conditions at the electrode, and the nature of the perturbation applied, often make analytical solutions difficult to obtain. The nonlinearity arises from the reaction kinetics occurring at the electrode/solution interface.

All variables are now expressed in non-dimensional form. Let

\[ \tilde{C}_j = \frac{C_j}{C_j^b}, \quad \tilde{t}_j = \frac{t}{\tau_j}, \quad \tilde{x} = \frac{x}{\delta}, \quad \text{and} \quad \tilde{i}_j = \frac{i_j}{i_{L_j}}, \]
where 

\[ \tau_j = \frac{\delta^2}{D_j}, \quad \text{and} \quad i_{L_j} = n_j F D_j \frac{C_j^b}{\delta}, \]

\( \tau_j \) is a measure of the time taken to reach steady state and \( i_{L_j} \) is the limiting current density (L.C.D) of species \( j \), which occurs when the surface concentration of species \( j \), is zero. Using the above, the boundary value problems (2.33)-(2.36) can be rewritten in non-dimensional form as

\[
\frac{\partial \bar{C}_j}{\partial \bar{t}_j} = \frac{\partial^2 \bar{C}_j}{\partial \bar{x}^2}, \quad (2.37)
\]

\[
\bar{C}_j(\bar{x}, 0) = \bar{C}_j(0, 0) + (1 - \bar{C}_j(0, 0))\bar{x}, \quad (2.38)
\]

\[
\bar{C}_j(1, \bar{t}_j) = 1, \quad (2.39)
\]

\[
\frac{\partial \bar{C}_j(0, \bar{t}_j)}{\partial \bar{x}} = -\bar{i}_j. \quad (2.40)
\]

It should also be noted that the important relationship between the corrosion current density, \( i_k \) and the initial surface concentrations, is given by

\[
\frac{i_k}{i_{L_j}} = 1 - \bar{C}_j(0, 0). \quad (2.41)
\]
Chapter 3

Steady State Methods: A
Modified Polarization Equation for
Corrosion Measurements

3.1 Introduction

Corrosion analysis routines have been a marked improvement in the determination of corrosion rate parameters from low polarization data. Such routines provide methods for determining Tafel slope constants in order to convert polarization resistance to corrosion current.

Examples are the 3-point method of Barnartt [8, 9, 10], the graphical method of Oldham and Mansfeld [67], the curve fitting method of Mansfeld [53], and the CORFIT [54] and POLFIT [82] programs. The latter use non-linear, least squares analysis techniques to fit low polarization data to the steady state current/potential...
polarization equation [54, 82]. Numerous other methods, utilising a range of algorithms, have also been suggested [29, 41, 42, 74, 77, 78, 79, 80, 87, 105]. However, all of these methods are based on only charge-transfer kinetics as per Equation (2.28), and diffusion effects are not considered. A special case of Equation (2.28) which is also commonly used [99], is a polarization equation derived for complete diffusion control for the cathodic reaction [87] and is given by

\[ i = i_k \{ e^{\Delta E/b_{a1}} - 1 \}. \]  

(3.1)

In some practical situations, e.g. corrosion of zinc in near neutral solutions [98, 99, 100], these routines (mentioned above) can produce significant errors in the calculated values of the corrosion rate.

The case of mixed charge-transfer and diffusion control, which occurs in many practical situations, has been investigated by a number of authors [17, 27, 39, 56, 57] and a number of modified polarization equations were presented. All of these equations were either limited in their application, or required the determination of additional parameters, which may be difficult to obtain in many practical situations. The most general polarization equation that incorporates the effect of mass transport was derived by Nagy and Thomas in 1986 [64]. This equation is general in that it describes the polarization curve when the cathodic (hydrogen ion reduction) partial reaction is under charge-transfer control \( (i_{L2} = \infty) \), mass transport control \( (i_{L2} = i_k) \), or mixed control \( (i_{L2} > i_k) \). Mass transport of the anodic process was not considered because the anodic reactant for a corrosion reaction is a solid metal, i.e. Nagy and Thomas considered the corrosion reaction given by Equations (2.21) and (2.22), where the back reactions are assumed negligible.
While in most practical situations, the corrosion potential is far removed from the equilibrium potential of the cathodic reaction (e.g. H₂ evolution or O₂ reduction), which validates neglecting the corresponding back reaction, it is not necessarily true for the anodic reaction. In cases where the corrosion potential is close to the equilibrium potential of the anodic reaction, the effects of the metal-ion deposition partial reaction need to be considered. It has been reported earlier [55, 99] that neglecting the metal-ion deposition partial reaction could cause errors as large as 50-100%, and a modified polarization equation was presented. However this was based on complete charge-transfer control. In other cases [99], even if the equilibrium potential of the metal is far from the corrosion potential, the build-up of metal-ions at the electrode surface (due to metal dissolution) causes the back reaction to have a more significant effect. In fact Walter [99], using the standard charge-transfer polarization equation, has found that for zinc and zinc coatings in near-neutral chloride solutions, neglecting the metal-ion deposition partial reaction resulted in electrochemically (theoretical) calculated mass losses being typically 50-60% higher than the solution analysis (experimental) derived mass loss. By including the metal-ion deposition partial reaction, the electrochemically calculated mass losses were reduced by up to 20%. It is believed that using a polarization equation derived for mixed charge-transfer and diffusion conditions will further reduce this error.

Although Nagy et al. [61, 63, 64] correctly point out that anodic metal dissolution is not affected by mass transport, cathodic metal-ion deposition is. A corroding metal produces a buildup of metal-ions adjacent to the metal surface. It is this buildup that may cause the metal-ion deposition partial reaction (back reaction)
to be more important in corrosion rate calculations for some practical situations. The present chapter introduces a modified polarization equation based on mixed charge-transfer and diffusion control, and includes the back reaction. Unlike earlier modifications, this equation is derived by including the concentration terms and solving the steady state Fick's diffusion equation for the steady state concentration response to a potential step, $\Delta E$. An error analysis is presented that demonstrates the errors involved in neglecting the back reaction in calculating corrosion rates from steady state polarization data, under conditions of mixed charge-transfer and diffusion control.

### 3.2 The Modified Polarization Equation

Consider a corrosion reaction which consists of two cathodic partial reactions (hydrogen evolution and metal-ion deposition) and one anodic partial reaction (metal dissolution) according to Equations (3.2) and (3.3),

$$
M \rightleftharpoons M^{n+} + n_1e^- \quad (3.2)
$$

$$
H^+ + e^- \rightarrow \frac{1}{2}H_2 \quad (3.3)
$$

For simplicity, it is assumed that there are no coupled homogeneous chemical reactions. Let $C_1$ and $C_2$ represent the concentrations of $M^{n+}$ and $H^+$ ions respectively. The current density $i$ at a potential $E$, is given by $i = i_1 + i_2$, where $i_1$ and $i_2$ are the anodic and cathodic c.d.'s respectively and are given by the Butler-Volmer kinetic equation for mixed control (see Section 2.1.1)

$$
i_1 = \dot{i}_0 \left\{ e^{(E-E_0_1)/b_{a_1}} - \frac{C_1(0,t)}{C_1^b} e^{-(E-E_0_1)/b_{c_1}} \right\}, \quad (3.4)\n$$
\[ i_2 = -i_{02} \frac{C_2(0, t)}{C_2^b} e^{-\frac{(E-E_{02})}{b_{c2}}}, \tag{3.5} \]

where \( C_j(0, t) \) refers to the concentrations of the ionic species at the electrode surface, and all the other symbols have their usual meaning. Using the same approach as in Section 2.1.2, we have zero total current at the corrosion potential, \( E_k \). Thus the current density from Equation (3.2) is equal in magnitude to that from Equation (3.3), \( i_1 = |i_2| = i_k \). Thus

\[ i_k = i_{01} \left\{ e^{\frac{(E_k-E_{01})}{b_{c1}}} - \frac{C_1(0, 0)}{C_1^b} e^{-\frac{(E_k-E_{01})}{b_{c1}}} \right\}, \tag{3.6} \]

\[ i_k = i_{02} \frac{C_2(0, 0)}{C_2^b} e^{-\frac{(E_k-E_{02})}{b_{c2}}}, \tag{3.7} \]

where \( C_j(0, 0) \) refers to the surface concentrations of ionic species, \( j \) at the corrosion potential, \( E_k \). Rearranging Equations (3.6) and (3.7) and substituting into Equations (3.4) and (3.5) respectively, and noting that [55]

\[ \frac{1}{b_{a1}} + \frac{1}{b_{c1}} = \frac{n_1 F}{RT} = \gamma, \tag{3.8} \]

yields

\[ i_1 = i_k \left[ \frac{C_1^b - C_1(0, t)e^{-\gamma \Delta E_k}}{C_1^b - C_1(0, 0)e^{-\gamma \Delta E_k}} \right] e^{\Delta E/b_{a1}}, \tag{3.9} \]

\[ i_2 = -i_k \frac{C_2(0, t)}{C_2(0, 0)} e^{-\Delta E/b_{c2}}. \tag{3.10} \]

Therefore, the total current density is given by

\[ i = i_k \left\{ \left[ \frac{C_1^b - C_1(0, t)e^{-\gamma \Delta E_k}}{C_1^b - C_1(0, 0)e^{-\gamma \Delta E_k}} \right] e^{\Delta E/b_{a1}} - \frac{C_2(0, t)}{C_2(0, 0)} e^{-\Delta E/b_{c2}} \right\}, \tag{3.11} \]
Chapter 3. A Modified Polarization Equation for Corrosion Measurements

where

\[ \Delta E = E - E_k, \quad \Delta E_1 = E - E_{01}, \quad \Delta E_{1k} = E_k - E_{01}. \]

At high polarization values, such that

\[ \Delta E_{1k} \gg RT/n_1F, \quad \text{and} \quad \Delta E_1 \gg RT/n_1F, \]

then the metal-ion deposition partial reaction (back reaction) can be neglected and Equation (3.11) reduces to

\[ i = i_k \left\{ \exp \left( \frac{\Delta E}{b_{a_1}} \right) - \frac{C_2(0, t)}{C_2(0, 0)} e^{-\Delta E/b_{a_2}} \right\}. \quad (3.12) \]

In order to derive an equation for the polarization curve (i.e. relating steady state current density to the electrode potential), steady state surface concentrations of the reactive ions must first be calculated, then substituted into Equation (3.11). The steady state concentration profiles are obtained by solving the steady state diffusion equations. In nondimensional form (see Section 2.3), these are given by

\[ \frac{d^2 C_j}{dx^2} = 0, \quad (3.13) \]

\[ C_j(1) = 1, \quad (3.14) \]

\[ \frac{dC_j}{dx}(0) = -\bar{i}_j, \quad (3.15) \]

where \( C_j(x) \) and \( \bar{i}_j \) are the nondimensional steady state concentration profile, and partial current density of species j, obtained by scaling equations (3.9) and (3.10). Solving the above boundary value problem, it is can easily be shown that the concentration profiles are given by

\[ C_1(x) = 1 + \left( e^{-\gamma \Delta E_1} - 1 \right) \left( \eta e^{-\Delta E/b_{a_1}} + e^{-\gamma \Delta E_1} \right)^{-1} (x - 1), \quad (3.16) \]
\[ C_2(x) = 1 + \left( 1 + \frac{C_2(0,0)}{1-C_2(0,0)} e^{\frac{\Delta E}{b c_2}} \right)^{-1} (x - 1), \] (3.17)

where upon making use of Equation (2.41), we obtain

\[ \eta = \frac{i_{L_1}}{i_k} (\beta - 1), \quad \beta = \left( 1 + \frac{i_k}{i_{L_1}} \right) e^{-\gamma \Delta E_{M,k}}. \]

Substituting \( x = 0 \) into Equations (3.16) and (3.17), the steady state surface concentrations of the reactive ions, \( M^{n+} \) and \( H^+ \) respectively, are obtained. Substituting these into Equation (3.11), yields

\[ i = i_k \left\{ \mu e^{\frac{\Delta E}{b a_1}} - \lambda e^{-\frac{\Delta E}{b c_2}} \right\}, \] (3.18)

where

\[ \mu = \alpha (1 - \beta) \left[ \eta e^{-\frac{\Delta E}{b a_1}} + e^{-\gamma \Delta E_1} \right], \]

\[ \alpha = e^{-\gamma \Delta E_1} \left( 1 - e^{-\gamma \Delta E_1} \right), \]

\[ \lambda = \left[ 1 - \frac{i_k}{i_{L_2}} + \frac{i_k}{i_{L_2}} e^{-\frac{\Delta E}{b c_2}} \right]^{-1}. \]

Note that \( \mu \) and \( \lambda \) represent correction factors for mixed control of the cathodic metal-ion deposition partial reaction (back reaction) and the cathodic hydrogen ion partial reaction, respectively. If the back reaction is negligible, then \( \mu \) is equal to unity, in which case Equation (3.18) reduces to that derived by Nagy and Thomas [64]. Furthermore, for near neutral aerated conditions, where the cathodic reaction is the diffusion limited oxygen reduction, Equation (3.18) reduces to

\[ i = i_k \left\{ \mu e^{\frac{\Delta E}{b a_1}} - 1 \right\}. \] (3.19)

Nagy et al. [61, 64] investigated the errors involved in using conventional charge-transfer methods (i.e. based on Equation (2.28)) for the evaluation of corrosion
parameters instead of a simplified version of Equation (3.18) with $\mu = 1$, which includes mass transport effects of the cathodic partial reaction only. They found that the errors in neglecting the mass transport effects of the cathodic reaction were a function of the two dimensionless parameters $i_k/i_{L2}$ and $b_{a1}/b_{c2}$. They showed that these errors can be significant, even for small values of $i_k/i_{L2}$, if the ratio $b_{a1}/b_{c2}$ is high. However, if $b_{a1}/b_{c2} \leq 0.5$, which is the case for many practical corrosion systems, the maximum error of conventional data evaluation methods was found to be 33%. They pointed out that errors increase with increasing $b_{a1}/b_{c2}$, because only the cathodic reaction is influenced by mass transport. Consequently, increasing $b_{a1}$ while keeping $b_{c2}$ constant, increases the relative importance of the cathodic term, thus increasing the overall error. On the other hand, increasing $b_{c2}$ while keeping $b_{a1}$ constant decreases the relative importance of the cathodic term, thus decreasing the overall error.

Equation (3.18), based on mixed kinetics, and including the back reaction, and can be easily incorporated in a multi-dimensional nonlinear least squares algorithm to calculate kinetic parameters such as corrosion current and Tafel slopes, without making any assumptions about the corrosion kinetics. In the next section, an error analysis is presented in order to determine the errors involved in predicting corrosion rates and Tafel slopes, under mixed control kinetics, when the back reaction is neglected. It is shown that this can lead to larger errors in calculated values of the corrosion parameters than the corresponding values under complete charge-transfer control, especially if diffusion effects are dominant or if corrosion rates are large.
3.3 Effect of neglecting the back reaction

Synthetic current/potential polarization data were generated using Equation (3.18), which includes the metal-ion deposition partial reaction (back reaction), using input values of the corrosion parameters, $i_k$, $b_{a_1}$, and $b_{c_2}$. The specific case of this equation with $\mu = 1$ (i.e. neglecting metal-ion deposition) was then fitted to the $i/E$ data using a multi-parameter nonlinear least squares program based on the Levenberg-Marquardt algorithm [71]. Calculated values of the corrosion parameters, were then compared to their input values, and a relative error due to neglecting the back reaction was calculated. The curve-fitting was carried out for a range of the kinetic parameter values, $i_k$, $b_{a_1}$, and $b_{c_2}$ as follows. The corrosion current density is represented by the non-dimensional parameter $i_k/i_{L2}$, which is varied between 0.01 and 1.0 (where 1.0 indicates that the cathodic hydrogen ion reduction partial reaction is under complete diffusion control). Values used for anodic Tafel slope, $b_{a_1}$, were varied between 30 and 60mV/decade, while values for the cathodic Tafel slope, $b_{c_2}$, were varied between 60 and 240mV/decade, these being typical values which often arise in practical situations [21, 51, 90]. The relative errors in neglecting the back reaction, for each parameter, $i_k$, $b_{a_1}$ and $b_{c_2}$, are presented in Figures 3.1-3.3, respectively. Below, results of the error analysis and explanations of these are presented.

Note that the maximum error due to neglect of the back reaction occurs at $i_k = i_{L2}$, i.e. when the cathodic hydrogen ion partial reaction is diffusion limited, and Equation (3.18) reduces to Equation (3.19). Subsequent discussion about maximum errors refers to this point.
Effect of $\Delta E_{1k}(= E_k - E_{01})$ — The error analysis demonstrates that errors due to neglect of the metal-ion deposition partial reaction, under mixed kinetics, can be significantly larger than the corresponding values under charge-transfer controlled kinetics, even for values of $E_k$ well removed from $E_{01}$. For example, the errors in calculated corrosion rates due to neglecting metal-ion deposition under charge-transfer controlled conditions were reported to be [51, 55] approximately 5% for $\Delta E_{1k} = 64$ mV, and 1% for $\Delta E_{1k} = 90$ mV. For the same values of $\Delta E_{1k}$, under conditions of mixed control, these errors can be as large as (Figure 3.1) $-65\%$ and $-53\%$ (at $i_k = i_{L2}$), respectively. By inspection of Figures 3.2 and 3.3, the corresponding errors in calculated Tafel slopes, $b_{c2}$ and $b_{a1}$, are $-70\%$, $-85\%$, and $-30\%$, $-42\%$, respectively.

Effect of corrosion current density, $i_k$ — By inspection of Figures 3.1-3.3, it is seen that, under mixed kinetics, the relative errors in all parameters increase, even for values of $E_k$ far removed from $E_{01}$, as $i_k \rightarrow i_{L2}$. For example, relative errors in corrosion current density, $i_k$, at $\Delta E_{1k} = 90$ mV, are $-10\%$ at $i_k = 0.2i_{L2}$, increasing to $-53\%$ at $i_k = i_{L2}$ (Figure 3.1). Note that errors in $i_k$ are always negative, indicating that calculated corrosion rates underestimate actual rates. This is an unsatisfactory state in practical situations to have actual corrosion rates higher than predicted. Under the same conditions (i.e. $\Delta E_{1k} = 90$ mV ), relative errors in the anodic and cathodic Tafel slopes, $b_{a1}$ and $b_{c2}$, were $-5\%$ and $-20\%$ at $i_k = 0.2i_{L2}$, and $-30\%$ and $-70\%$ at $i_k = i_{L2}$, respectively (Figures 3.2 and 3.3). As $i_k$ approaches $i_{L2}$, the build up of metal-ions at the metal surface increase further.
Because of the slow mass transport of metal-ions away from the metal surface, the back reaction has a more significant effect, hence errors due to neglect of the back reaction increase.

**Effect of Tafel slopes $b_{a_1}$ and $b_{c_2}$** — Figures 3.4 and 3.5 demonstrate the dependence of the relative error in $i_k$ on $b_{a_1}$ and $b_{c_2}$. It can be observed that increasing $b_{a_1}$ (or $b_{c_2}$), while keeping $b_{c_2}$ (or $b_{a_1}$) constant, causes an increase in the error in $i_k$. Note also that the errors are more sensitive to variation of the anodic Tafel slope, $b_{a_1}$, than they are to the cathodic Tafel slope, $b_{c_2}$. The effect of the Tafel slopes can be understood by noting that the errors are due to neglect of the cathodic metal-ion deposition partial reaction. An increase in $b_{a_1}$ will cause the metal dissolution term (first exponential term of Equation (3.6)) to decrease. This will also cause a decrease in $b_{c_1}$ (by inspection of Equation (3.8)) which will cause the relative importance of the metal-ion deposition term to increase. Thus increasing $b_{a_1}$ will cause an increase in the error due to neglect of the back reaction. If $b_{c_2}$ increases, then the relative importance of the second exponential term (hydrogen evolution) in Equation (3.13) decreases, and hence the metal partial reaction becomes more significant. As this is the term containing the back reaction, an increase in $b_{c_2}$ will cause an increase in the error due to neglect of the back reaction. The above effects result in minimum errors occurring as $b_{a_1}/b_{c_2} \rightarrow 1$, and maximum errors for both $b_{a_1}/b_{c_2} \gg 1$ and $\ll 1$.

**Effect of neglecting mass transport and the back reaction** — The maximum errors in calculated corrosion rate values due to neglecting the back reaction, under
Figure 3.1: Errors due to neglect of the back reaction under mixed kinetic conditions, in corrosion current density, $i_k$, with $b_{a_1} = 60 \text{mV}$, $b_{c_2} = 120 \text{mV}$; (a) $\Delta E_{1k} = 10RT/n_1F$ (128 mV); (b) $\Delta E_{1k} = 7RT/n_1F$ (90 mV); and (c) $\Delta E_{1k} = 5RT/n_1F$ (64 mV). Numbers in brackets represent $\Delta E_{1k}$ at room temperature and $n_1 = 2$. 
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Figure 3.2: Errors due to neglect of the back reaction under mixed kinetic conditions, in cathodic Tafel slope, $b_{c2}$, with $b_{a1} = 60\text{mV}$, $b_{c2} = 120\text{mV}$; (a) $\Delta E_{1k} = 10RT/n_1F$ (128 mV); (b) $\Delta E_{1k} = 7RT/n_1F$ (90 mV); and (c) $\Delta E_{1k} = 5RT/n_1F$ (64 mV). Numbers in brackets represent $\Delta E_{1k}$ at room temperature and $n_1 = 2$. 
Figure 3.3: Errors due to neglect of the back reaction under mixed kinetic conditions, in anodic Tafel slope, \( b_{a1} \), with \( b_{a1} = 60 \text{mV} \), \( b_{c2} = 120 \text{mV} \); (a) \( \Delta E_{1k} = 10RT/n_1F \) (128 mV); (b) \( \Delta E_{1k} = 7RT/n_1F \) (90 mV); and (c) \( \Delta E_{1k} = 5RT/n_1F \) (64 mV). Numbers in brackets represent \( \Delta E_{1k} \) at room temperature and \( n_1 = 2 \).
Figure 3.4: Dependence of relative error, due to neglect of the back reaction under mixed kinetic conditions, in corrosion current density, \( i_k \), on cathodic Tafel slope, \( b_{c2} \), with \( b_{a1} = 60 \text{mV} \), and \( \Delta E_{1k} = 64 \text{mV} \); (a) \( b_{c2} = 60 \text{mV} \); (b) \( b_{c2} = 120 \text{mV} \); and (c) \( b_{c2} = 240 \text{mV} \)
Figure 3.5: Dependence of relative error, due to neglect of the back reaction under mixed kinetic conditions, in corrosion current density, $i_k$, on anodic Tafel slope, $b_{a,M}$, with $b_{c,H}=0.120\,\text{V/decade}$, and $\Delta E_{k,M} = 64\,\text{mV}$; (a) $b_{a_1} = 60\,\text{mV}$; (b) $b_{a_1} = 40\,\text{mV}$; (c) $b_{a_1} = 30\,\text{mV}$
mixed kinetics, for the common practical case of $b_{a1}/b_{c2} \leq 0.5$, was found to be
-10% ($\Delta E_{1k} = 128\text{mV}$), -30% ($\Delta E_{1k} = 90\text{mV}$) and -45% ($\Delta E_{1k} = 64\text{mV}$) for $i_k = i_{L2}$, while for values of $i_k/i_{L2} = 0.5$, the errors were found to be -5%, -20%, and -30% respectively. If both the back reaction and mass transport effects are neglected (i.e. calculating corrosion parameters using Equation (2.28) instead of Equation (3.13)), the errors above can increase by a further 20 − 33% [61], leading to calculated corrosion rates being significantly lower than actual rates.

3.4 Conclusion

A modified polarization equation, is derived, based on mixed charge-transfer plus diffusion control of anodic and cathodic reactions, and including the metal-ion deposition partial reaction. Unlike the polarization equation derived by Nagy and Thomas [64], this equation takes into account diffusion of metal-ions away from the electrode surface as well as diffusion of hydrogen ions towards the electrode. This equation is necessary for corrosion rate measurements from polarization data if the corrosion potential is close to the equilibrium potential of the metal, or if the corrosion rate is high such that metal-ion build up at the surface causes the back reaction to have a more significant effect.

It was found that errors due to neglect of the metal-ion deposition partial reaction, under mixed kinetics, can be significantly larger than the corresponding values under charge-transfer controlled kinetics, even for values of $E_k$ well removed from $E_{01}$ (e.g. at $E_{k,M} = 64\text{mV}$, errors were 5% compared to −65%). Errors were found to increase as the corrosion current density, $i_k$, approaches the limiting current den-
sity of the cathodic hydrogen evolution partial reaction, $i_{L2}$, and by increasing either of the Tafel slopes, holding the other constant. As $i_k$ approaches $i_{L2}$, the build up of metal-ions at the metal surface increases further. Because of slow mass transport of metal-ions away from the metal surface, the back reaction has a more significant effect, hence errors due to neglect of the back reaction increase. This modified equation can be used under complete charge-transfer, mixed charge-transfer plus diffusion, or complete diffusion controlled conditions. This equation can be used as a basis of a nonlinear least squares curve-fitting routine for measuring corrosion rates and Tafel slopes from polarization data. This should result in more accurate calculations of the kinetic parameters $i_k$, $b_\alpha$, and $b_{c2}$, compared to the conventional charge-transfer polarization equation (i.e. Equation (2.28)) and the polarization equation derived by Nagy and Thomas (i.e. Equation (3.18) with $\mu = 1$).
Chapter 4

Transient Methods: Controlled Potential Methods

4.1 Introduction

In this chapter, electrochemical techniques where the working electrode (metal) potential is controlled and the current transient is recorded, will be investigated. In particular, we consider two of the most widely used techniques for studying electrochemical reactions, namely the potentiostatic and potentiodynamic (or linear sweep voltammetry) techniques. In both cases, we solve the resulting boundary value problems to obtain analytic expressions for the current density as a function of time. This will facilitate the curve fitting process, in order to calculate the corrosion parameters (corrosion rate and Tafel slopes). It will be shown that for the potentiostatic experiment, the resulting boundary conditions are linear and thus exact analytical solutions are obtained. For the potentiodynamic experiment, while
the boundary conditions are also linear, exact analytical solutions could not be found due to the unusual nature of the boundary conditions. In this case we perform a perturbation analysis to obtain some approximate analytical solutions for the concentrations of the reacting ions and the current transients.

4.2 The Potentiostatic Method

The potentiostatic method was first proposed for studying the kinetics of electrode processes, by the German electrochemists Gerischer and Vielstich in 1955 [22]. In this method, the potential of the electrode is suddenly changed from an initial equilibrium (or steady state in the case of corrosion reactions) value to some other constant value (Figure 4.1), measured against a suitable reference electrode [22, 25, 37, 46, 94]. The reference electrode is made from a special material/electrolyte combination (e.g. Hg/HgCl in saturated KCl solution, known as the calomel electrode) which maintains a stable potential for a wide range of currents, such that this can be used as a reference point for potential measurements.

The resulting current is then measured as a function of time, using a fast response galvanometer. The sudden change in potential is achieved by means of a potentiostat, the function of which is to maintain a prescribed potential between the working electrode and the reference electrode by applying a variable current between the working electrode and a counter electrode (usually made from an inert material such as platinum, such that no electrochemical reactions occur at its surface). A schematic diagram of a simple potentiostat is given in Figure 4.3, while the potentiostatic setup is illustrated in Figure 4.2.
In this section, we present an analytical (exact) solution for the current transient response to a potentiostatic step applied to a metal electrode which is corroding in an acidic electrolyte, given by Equations (3.2) and (3.3). The model is based on mixed charge-transfer and diffusion control and includes the metal-ion deposition partial reaction (back reaction). The effect of the back reaction, on the overall current transient response is investigated. In the potentiostatic step experiment, the system is initially at steady state, where the electrode potential is the corrosion potential, $E_k$. The electrode potential is then stepped to a new constant value, $E$ (see Figure 4.1). From the solution of this model, concentrations of the electroactive species can be determined and hence the current transient response to a potentiostatic step can be determined.

The finite diffusion model (not including the back reaction) has previously been solved numerically [63]. The present analytical solution is believed to be the first analytic solution to be published. Even though diffusion models can be solved with
Figure 4.2: A schematic diagram of the potentiostatic test set-up [30]. Here W.E. denotes the working electrode and Aux. denotes the auxiliary (or counter) electrode, and R is a resistor of variable resistance.
Figure 4.3: A schematic diagram of a simple potentiostat [37].
confidence by numerical equation solvers, analytic solutions still have an important role. Analytic expressions have the general advantage over purely numerical models that they exactly represent the solution of a problem, without the complication of discretization errors, which are inherent with numerical solutions and depend on the grid spacings. Numerical solutions satisfy the governing equations and boundary conditions only in an approximate sense. Often it is difficult to prove that a numerical solution converges in the limit of small grid size or indeed that the limit, even if it exists, is a bona fide solution of the original problem, uncorrupted by the idiosyncrasies of the chosen numerical scheme. Errors in the evaluation of open form analytic solutions, which arise mainly in the evaluation of special functions or in summation of series, are usually more readily estimated and controlled. Hence they provide valuable bench tests for the wide variety of numerical approximation schemes currently in use. Finally, analytical solutions have the advantage over numerical solutions that they can be used to curve-fit experimental data to theoretical models much more efficiently, which results in quick measurements of the corrosion rate either in the laboratory or in the field. This is particularly useful for commercial corrosion software, which often have to be concise and fast, in order to operate efficiently over a wide range of personal computers.

### 4.2.1 The mathematical model

Using the results of Section 2.3, the mathematical model representing the corrosion reaction given by Equations (3.2) and (3.3), is given in nondimensional form by Equations (2.37)-(2.40), where the nondimensional partial current densities, $\tilde{i}_1$ and
\( \tilde{i}_2 \), obtained by expressing Equations (3.9) and (3.10) in nondimensional form, are given by

\[
\tilde{i}_1(\tilde{t}_1) = \frac{i_k}{i_L} \left\{ \frac{1 - \tilde{C}_1(0, \tilde{t}_1)}{1 - \tilde{C}_1(0, 0)} e^{-\gamma \Delta E_1} \right\} e^{(E - E_k)/b_{a1}},
\]

(4.1)

\[
\tilde{i}_2(\tilde{t}_2) = \frac{i_k}{i_{L2}} \frac{\tilde{C}_2(0, 0)}{\tilde{C}_2(0, t)} e^{-(E - E_k)/b_{c2}},
\]

(4.2)

where \( \Delta E_1 = E - E_0 \) and \( \Delta E_{1k} = E_k - E_{01} \). It should be recalled that if the applied potential is such that \( \Delta E_{1k} \gg RT/n_1 F \) and \( \Delta E_1 \gg RT/n_1 F \), then metal-ion deposition is neglected, and Equation (4.1) above reduces to

\[
\tilde{i}_1(\tilde{t}_1) = \frac{i_k}{i_L} e^{(E - E_k)/b_{a1}}.
\]

(4.3)

Now to simplify the boundary value problems as much as possible before an exact solution is attempted, two substitutions will be made. The first substitution is to replace \( \tilde{C}_j(\tilde{x}, \tilde{t}_j) \) by \( \theta_j \), where

\[
\theta_j = \tilde{C}_j(\tilde{x}, \tilde{t}_j) - \left( \tilde{C}_j(0, 0) + \left[ 1 - \tilde{C}_j(0, 0) \right] \tilde{x} \right),
\]

(4.4)

represents the deviation of the non-dimensional concentration of species \( j \) from its initial non-dimensional steady state value. The second substitution is to replace \( \tilde{x} \) by the non-dimensional variable \( \xi \), which is given by

\[
\xi = 1 - \tilde{x},
\]

(4.5)

such that \( \xi = 1 \) corresponds to the electrode surface and \( \xi = 0 \) corresponds to the outer edge of the diffusion layer. Using Equations (4.1), (4.2), (4.4) and (4.5), the boundary value problem (b.v.p) given by Equations (2.37)-(2.40) may be rewritten
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\[ \frac{\partial \theta_j}{\partial t_j} = \frac{\partial^2 \theta_j}{\partial \xi^2}, \]  
\[ \theta_j(\xi, 0) = 0, \]  
\[ \theta_j(0, \xi_j) = 0, \]  
\[ \frac{\partial \theta_j(1, \xi_j)}{\partial \xi} = \lambda_j + \mu_j \theta_j(1, \xi_j), \]

where

\[ \mu_1 = -\alpha \, e^{\gamma \Delta E_1 (\tilde{C}_1(0, 0) - 1)e^{\Delta E/b_{e1}}, \]
\[ \lambda_1 = (\tilde{C}_1(0, 0) - 1) \left( \alpha[1 - e^{\gamma \Delta E_1 \tilde{C}_1(0, 0)e^{\Delta E/b_{e1}} - 1} \right), \]
\[ \alpha = \left( 1 - \tilde{C}_1(0, 0)e^{-\gamma \Delta E_{ik}} \right)^{-1}, \]
\[ \mu_2 = -\left( \frac{1 - \tilde{C}_2(0, 0)}{\tilde{C}_2(0, 0)} \right) e^{-(E-E_k)/b_{c2}}, \]
\[ \lambda_2 = \left( 1 - \tilde{C}_2(0, 0) \right) \left( 1 - e^{-(E-E_k)/b_{c2}} \right). \]

Note that under potentiostatic conditions, where the electrode potential is held constant, \( \lambda_1, \lambda_2, \mu_1, \) and \( \mu_2 \) are all constant. Also, note that \( \tilde{C}_j(1, 0) \) is the nondimensional initial surface concentration of species \( j \). The b.v.p is now simplified and the Laplace Transform can be utilized to obtain the solution.

Taking the Laplace Transform of Equation (4.6) and using the initial condition (4.7) yields

\[ \frac{d^2 \tilde{\theta}_j}{d\xi^2} = s\tilde{\theta}_j(\xi, s), \]

where \( \tilde{\theta}_j(\xi, s) \) is the Laplace transform of \( \theta_j(\xi, \xi_j) \), the solution of which is given by

\[ \tilde{\theta}_j(\xi, s) = A(s)e^{-s^{1/2}\xi} + B(s)e^{s^{1/2}\xi}. \]
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Applying boundary conditions (4.8) and (4.9) yields

\[
\tilde{\theta}_j(\xi, s) = \frac{\lambda_j}{s} \frac{e^{-s^{1/2}\xi} - e^{s^{1/2}\xi}}{[\mu_j - s^{1/2}][e^{s^{1/2}} - [\mu_j + s^{1/2}]e^{-s^{1/2}}].}
\] (4.10)

The Inverse Laplace transform of the above equation will yield \( \theta_j(\xi, \tau_j) \), which is the solution of the b.v.p (4.6)-(4.9). Equation (4.10) can be rewritten as

\[
\tilde{\theta}_j(\xi, s) = \frac{\lambda_j}{s} \frac{\sinh(\xi \sqrt{s})}{\sqrt{s} \cosh(\sqrt{s}) - \mu_j \sinh(\sqrt{s})}.
\] (4.11)

Applying the Inversion Theorem for the Laplace transformation [18], the solution is given by,

\[
\theta_j(\xi, \tau_j) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} e^{zt} \tilde{\theta}_j(\xi, z) dz,
\] (4.12)

where \( \gamma \) is so large that all the singularities of \( \tilde{\theta}_j(\xi, z) \) lie to the left of the line \( (\gamma - i\infty, \gamma + i\infty) \) and \( z \) is a complex variable. To evaluate this integral, we consider the closed contour \( C \), which is a semi-circle of radius \( R \), consisting of the line \( (\gamma - iR, \gamma + iR) \) and the arc \( \Gamma \), which extends to the left of \( \gamma \). It can be shown [18] that in the limit, as \( R \to \infty \), the integral over \( \Gamma \) vanishes. Thus, using Cauchy's Residue theorem [106], the line integral (4.12) is equal to \( 2\pi i \) times the sum of the residues at the poles of its integrand. Thus,

\[
\theta_j(\xi, \tau_j) = \sum_{n=0}^{N} \text{Res}(H(z), z_n)
\] (4.13)

where \( H(z) = e^{zt} \tilde{\theta}_j(\xi, z) \) is an analytic function on \( C \), except at isolated singularities (poles) at the points \( z_n, n = 1, 2, \cdots N \). We can rewrite \( H(z) \) as,

\[
H(z) = \frac{F(z)}{G(z)},
\]
where
\[ F(z) = \frac{\lambda_j e^{\xi z} \sinh(\xi \sqrt{z})}{z}, \]
\[ G(z) = \sqrt{z} \cosh(\sqrt{z}) - \mu_j \sinh(\sqrt{z}). \]

Thus, \( H(z) \) has simple poles at \( z = 0 \), and at the zeroes of \( G(z) \). Substituting
\[ z = -\alpha_n^2 \ (\sqrt{z} = i\alpha_n), \]
\( G(z) \) can be rewritten as
\[ G(-\alpha_n^2) = i\alpha_n \cos(\alpha_n) - i\mu_j \sin(\alpha_n), \]
and thus, the zeroes of \( G(z) \) are given by the increasing sequence of roots of the equation
\[ \alpha_n = \mu_j \tan(\alpha_n), \quad n = 1, 2, \ldots, \infty, \]  
which are easily evaluated and many of them have previously been evaluated for a range of values of \( \mu_j \), see for example [1, 18]. Now, we calculate the residues of \( H(z) \) at the poles. The residue at \( z = 0 \), is given by [106]
\[ \operatorname{Res}(H(z), 0)) = \lim_{z \to 0} z H(z) \]
\[ = \left. \frac{\lambda_j \sinh(\xi \sqrt{z})}{\sqrt{z} \cosh(\sqrt{z}) - \mu_j \sinh(\sqrt{z})} \right|_{z=0} \]
\[ = \frac{\lambda_j \xi}{1 - \mu_j}, \]  
upon using L'Hôpital's rule. The residue at the pole \( \alpha_n \) is given by
\[ \operatorname{Res}(H(-\alpha_n^2)) = \frac{F(-\alpha_n^2)}{G'(-\alpha_n^2)} \]
\[ = \frac{-2\lambda_j e^{-\alpha_n^2 \xi} \sin(\alpha_n \xi)}{\alpha_n (\mu_j - 1) \cos(\alpha_n) + \alpha_n^2 \sin(\alpha_n)}. \]  
Therefore, upon substituting Equations (4.15) and (4.16) into (4.13), the solution to the boundary value problem (4.6)-(4.9) is given by
\[ \theta_j(\xi, \bar{\xi}) = \frac{\lambda_j \xi}{1 - \mu_j} - 2\lambda_j \sum_{n=1}^{\infty} \frac{e^{-\alpha_n^2 \xi} \sin(\alpha_n \xi)}{\alpha_n (\mu_j - 1) \cos(\alpha_n) + \alpha_n^2 \sin(\alpha_n)}. \]
Using Equation (4.5) yields,

\[ \theta_j(x, \bar{t}_j) = \frac{\lambda_j}{1 - \mu_j} \left( 1 - \bar{x} \right) - 2\lambda_j \sum_{n=1}^{\infty} \frac{e^{-\alpha_n^2t_j} \sin(\alpha_n(1 - \bar{x}))}{\alpha_n(\mu_j - 1) \cos(\alpha_n) + \alpha_n^2 \sin(\alpha_n)}. \]  (4.18)

Thus, upon using Equation (4.4), the non-dimensional surface concentrations are given by

\[ \bar{C}_j(0, \bar{t}_j) = \bar{C}_j(0, 0) + \frac{\lambda_j}{1 - \mu_j} - 2\lambda_j \sum_{n=1}^{\infty} \frac{e^{-\alpha_n^2t_j} \sin(\alpha_n)}{\alpha_n(\mu_j - 1) \cos(\alpha_n) + \alpha_n^2 \sin(\alpha_n)}, \]  (4.19)

where \( \alpha_n \) are the roots of Equation (4.14). Equation (4.19) can be re-written in a more convenient form as

\[ \bar{C}_j(0, \bar{t}_j) = \bar{C}_j(0, 0) + \frac{\lambda_j}{1 - \mu_j} - 2\lambda_j \sum_{n=1}^{\infty} A_j(\alpha_n)e^{-\alpha_n^2t_j}, \]  (4.20)

where

\[ A_j(\alpha_n) = \frac{\sin(\alpha_n)}{\alpha_n(\mu_j - 1) \cos(\alpha_n) + \alpha_n^2 \sin(\alpha_n)}. \]  (4.21)

Substituting Equation (4.20) into Equations (4.1) and (4.2), the anodic and cathodic partial current transients due to a potential step, \( \Delta E \), are given respectively by

\[ \bar{i}_1(\bar{t}_1) = i_k \left\{ \kappa_{11} + \kappa_{12} \sum_{n=1}^{\infty} A_1(\alpha_n)e^{-\alpha_n^2\bar{t}_1} \right\} e^{\Delta E/b_{\alpha_1}}, \]  (4.22)

\[ \bar{i}_2(\bar{t}_2) = -i_k \left\{ \kappa_{21} + \kappa_{22} \sum_{n=1}^{\infty} A_2(\alpha_n)e^{-\alpha_n^2\bar{t}_2} \right\} e^{-\Delta E/b_{\alpha_2}}, \]  (4.23)

where

\[ \kappa_{11} = \frac{\alpha}{\bar{i}_{L_1}} \left\{ 1 - \left( \bar{C}_1(0, 0) + \frac{\lambda_1}{1 - \mu_1} \right) e^{-\gamma\Delta E_1} \right\}, \]

\[ \kappa_{12} = 2\alpha \lambda_1 e^{-\gamma\Delta E_1}/\bar{i}_{L_1}, \]

\[ \kappa_{21} = \left( \bar{i}_{L_2} \bar{C}_2(0, 0) \right)^{-1} \left( \bar{C}_2(0, 0) + \frac{\lambda_2}{1 - \mu_2} \right), \]

\[ \kappa_{22} = 2 \left( \bar{i}_{L_2} \bar{C}_2(0, 0) \right)^{-1} \lambda_2. \]
Now, to calculate the total non-dimensional current transient, care is needed since the partial currents are non-dimensionalized with respect to two different limiting current densities \( i_{L_1} \) and \( i_{L_2} \). Therefore, for consistency, the total current must be non-dimensionalized with respect to either \( i_{L_1} \) or \( i_{L_2} \). The cathodic limiting current density, \( i_{L_2} \) is chosen as the current scale. This is chosen because it is physically meaningful, being the maximum rate at which the hydrogen evolution reaction may proceed. On the other hand, \( i_{L_1} \) represents the limiting rate at which the metal-ion deposition reaction may proceed, which is of no physical interest for our purposes, since this would require a very large cathodic (i.e. negative) potential step, such that metal dissolution is negligible compared to metal-ion deposition. Time is also normalized using \( \tau_2 \). Therefore

\[
\tilde{i}(\tilde{t}_2) = \frac{i(\tilde{t}_2)}{i_{L_2}} = \hat{D}\tilde{i}_1(\hat{\tau}\tilde{t}_1) + \tilde{i}_2(\tilde{t}_2), \tag{4.24}
\]

where \( \tilde{i}_1(\tilde{t}_1) \) and \( \tilde{i}_2(\tilde{t}_2) \) are given by Equations (4.22) and (4.23) respectively,

\[
\hat{D} = \frac{n_1 D_1 C_1^b}{n_2 D_2 C_2^b}, \quad \text{and} \quad \hat{\tau} = \tau_2/\tau_1.
\]

Equation (4.24) represents the total non-dimensional current transient of the corrosive system represented by Equations (3.2) and (3.3), due to a potentiostatic step, \( \Delta E \). Typical current transients obtained using Equation (4.24) and the effect of the back reaction are shown in Figures 4.5 and 4.6.

### 4.2.2 Results and Discussion

Parameters used in all calculations are as follows; \( D_1 = 0.72 \times 10^{-5} \text{cm}^2\text{s}^{-1} \), \( D_2 = 9.13 \times 10^{-5} \text{cm}^2\text{s}^{-1} \), \( b_a = 36\text{mV} \), \( b_c = 120\text{mV} \) (which are typical values for
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$Zn^{2+}$ and $H^+$ ions respectively) [69] and $C_1^b = C_2^b$ (note that values for $C_1^b$ and $C_2^b$ are not needed, since the concentrations are expressed in non-dimensional form).

The equilibrium potential of the metal, $E_{01}$, was calculated using the bulk concentration, $C_1^b$ in the Nernst equation (Equation (2.18)). The exact solution for the non-dimensional hydrogen concentration (Equations (4.20)-(4.21), using the first 3 terms) was used to verify the numerical solution obtained by the well known Crank-Nicholson method [33] (Figure 4.4). Excellent agreement of the two solutions was observed. Note that the concentration of the metal ions is not shown, since the purpose of this is to compare exact analytical and numerical solutions, and that the boundary value problems for both ions (i.e. hydrogen and metal ions) are of identical form.

The effect of neglecting the back reaction (metal-ion deposition) on the overall current transients is demonstrated in Figures 4.5-4.6. The relative error in neglecting the back reaction, was found to depend on $i_k$, $\Delta E (= E - E_k)$ and $\Delta E_{1k} (= E_k - E_{01})$.

The error due to neglecting the back reaction when $\Delta E_{1k} = 50\text{mV}$ and $i_k = 0.5i_{L2}$, was found to be approximately 12% and 33% for an applied potential step, $\Delta E = \pm 30\text{mV}$ respectively. Increasing the potential step to $\Delta E = \pm 60\text{mV}$ resulted in the errors being 10% and 60% respectively, while increasing $i_k$ to $0.9i_{L2}$ resulted in errors of 20% and 50% for $\Delta E = \pm 30\text{mV}$ respectively. Using $\Delta E_{1k} = 80\text{mV}$ resulted in a maximum error of approximately 8% for the conditions mentioned above (i.e. $\Delta E = \pm 30\text{mV}$ and $\Delta E = \pm 60\text{mV}$).

From the above errors, it can be seen that when anodic (positive) potential steps are applied, the effect of the back reaction becomes less significant as the
Figure 4.4: Comparison of non-dimensional surface concentration obtained from the Exact solution (Equations (4.20)-(4.21), using the first 3 terms) and that obtained using the Crank-Nicholson method [33], for $i_k = 0.4i_{L_2}$ and an applied potentiostatic step: (a) $\Delta E = -30\text{mV}$ and (b) $\Delta E = 30\text{mV}$. 
Figure 4.5: Effect of the metal-ion deposition partial reaction (back reaction) on the non-dimensional current transients. $\Delta E = \pm 30 \text{mV}$, $i_k = 0.5i_{L_2}$; (a) back reaction not included; (b), (c) back reaction included with $E_k - E_{0i} = 80 \text{mV}$ and $50 \text{mV}$ respectively.
Figure 4.6: Effect of the metal-ion deposition partial reaction (back reaction) on the non-dimensional current transients. $\Delta E = \pm 60\text{mV}$, $i_k = 0.5i_{L2}$; (a) back reaction not included; (b), (c) back reaction included with $E_k - E_{01} = 80\text{mV}$ and $50\text{mV}$ respectively.
potential step size is increased, thus reducing the errors involved in neglecting the back reaction, e.g. neglecting the back reaction when \( E_k - E_{01} = 50 \text{mV} \), results in an error of 12% for \( \Delta E = 30 \text{mV} \) and 10% for \( \Delta E = 60 \text{mV} \).

This is to be expected, since anodic steps cause the metal to corrode at a higher rate, in which case the metal dissolution reaction would be much more significant than the metal-ion deposition (back) reaction. In contrast, cathodic (negative) potential steps cause the back reaction to have a more significant effect, and thus increasing the step size causes an increase in the errors involved in neglecting the back reaction, e.g. neglecting the back reaction when \( E_k - E_{01} = 50 \text{mV} \), results in an error of 33% for \( \Delta E = -30 \text{mV} \) and 60% for \( \Delta E = -60 \text{mV} \).

Another way of understanding the effect of \( \Delta E \) on the errors due to neglecting the back reaction is as follows. Consider Equation (4.1),

\[
\tilde{i}_1(\tilde{t}_1) = \frac{i_k}{i_{L1}} \left\{ \frac{1 - \tilde{C}_1(0, \tilde{t}_1) e^{-\gamma \Delta E_1}}{1 - \tilde{C}_1(0, 0) e^{-\gamma \Delta E_{1k}}} \right\} e^{(E_k - E_{01})/b_{a1}}.
\]

Now if the corrosion potential, \( E_k \), is far removed from the equilibrium potential of the metal-ions, \( E_{01} \), such that \( \Delta E_{1k} \gg RT/n_1F \), then the above equation reduces to

\[
\tilde{i}_1(\tilde{t}_1) = \frac{i_k}{i_{L1}} \left\{ 1 - \tilde{C}_1(0, \tilde{t}_1) e^{-\gamma \Delta E_1} \right\} e^{(E_k - E_{01})/b_{a1}},
\]

which further reduces to Equation (4.3) below if \( \Delta E_1(= E - E_{01}) \gg RT/n_1F \),

\[
\tilde{i}_1(\tilde{t}_1) = \frac{i_k}{i_{L1}} e^{(E_k - E_{01})/b_{a1}}.
\]

This condition is satisfied if large anodic (positive) potential steps are applied. However, if large cathodic (negative) potential steps are applied then the above condition
for $\Delta E_1$ is not satisfied, and Equation (4.3) should not be used. Hence for large cathodic potential steps are applied, Equation (4.3) leads to large errors, even for large values of $\Delta E_{ik}$.

Finally, independent of the step applied, large errors due to neglecting the back reaction were observed as the corrosion current density $i_k$ approaches the limiting current density of the cathodic species, $i_{L_2}$ (i.e. as the cathodic reaction approaches conditions of pure diffusion control). At the limiting current, the corrosion reaction is proceeding at its maximum rate, and thus the surface concentration of the metal ions, due to metal dissolution, becomes relatively large. This promotes the metal-ion deposition reaction, which is proportional to the metal-ion concentration at the electrode surface.

It should be noted that the exact analytical solutions obtained converge rapidly, and have the advantage over the previous numerical solution, that they can be used to curve-fit experimental data to theoretical models much more efficiently, which results in quick measurements of the corrosion rate. The potentiostatic (transient) method has a number of advantages, compared to steady state methods, some of which are:

- Kinetic parameters can be predicted from current transients, thus greatly reducing measurement times involved, especially for reactions with large times to steady state.

- No assumptions about the system reaching a steady state are required, since actual current transients are used for the analysis.

- Because measurements are carried out in short intervals of time, coupled chem-
ical reactions (e.g. $\text{Zn}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Zn(OH)}_2$, and passivating film formation on steel) would have minimal effects.

### 4.3 The Potentiodynamic Method

In the potentiodynamic experiment, the electrode potential is varied linearly in time from the corrosion potential, $E_k$, according to the relationship $E = E_k + Vt$, where $V$ is the scan rate, as illustrated in Figure 4.7. The current produced is then measured, and a polarization curve is constructed, from which the corrosion current and Tafel slopes can be calculated. Unfortunately, however, it is common to fit an non-steady state polarization curve obtained in this manner to a steady state polarization equation as in Chapter 3 [83, 93], which of course can lead to large errors. Walter [100] has previously examined this problem and showed that, for pure zinc in aerated and deaerated 0.1M NaCl solutions, the polarization resistance, $R_p$ (which is inversely proportional to the corrosion current density) generally decreased with faster scan rates (larger values of $V$). That is, Walter showed that corrosion rates calculated from such polarization curves were dependent on the scan rate used.

A number of authors [43, 76, 92] have proposed methods of obtaining the maximum scan rate, such that steady state polarization data may be obtained. These however, were based on analysing equivalent circuit representations, which assume pure charge-transfer control. For mixed diffusion and charge-transfer control, determining the maximum allowable scan rate for steady state conditions, would be much more complicated. Instead, we take a different approach, where we solve the diffusion equation as in the previous section with the appropriate boundary conditions,
which leads to an expression for the current density as a function of time and the applied scan rate, $V$. Once this expression is obtained, one can then fit the resulting experimental polarization data to it without making any assumptions about steady state at all.

### 4.3.1 The mathematical model

Substituting $E = E_k + Vt$, Equations (4.1) and (4.2) can be rewritten as

$$
\tilde{i}_1(\tilde{t}_1) = \frac{i_k}{i_{L_1}} \left( e^{V\tau_1}\tilde{t}_1/b_{a_1} - \tilde{C}_1(0, \tilde{t}_1)e^{-\gamma\Delta E_{k}}e^{-V\tau_1}\tilde{t}_1/b_{c_1} \right), \quad (4.26)
$$

$$
\tilde{i}_2(\tilde{t}_2) = \frac{i_k}{i_{L_2}} \frac{\tilde{C}_2(0, \tilde{t})}{\tilde{C}_2(0, 0)} e^{-V\tau_2}\tilde{t}_2/b_{c_2}, \quad (4.27)
$$

where $\alpha = \left[ 1 - \tilde{C}_1(0, 0) e^{-\gamma\Delta E_{k}} \right]^{-1}$. Using Equations (4.4) and (4.5) and introducing the nondimensional parameter $\nu = V\tau_2/b_{c_2}$, we obtain the boundary value
problem given by

\[
\frac{\partial \theta_j}{\partial \bar{t}_j} = \frac{\partial^2 \theta_j}{\partial \xi^2},
\]  

(4.28)

\[
\theta_j(\xi,0) = 0,
\]  

(4.29)

\[
\theta_j(0,\bar{t}_j) = 0,
\]  

(4.30)

\[
\frac{\partial \theta_j}{\partial \xi}(1,\bar{t}_j) = a_j e^{\alpha_j \bar{t}_j} + b_j (\theta_j(1,\bar{t}_j) + C_j 0) e^{-\beta_j \bar{t}_j} + \gamma_j,
\]  

(4.31)

where

\[
\alpha_j = \left(\tau_j/\tau_2\right)(b_{c_2}/b_a), \quad \beta_j = \left(\tau_j/\tau_2\right)(b_{c_2}/b_c), \quad C_{j0} = \tilde{C}_j(0,0), \quad a_1 = \alpha_i k/i L_1
\]

\[
a_2 = 0, \quad \gamma_j = 1 - C_{j0}, \quad b_1 = -\alpha_i k e^{-\gamma \Delta \varepsilon_{1e}} / i L_1, \quad b_2 = -i_k / (i L_2 \tilde{C}_2(0,0)).
\]

Even though the above boundary value problem (b.v.p) is linear, analytical solutions were not possible to obtain due to the nature of the boundary conditions. In order to obtain some approximate solutions, we perform a perturbation analysis as follows.

Assuming that the scan rate is low, i.e. \(|V| \ll 1\), we substitute the following expansion for \(\theta_j\)

\[
\theta_j(x,t) = v \theta_j^{(1)}(x,t) + v^2 \theta_j^{(2)}(x,t) + \ldots,
\]  

(4.32)

into equations (4.28)-(4.31) and approximate exponential terms using a first order Taylor series. Note that the factor \(\tau_2/b_{c_2} \leq 1\) for all physically relevant values of \(\tau_2\) and \(b_{c_2}\), therefore \(|V| \ll 1\) implies that \(|v| \ll 1\). Considering the leading order b.v.p, we obtain

\[
\frac{\partial \theta_j^{(1)}}{\partial \bar{t}_j} = \frac{\partial^2 \theta_j^{(1)}}{\partial \xi^2},
\]  

(4.33)

\[
\theta_j^{(1)}(\xi,0) = 0,
\]  

(4.34)
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\[ \theta_j^{(1)}(0, \tilde{t}_j) = 0, \quad (4.35) \]
\[ \frac{\partial \theta_j^{(1)}}{\partial \xi} (1, \tilde{t}_j) = \omega_j \tilde{t}_j + b_j \theta_j^{(1)}(1, \tilde{t}_j), \quad (4.36) \]

where \( \omega_j = a_j \alpha_j - b_j C_j \alpha_j \). Taking Laplace transform of (4.33) and applying (4.34)-(4.35) as before we get

\[ \tilde{\theta}_j^{(1)}(\xi, s) = A_j(s) \sinh \left( \xi s^{1/2} \right). \quad (4.37) \]

Now taking Laplace transform of (4.36), yields

\[ \frac{d\tilde{\theta}_j^{(1)}}{d\xi} (1, s) = \frac{\omega_j}{s^2} + b_j \tilde{\theta}_j^{(1)}(1, s), \quad (4.38) \]

which upon using Equation (4.37) yields

\[ A_j(s) = \frac{\omega_j}{s^2 \left[ s^{1/2} \cosh \left( s^{1/2} \right) - b_j \sinh \left( s^{1/2} \right) \right]}, \quad (4.39) \]

and thus

\[ \tilde{\theta}_j(\xi, s) = \frac{\omega_j \sinh \left( \xi s^{1/2} \right)}{s^2 \left[ s^{1/2} \cosh \left( s^{1/2} \right) - b_j \sinh \left( s^{1/2} \right) \right]}. \quad (4.40) \]

Applying the Inversion theorem as before, we may readily deduce that

\[ \theta_j^{(1)}(\xi, \tilde{t}_j) = \frac{\omega_j \left[ (b_j - 3) + (b_j - 1) \left( \xi^2 + 6 \tilde{t}_j \right) \right]}{6 (b_j - 1)^2} \]

\[ - 2 \omega_j \sum_{n=0}^{\infty} \frac{e^{-\lambda_n^2 \tilde{t}_j} \sin (\lambda_n \xi)}{(1 - b_j) \lambda_n^2 \cos (\lambda_n) - \lambda_n^4 \sin (\lambda_n)}, \quad (4.41) \]

where \( \lambda_n \) are the increasing sequence of roots of the equation

\[ \lambda_n = b_j \tan (\lambda_n). \quad (4.42) \]

Therefore, the nondimensional surface concentrations are approximated, for relatively small values of \( \nu \), by

\[ C_j(0, \tilde{t}_j) = C_j(0, 0) + \nu \omega_j \left[ \frac{(b_j - 3) + (b_j - 1) \left( 1 + 6 \tilde{t}_j \right)}{6 (b_j - 1)^2} + \sum_{n=0}^{\infty} B_j(\lambda_n) e^{-\lambda_n^2 \tilde{t}_j} \right], \quad (4.43) \]
where \( B_j(\lambda_n) \) is given by

\[
B_j(\lambda_n) = \frac{\sin(\lambda_n)}{(1 - b_j) \lambda_n^3 \cos(\lambda_n) - \lambda_n^4 \sin(\lambda_n)}.
\]

The above results, are then substituted into Equations (4.26) and (4.27) to obtain the partial current densities. These are then substituted into Equation (4.24) to calculate the total current density as a function of time as in Section 4.2.1.

### 4.3.2 Results and Discussion

Using the same physical values of all parameters [69], as discussed earlier in Section 4.2.2, a comparison between the approximate analytical and numerical solutions was performed. The approximate solutions produced very good results for scan rates of magnitude up to 1 mV/sec. Maximum errors between numerical and approximate analytical surface concentrations were found to be less than 3% for \(|V| = 1\text{mV/sec}.\)

Typical surface concentrations for the metal-ions are shown in Figures 4.8 and 4.9. Errors in the hydrogen ion concentrations were found to be significantly lower than the corresponding values for the metal-ions, and as such are not shown here, since we are only interested in the maximum errors only. This is to be expected, since the metal-ions have a time constant \((\tau_1 = \delta^2/D_1)\) which is approximately one order of magnitude larger than that of the hydrogen ions (note that these time constants appear in the exponential terms in Equation (4.31)). Finally, it can be seen from Figures 4.8 and 4.9, that the surface concentration of the metal ions increases with time for a positive (anodic) scan, and decreases for a negative (cathodic) scan. This is also expected, since an anodic scan causes metal dissolution to proceed at a higher rate compared to the (initial) corrosion rate, \( i_k \), hence an increase in
Figure 4.8: Comparison of non-dimensional surface concentration obtained from the approximate solution (---) (Equations (4.43)-(4.44), using the first 3 terms) and that obtained using the Crank-Nicholson method [33] (-----), for $i_k = 0.5i_{L_2}$; (a) $V = 0.1$ mV and (b) $V = -0.1$ mV.
Figure 4.9: Comparison of non-dimensional surface concentration obtained from the approximate analytical solution (---)(Equations (4.43)-(4.44), using the first 3 terms) and that obtained using the Crank-Nicholson method [33] (--), for $i_k = 0.5i_{LS}$; (a) $V = 1$ mV (anodic scan) and (b) $V = -1$ mV (cathodic scan).
metal-ion surface concentration. Similarly, a cathodic scan causes metal dissolution to proceed a lower rate compared to $i_k$, and hence a decrease in metal-ion surface concentration.

Given that it is common to use scan rates as low as 0.1 mV/sec, in laboratory experimentation (author's experience at BHP Research laboratories), to prevent destruction of the working sample (i.e. nondestructive corrosion testing) and to achieve pseudo-steady state conditions, these approximate solutions can be used with confidence to represent the physical processes (concentration variation of reacting ions and hence the current density response) during such experiments. Furthermore, it is expected that analysing experimental transients using these solutions would produce greater accuracy in calculated corrosion rates, than the conventional procedure of using a steady state polarization equation.
Chapter 5

Transient Methods: The Galvanostatic Method

5.1 Introduction

The galvanostatic electrochemical method is one of the basic and most commonly used methods for the determination of electrochemical reaction rates. The main advantage of this method is the fact that the experimental arrangement for galvanostatic measurements is generally simple [94], compared to other methods. However, it is not often used in corrosion measurements because the electrode potential is not always a single valued function of the current (as in passivation). In this method, the cell current is varied from zero to a constant value, and the transient electrode over-voltage is measured against a suitable reference electrode. The earliest use of this method was by Sand and Karaoglanoff [26] on diffusion controlled reactions, and by Bowden and Rideal [16], who were the first to use charging curves at constant cur-
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rent. In 1954, Berzins and Delahay [22], independently, showed how fast reactions could be studied by this method and considered conditions of mixed charge-transfer and diffusion control. In 1961, Bockris and Kita [13] used the galvanostatic method to investigate the coverage of electrodes by adsorbed species during the corrosion of iron. The galvanostatic method has also been used for studying corrosion reactions by Walter [96, 98, 99, 100], Jones and Greene [43], Azzari [2, 3] and Giuliani [34]. All of these were based on either pure charge-transfer control, or mixed charge-transfer and transport (semi-infinite diffusion) control.

In this chapter, the galvanostatic method applied to the corrosion reaction, given by Equations (3.2) and (3.3), is considered. The reaction is initially at steady state and the current step is applied at time \( t = 0 \). The mathematical model representing the corrosion reaction is described by a system of two boundary value problems which are nonlinearly coupled at the electrode surface. To the knowledge of the author, no numerical or analytical solutions have been presented for this model (i.e. representing the corrosion reaction given by Equations (3.2) and (3.3)) in the literature. The solution of this model will enable us to calculate the potential response of the electrode, which can then be fitted to experimental potential transients in order to calculate the corrosion current and the Tafel slopes. Numerical and leading order perturbation solutions to the resulting boundary value problems will be presented for two special cases. In the first case, it is assumed that metal dissolution only occurs, while in the second case both metal dissolution and metal-ion deposition occur. As a result of the perturbation analysis, we are able to decouple the boundary value problems for the case of metal dissolution only, thus obtaining solutions
for the leading order boundary value problems. If the metal-ion deposition reaction is also included, then the perturbation analysis leads to a system of two linearly coupled boundary value problems for which analytical solutions are also obtained. Numerical solutions are obtained using the method of lines [58], along with a special treatment to evaluate the nonlinear boundary conditions. Comparison between perturbation and numerical solutions will also be discussed.

5.2 Model development

The current density produced by reactions (3.2) and (3.3), are given by Equations (3.9) and (3.10), respectively. Rearranging Equations (3.9) and (3.10), and using Equation (3.8), the current densities can be rewritten as

\[ i_1 = \dot{\zeta} i_k \left( e^{\eta(t)/b_{a1}} - \xi C_1(0, t) e^{-\eta(t)/b_{c1}} \right), \]  

\[ i_2 = -i_k \frac{C_2(0, t)}{C_2(0, 0)} e^{-\eta(t)/b_{c2}}, \]

where \( \eta(t) = E(t) - E_k \), is the electrode polarization,

\[ \dot{\varsigma} = e^{-\gamma(E_k-E_0_1)/C_1^b}, \quad \dot{\zeta} = (1 - \dot{\xi} C_1(0, 0))^{-1}, \]

and \( \gamma \) is given by Equation (3.8). If the metal-ion deposition partial reaction is assumed to be negligible compared to the metal dissolution partial reaction, then \( \dot{\varsigma} \) in Equation (5.1) becomes zero. In this chapter, we show that when a galvanostatic step is applied to the electrode surface, a perturbation analysis results in boundary conditions which are linearized and decoupled for the case of metal dissolution only.
However, if the metal dissolution and metal-ion deposition are included, this leads to linearly coupled boundary conditions.

The mathematical model representing the corrosion reaction is given by Equations (2.33)- (2.36). Noting that the total current is the sum of the partial currents, and applying the galvanostatic condition, we have an extra condition

\[ I = i_1(t) + i_2(t), \]  

where \( I \) is the constant current applied across the electrode/solution interface. Using boundary conditions (2.36), the above condition can be rewritten as

\[ I = -n_1FD_1 \frac{\partial C_1(0, t)}{\partial x} - n_2FD_2 \frac{\partial C_2(0, t)}{\partial x}. \]  

It should be noted that it is the above condition, and the nonlinearity of Equations (5.1) and (5.2), which give rise to the nonlinear coupling of the boundary value problems, as shown below. This is in contrast to the case of a single electrochemical reaction, where galvanostatic conditions result in a constant flux boundary condition, which simplifies the mathematical model.

To facilitate the analysis, the following nondimensional variables are introduced,

\[ \bar{C}_j = \frac{C_j}{C^b}, \quad \bar{t} = \frac{t}{\tau_2}, \quad \bar{x} = \frac{x}{\delta}, \quad \bar{i}_j = \frac{i_j}{i_{L2}}, \quad \bar{I} = \bar{i}_1 + \bar{i}_2, \]

where

\[ \tau_2 = \frac{\delta^2}{D_2}, \quad i_{L2} = n_2FD_2 \frac{C^b}{\delta}. \]

Introducing the nondimensional parameters

\[ \epsilon = e^{-\gamma(E_k-E_{01})/\bar{C}_1^b}, \quad \zeta = (1 - \epsilon \bar{C}_1(0,0))^{-1}, \]
the system of boundary value problems can be written in nondimensional form as

\[
\frac{\partial C_j}{\partial t} = D_j \frac{\partial^2 C_j}{\partial x^2},
\]

(5.5)

\[
C_j(x,0) = C_j(0,0) + (C_j^* - C_j(0,0))x,
\]

(5.6)

\[
C_j(1, t) = C_j^*,
\]

(5.7)

\[
\frac{\partial C_1(0, t)}{\partial x} = -\mu \zeta_i k \left( e^{\eta(t)/b_{a_1}} - \epsilon C_1(0, t)e^{-\eta(t)/b_{c_1}} \right),
\]

(5.8)

\[
\frac{\partial C_2(0, t)}{\partial x} = -i_k C_2(0, t)e^{-\eta(t)/b_{c_2}},
\]

(5.9)

where \(D_1^* = D_1/D_2, D_2^* = 1, C_1^* = C_1^0, C_2^* = 1,\) and \(\mu = n_2 D_2/n_1 D_1.\) Also, Equation (5.4) becomes

\[
I = -\frac{1}{\mu} \frac{\partial C_1(0, t)}{\partial x} - \frac{\partial C_2(0, t)}{\partial x}.
\]

(5.10)

Using boundary condition (5.9), we get

\[
\eta(t) = \ln \left[ \frac{1}{i_k C_2(0, 0)} \frac{\partial C_2(0, t)}{\partial x} \right]^{-b_{c_2}},
\]

(5.11)

which upon substituting into boundary condition (5.8) and using Equation (5.10), yields the nonlinearly coupled boundary condition,

\[
\frac{\partial C_2(0, t)}{\partial x} = \zeta_i k \left[ \frac{h}{C_2(0, t)} \frac{\partial C_2(0, t)}{\partial x} \right]^{-\gamma_1} - \epsilon C_1(0, t) \left[ \frac{h}{C_2(0, t)} \frac{\partial C_2(0, t)}{\partial x} \right]^{\gamma_2} - I,
\]

(5.12)

where

\[
\gamma_1 = b_{c_2}/b_{a_1}, \quad \gamma_2 = b_{c_2}/b_{c_1}, \quad h = C_2(0, 0)/i_k.
\]

Equation (5.12) represents the nonlinearly coupled boundary condition, which arises from the fact that a constant current is applied to the electrode surface. Note that this is in contrast to the case where a potential step is applied to the electrode. In
the latter, the resulting boundary conditions are linear and exact analytical solutions were obtained. In the next section, a perturbation analysis is performed to simplify the boundary conditions. Approximate analytical solutions are presented for the two cases where metal dissolution only occurs and where both metal dissolution and metal-ion deposition occur.

5.3 Analysis of the Boundary Value Problems

First, we introduce the nondimensional variable $\theta_j$ such that

$$\theta_j(x, t) = C_j(x, t) - [C_j(0, 0) + (C^*_j - C_j(0, 0))x]. \quad (5.13)$$

Assuming that the applied current step is small in magnitude (compared to the cathodic limiting current density) such that $|I| \ll 1$, we substitute the expansion

$$\theta_j(x, t) = I\dot{\theta}_j^{(1)}(x, t) + I^2\dot{\theta}_j^{(2)}(x, t) + \cdots, \quad (5.14)$$

$$\eta(t) = I\eta^{(1)}(t) + I^2\eta^{(2)}(t) + \cdots, \quad (5.15)$$

into Equations (5.5)-(5.10) and approximate exponential terms using a first order Taylor series. Equating terms of the same order of magnitude leads to an infinite sequence of boundary value problems. Considering the leading order boundary value problem only, and substituting $\xi = 1 - x$, we obtain

$$\frac{\partial \theta_j^{(1)}}{\partial t} = D'_j \frac{\partial^2 \theta_j^{(1)}}{\partial \xi^2}, \quad (5.16)$$

$$\theta_j^{(1)}(\xi, 0) = 0, \quad (5.17)$$

$$\theta_j^{(1)}(0, t) = 0, \quad (5.18)$$

$$\frac{\partial \theta_j^{(1)}(1, t)}{\partial \xi} = \mu \zeta \epsilon_k \left( \omega \eta^{(1)}(t) - \epsilon \theta_j^{(1)}(1, t) \right), \quad (5.19)$$
Chapter 5. The Galvanostatic Method

\[
\frac{\partial \theta_2^{(1)}(1,t)}{\partial \xi} = i_k \left( \frac{\eta^{(1)}(t)}{b_{c_2}} - \frac{\theta_2^{(1)}(1,t)}{C_2(0,0)} \right), \tag{5.20}
\]

and

\[
1 = \frac{1}{\mu} \frac{\partial \theta_1^{(1)}(1,t)}{\partial \xi} + \frac{\partial \theta_2^{(1)}(1,t)}{\partial \xi}. \tag{5.21}
\]

We now present some analytical solutions to the above leading order system of boundary value problems, given by Equations (5.16)-(5.21), for the two cases where metal dissolution only occurs and where metal dissolution and metal-ion deposition occur. Solutions are obtained for the concentrations of both ions and for the potential response of the electrode, using the Laplace transform, details of which are presented in Sections 5.3.1 and 5.3.2, respectively.

### 5.3.1 Solution for metal dissolution only

If the metal-ion deposition partial reaction is assumed to be negligible compared to the metal dissolution partial reaction, then \( \epsilon = 0 \) (in Equation (5.1)), and hence \( \zeta = 1 \) and \( \omega = 1/b_{a_1} \). Therefore boundary condition (5.19) becomes,

\[
\frac{\partial \theta_1^{(1)}(1,t)}{\partial \xi} = \frac{\eta^{(1)}(t)}{b_{a_1}}. \tag{5.22}
\]

Using Equations (5.21) and (5.22), we get

\[
\eta^{(1)}(t) = \frac{b_{a_1}}{i_k} \left[ 1 - \frac{\partial \theta_2^{(1)}(1,t)}{\partial \xi} \right], \tag{5.23}
\]

which upon substituting into Equation (5.20) yields the linear boundary condition of the Robin type,

\[
\frac{\partial \theta_2^{(1)}(1,t)}{\partial \xi} = \gamma_1(1 + \gamma_1)^{-1} \left( \gamma_1^{-1} - \frac{i_k \theta_2^{(1)}(1,t)}{C_2(0,0)} \right). \tag{5.24}
\]
We now solve the boundary value problem given by Equations (5.16)-(5.18) and (5.24) for $\theta_{2}^{(1)}(\xi, t)$. Taking the Laplace transform of Equation (5.16) and using (5.17) we get

$$\tilde{\theta}_{2}^{(1)}(\xi, s) = A(s)e^{-\xi\sqrt{s}} + B(s)e^{\xi\sqrt{s}}.$$  \hspace{1cm} (5.25)

Applying boundary conditions (5.18) and (5.24) yields

$$\tilde{\theta}_{2}^{(1)}(\xi, s) = \frac{\omega}{s\sqrt{s}} \frac{\sinh(\xi\sqrt{s})}{\cosh(\sqrt{s}) - \lambda \sinh(\sqrt{s})},$$  \hspace{1cm} (5.26)

where $\tilde{\theta}_{j}^{(1)}(\xi, s)$ is the Laplace transform of $\theta_{j}^{(1)}(\xi, t)$, $\lambda = -\frac{1}{i}\left[(1 + \gamma_{1}^{-1})C_{2}(0, 0)\right]^{-1}$ and $\omega = (1 + \gamma_{1})^{-1}$. Equation (5.26) is analogous to Equation (4.11), and can be inverted using the same procedure. Therefore, we may readily obtain

$$\theta_{2}^{(1)}(x, t) = \frac{\omega}{1 - \lambda} \left(1 - \frac{x}{\lambda}\right) - 2\omega \sum_{n=1}^{\infty} \frac{e^{-\alpha_{n}^{2}t \sin(\alpha_{n}x)}}{\alpha_{n}(\lambda - 1) \cos(\alpha_{n}) + \alpha_{n}^{2} \sin(\alpha_{n})},$$  \hspace{1cm} (5.27)

where $\alpha_{n}$ are the increasing sequence of roots of the equation

$$\alpha_{n} = \lambda \tan(\alpha_{n}), \hspace{0.5cm} n = 1, 2, \ldots, \infty.$$  \hspace{1cm} (5.28)

Substituting Equation (5.27) into (5.23), we obtain

$$\eta^{(1)}(t) \approx \frac{b_a}{i_k} \left(1 - \frac{\omega}{1 - \lambda} + \sum_{n=1}^{\infty} \frac{2\omega e^{-\alpha_{n}^{2}t \cos(\alpha_{n})}}{\lambda - 1 \cos(\alpha_{n}) + \alpha_{n} \sin(\alpha_{n})}\right).$$  \hspace{1cm} (5.29)

The above equation is an approximate expression for the potential transient response to an applied galvanostatic step in the presence of mixed charge-transfer and diffusion control. As far as calculation of corrosion parameters is concerned, this equation is sufficient, i.e. this equation would be fitted to experimental potential transients. We now use the above result to calculate the concentration response of the metal ions, in order to compare these to the full numerical solution. We solve
the boundary value problem given by Equations (5.16)-(5.19) for $\theta_1^{(1)}(\xi, t)$. Taking the Laplace transform and applying the boundary conditions, we have

$$\tilde{\theta}_1(\xi, s) = \frac{\mu}{\nu} \left\{ \frac{\sinh(\nu \xi \sqrt{s})}{s^{3/2} \cosh(\nu \sqrt{s})} - \frac{\omega}{s \cosh(\nu \sqrt{s})} \frac{\sinh(\nu \xi \sqrt{s}) \cosh(\sqrt{s})}{\sqrt{s} \cosh(\sqrt{s}) - \lambda \sinh(\sqrt{s})} \right\}, \quad (5.30)$$

where $\nu = 1/\sqrt{D_1^2}$. We consider each term of $\tilde{\theta}_1(\xi, s)$ separately. Let

$$\tilde{u}(\xi, s) = \frac{\sinh(\nu \xi \sqrt{s})}{s^{3/2} \cosh(\nu \sqrt{s})}, \quad (5.31)$$

$$\tilde{v}(\xi, s) = \frac{\omega}{s \cosh(\nu \sqrt{s})} \frac{\sinh(\nu \xi \sqrt{s}) \cosh(\sqrt{s})}{\sqrt{s} \cosh(\sqrt{s}) - \lambda \sinh(\sqrt{s})}. \quad (5.32)$$

Expanding $\tilde{u}(\xi, s)$, we have

$$\tilde{u}(\xi, s) = \frac{1}{s^{3/2}} \left( \frac{e^{\nu \xi \sqrt{s}}}{e^{\nu \sqrt{s}} + e^{-\nu \sqrt{s}}} - \frac{e^{-\nu \xi \sqrt{s}}}{e^{\nu \sqrt{s}} + e^{-\nu \sqrt{s}}} \right). \quad (5.33)$$

Using the binomial theorem, the first term of $\tilde{u}(\xi, s)$ can be rewritten as

$$\frac{1}{s^{3/2}} \frac{e^{\nu \xi \sqrt{s}}}{e^{\nu \sqrt{s}} + e^{-\nu \sqrt{s}}} = \sum_{n=0}^{\infty} \frac{(-1)^{n+1} e^{-(2n+1) \xi \nu \sqrt{s}}}{s^{3/2}},$$

the inverse Laplace transform of which is given by

$$\sum_{n=0}^{\infty} (-1)^n \left\{ 2 \sqrt{\frac{t}{\pi}} \exp \left( -\frac{(2n+1-\xi)^2 \nu^2}{4t} \right) - (2n+1-\xi) \nu \text{erfc} \left( \frac{(2n+1-\xi) \nu}{2 \sqrt{t}} \right) \right\}.$$

Applying the same treatment to the second term of $\tilde{u}(\xi, s)$ yields,

$$u(\xi, t) = \sum_{n=0}^{\infty} (-1)^n \left\{ 2 \sqrt{\frac{t}{\pi}} \exp \left( -\frac{(2n+1-\xi)^2 \nu^2}{4t} \right) - (2n+1-\xi) \nu \text{erfc} \left( \frac{(2n+1-\xi) \nu}{2 \sqrt{t}} \right) - 2 \sqrt{\frac{t}{\pi}} \exp \left( -\frac{(2n+1+\xi)^2 \nu^2}{4t} \right) + (2n+1+\xi) \nu \text{erfc} \left( \frac{(2n+1+\xi) \nu}{2 \sqrt{t}} \right) \right\}. \quad (5.34)$$
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We now find the inverse Laplace transform of $\tilde{u}(\xi, s)$ using the inversion theorem and the Cauchy residue theorem as in Section 4.2.2. Thus

$$v(\xi, t) = \sum_{n=0}^{N} \text{Res}(J(z), z_n),$$

(5.35)

where

$$J(z) = \frac{\omega K(z)}{\lambda L(z) \cosh(\nu \sqrt{z})},$$

$$K(z) = \sinh(\nu \xi \sqrt{z}) \cosh(\sqrt{z}) e^{zt},$$

$$L(z) = \sqrt{z} \cosh(\sqrt{z}) - \lambda \sinh(\sqrt{z}).$$

Thus $J(z)$ has simple poles at $z = 0$, $\cosh(\nu \sqrt{z}) = 0$ and $L(z) = 0$. The residue at $z = 0$ is given by

$$\text{Res}_1 = \lim_{z \to 0} \frac{\omega K(z)}{L(z) \cosh(\nu \sqrt{z})} = \frac{\omega \nu \xi}{1 - \lambda}.$$ 

(5.36)

Now to calculate the zeroes of $\cosh(\nu \sqrt{z})$, we substitute $z = -\beta_n^2$, therefore

$$\cos(\nu \beta_n) = 0 \implies \beta_n = \frac{(2n + 1) \pi}{2 \nu}, n = 0, 1, 2, \ldots.$$ 

Therefore, the residues at $\beta_n$ are given by

$$\text{Res}_2 = \frac{\omega K(-\beta_n^2)}{-\beta_n^2 L(-\beta_n^2) \left( \frac{d}{dz} (\cosh(\nu \sqrt{z})) \right)_{-\beta_n^2}}$$

$$= \frac{-2\omega \sin(\nu \beta_n \xi) \cos(\beta_n) e^{-\beta_n^2 t}}{\nu \beta_n \sin(\nu \beta_n) [\beta_n \cos(\beta_n) - \lambda \sin(\beta_n)]}.$$ 

(5.37)

Finally, the zeroes of $L(z)$ occur at $z = -\alpha_n^2$, where $\alpha_n$ are given by Equation (5.28).

Therefore, the residues at $\alpha_n$ are given by

$$\text{Res}_3 = \frac{\omega K(-\alpha_n^2)}{-\alpha_n^2 \cos(\nu \alpha_n) L'(-\alpha_n^2)}$$

$$= \frac{-2\omega \sin(\nu \alpha_n \xi) \cos(\alpha_n) e^{-\alpha_n^2 t}}{\alpha_n \cos(\nu \alpha_n) [(\lambda - 1) \cos(\alpha_n) + \alpha_n \sin(\alpha_n)]}.$$ 

(5.38)
Substituting Equations (5.36)-(5.38) into Equation (5.35), we get

\[ v(\xi, t) = \frac{\omega \nu \xi}{1 - \lambda} - 2\omega \left\{ \frac{\sin(\nu \beta_n \xi) \cos(\beta_n) e^{-\beta_n^2 t}}{\nu \beta_n \sin(\nu \beta_n) [\beta_n \cos(\beta_n) - \lambda \sin(\beta_n)]} \right. \\
+ \frac{\sin(\nu \alpha_n \xi) \cos(\alpha_n) e^{-\alpha_n^2 t}}{\alpha_n \cos(\nu \alpha_n) [(\lambda - 1) \cos(\alpha_n) + \alpha_n \sin(\alpha_n)]} \left\} \right. \\
\] (5.39)

Finally, combining Equations (5.34) and (5.39) and substituting \( \xi = 1 - x \), yields

\[ \theta_1^{(1)}(x, t) = \frac{\mu}{\nu} \sum_{n=1}^{\infty} \left\{ (-1)^n \left[ (2(n+1) - x) \nu \operatorname{erfc} \left( \frac{2(n+1) - x}{2\sqrt{t}} \right) \right. \\
- (2n + x) \nu \operatorname{erfc} \left( \frac{2n + x}{2\sqrt{t}} \right) \left] + \frac{2\omega \sin(\nu \beta_n (1 - x)) \cos(\beta_n) e^{-\beta_n^2 t}}{\nu \beta_n \sin(\nu \beta_n) [\beta_n \cos(\beta_n) - \lambda \sin(\beta_n)]} \right\} + \frac{\mu \omega (x - 1)}{1 - \lambda}. \] (5.40)

The solutions obtained above are due to the perturbation analysis, which resulted in linearizing and decoupling the boundary conditions for each ion (i.e. metal and hydrogen ions). These solutions are relatively simple, involving elementary functions and error functions which are readily evaluated by well established algorithms [1].

Below, we examine the boundary value problems which arise if metal-ion deposition is also included. It will be shown that the situation is slightly different in this case.

### 5.3.2 Solution for metal dissolution and metal-ion deposition

We now solve the boundary value problems given by Equations (5.16)-(5.21) with both metal dissolution and metal-ion deposition occurring at the electrode surface.
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Rearranging Equation (5.21) yields,
\[ \frac{\partial \theta_1^{(1)}(1,t)}{\partial \xi} = \mu \left( 1 - \frac{\partial \theta_2^{(1)}(1,t)}{\partial \xi} \right), \]  
(5.41)

which upon substituting into Equation (5.19) and rearranging yields,
\[ \eta^{(1)}(t) = \zeta^* \left( 1 - \frac{\partial \theta_2^{(1)}(1,t)}{\partial \xi} \right) + \frac{\mu}{\omega} \theta_1^{(1)}(1,t), \]  
(5.42)

where \( \zeta^* = (\omega \zeta_i k)^{-1} \). Note that by including the metal-ion deposition partial reaction, the potential transients now depend on both the metal ion and hydrogen ion surface concentrations. Finally, substituting Equation (5.42) into boundary condition (5.20), yields the linearly coupled boundary condition,
\[ \frac{\partial \theta_2^{(1)}(1,t)}{\partial \xi} = \alpha \theta_1^{(1)}(1,t) + \beta \theta_2^{(1)}(1,t) + \gamma, \]  
(5.43)

where
\[
\alpha = \epsilon i_k (\omega \zeta_{b_{c_2}})^{-1} k, \quad \beta = -h^{-1} k, \quad \gamma = (\omega \zeta_{b_{c_2}})^{-1} k, \quad k = (1 + (\omega \zeta_{b_{c_2}})^{-1})^{-1}.
\]

Unlike the boundary value problems in Section 5.3.1, Equations (5.16)-(5.18), (5.41) and (5.43) constitute a system of linearly coupled boundary value problems. Upon applying the Laplace transform as before, we may eventually deduce that (see Appendix A for details)
\[ \tilde{\theta}_1^{(1)}(\xi, s) = s^{-3/2} \left[ \sqrt{s} \left( 1 - \gamma \right) \cosh(\sqrt{s}) - \beta \sinh(\sqrt{s}) \right] \sinh(\nu_1 \sqrt{s} \xi) \mu^{-1} \nu_1 \cosh(\nu_1 \sqrt{s}) \left[ \sqrt{s} \cosh(\sqrt{s}) - \beta \sinh(\sqrt{s}) \right] + \alpha \sinh(\nu_1 \sqrt{s}) \cosh(\sqrt{s}), \]  
(5.44)

and
\[ \tilde{\theta}_2^{(1)}(\xi, s) = \alpha \left[ \sqrt{s} \left( 1 - \gamma \right) \cosh(\sqrt{s}) - \beta \sinh(\sqrt{s}) \right] \sinh(\nu_1 \sqrt{s}) \sinh(\sqrt{s} \xi) \mu^{-1} \nu_1 \cosh(\nu_1 \sqrt{s}) \left[ \sqrt{s} \cosh(\sqrt{s}) - \beta \sinh(\sqrt{s}) \right] + \alpha \sinh(\nu_1 \sqrt{s}) \cosh(\sqrt{s}) \]
\begin{align*}
\times \frac{s^{-3/2}}{\sqrt{s} \cosh(\sqrt{s}) - \beta \sinh(\sqrt{s})} + \frac{\gamma}{s} \frac{\sinh(\sqrt{s} \xi)}{\sqrt{s} \cosh(\sqrt{s}) - \beta \sinh(\sqrt{s})}.
\end{align*}

(5.45)

Again, use is made of the inversion theorem as before. First, we consider \( \bar{\phi}_1^{(1)}(\xi, s) \).

We let \( H(z) = \bar{\phi}_1^{(1)}(\xi, z) e^{zt} = F(z) z^{-3/2} / G(z) \), where

\begin{align*}
F(z) &= \left[ \sqrt{z} (1 - \gamma) \cosh(\sqrt{z}) - \beta \sinh(\sqrt{z}) \right] \sinh(\nu_1 \sqrt{z} \xi) e^{zt}, \\
G(z) &= \frac{\nu_1}{\mu} \cosh(\nu_1 \sqrt{z}) \left[ \sqrt{z} \cosh(\sqrt{z}) - \beta \sinh(\sqrt{z}) \right] + \alpha \sinh(\nu_1 \sqrt{z}) \cosh(\sqrt{z}).
\end{align*}

Thus, \( H(z) \) has simple poles at \( z = 0 \) and \( G(z) = 0 \). The residue at \( z = 0 \) is given by

\[ \text{Res}_{z=0} = \lim_{z \to 0} \frac{F(z)}{z^{1/2} G(z)} = A_{10}(\xi), \]

where

\[ A_{10} = \frac{\mu(1 - \beta - \gamma) \xi}{(1 - \beta + \alpha \mu)} \]

(5.47)

Now, we need to find the zeroes of \( G(z) \). Substituting \( z = -\rho_n^2 \), we have

\[ \nu_1 \cos(\nu_1 \rho_n) \left[ \rho_n \cos(\rho_n) - \beta \sin(\rho_n) \right] + \mu \alpha \cos(\rho_n) \sin(\nu_1 \rho_n) = 0. \]

(5.48)

We can show, provided that \( \nu_1 \neq 2k + 1 \), for integer values of \( k \), that values of \( \rho_n \) satisfying \( \cos(\nu_1 \rho_n) = 0 \), do not satisfy Equation (5.48) above. Thus, for physical values of \( \nu_1 \), we can divide through by \( \cos(\nu_1 \rho_n) \), and (5.48) becomes

\[ \nu_1 \left[ \rho_n \cos(\rho_n) - \beta \sin(\rho_n) \right] + \mu \alpha \cos(\rho_n) \tan(\nu_1 \rho_n) = 0, \]

which upon dividing by \( \cos(\rho_n) \), finally yields

\[ \rho_n - \beta \tan(\rho_n) + \frac{\mu \alpha}{\nu_1} \tan(\nu_1 \rho_n) = 0. \]

(5.49)
Thus, the zeroes of $G(z)$ are given by the roots of Equation (5.49). The residues at $z = i\rho_n$ are given by

\[
\text{Res}_{11} = \frac{-F(i\rho_n)}{i\rho_n^3 G'(i\rho_n)} = A_{11}(\rho_n) \sin(\nu_1 \xi \rho_n) e^{-\rho_n^2 t},
\]

(5.50)

where

\[
A_{11}(\rho_n) = \frac{2\rho_n^{-2} [\rho_n(\gamma - 1) \cos(\rho_n) + \beta \sin(\rho_n)]}{\Gamma_1(\rho_n) \sin(\nu_1 \rho_n) + \Gamma_2(\rho_n) \cos(\nu_1 \rho_n)}
\]

(5.51)

where

\[
\Gamma_1(\rho_n) = \sigma_1 \sin(\rho_n) + \sigma_2 \rho_n \cos(\rho_n)
\]

\[
\Gamma_2(\rho_n) = \nu_1 \left[ \mu^{-1} \rho_n \sin(\rho_n) - \sigma_3 \cos(\rho_n) \right]
\]

Upon summing all the residues, given by Equations (5.46) and (5.50), and substituting back for $x$, we obtain

\[
\theta_1^{(1)}(x, t) = A_{10}(x) + \sum_{n=0}^{\infty} A_{11}(\rho_n) \sin(\nu_1 \rho_n(1 - x)) e^{-\rho_n^2 t},
\]

(5.52)

where \(\{\rho_n, n = 1, 2, \cdots\}\), are the sequence of roots of Equation (5.49). We now consider $\tilde{\theta}_2^{(1)}(\xi, s)$ given by (5.45). We let

\[
\tilde{\theta}_2^{(1)}(\xi, z) = \tilde{\psi}_1(\xi, z) + \tilde{\psi}_2(\xi, z),
\]

(5.53)

\[
\tilde{\psi}_1(\xi, z) = \frac{\gamma}{z} \frac{\sinh(\sqrt{z} \xi) e^{\pi t}}{[\sqrt{z} \cosh(\sqrt{z}) - \beta \sinh(\sqrt{z})]}
\]

(5.54)

\[
\tilde{\psi}_2(\xi, z) = \frac{N(\xi, z)}{z^{3/2} M(z) G(z)},
\]

(5.55)

where

\[
M(z) = \sqrt{z} \cosh(\sqrt{z}) - \beta \sinh(\sqrt{z}),
\]
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\[ G(z) = \frac{\nu_1}{\mu} \cosh(\nu_1 \sqrt{z}) \left[ \sqrt{z} \cosh(\sqrt{z}) - \beta \sinh(\sqrt{z}) \right] + \alpha \sinh(\nu_1 \sqrt{z}) \cosh(\sqrt{z}), \]
\[ N(\xi, z) = \alpha \left[ \sqrt{z} (1 - \gamma) \cosh(\sqrt{z}) - \beta \sinh(\sqrt{z}) \right] \sinh(\nu_1 \sqrt{z}) \sinh(\sqrt{z} \xi) e^{zt}. \]

From (5.53)-(5.55), we see that \( \tilde{\theta}_2^{(1)}(\xi, s) \) has simple poles at \( z = 0 \). The residue is given by

\[ \text{Res}_{20} = \frac{(\alpha \mu + \gamma) \xi}{1 - \beta + \alpha \mu} = A_2(\xi). \]  

(5.56)

Equation (5.54) for \( \tilde{\psi}_1(\xi, z) \), is analogous to Equation (5.26), and can be inverted in a similar fashion. Thus, we obtain

\[ \psi_1(\xi, t) = -2\gamma \sum_{n=1}^{\infty} \frac{e^{-r_n^2 t} \sin(r_n \xi)}{r_n(\beta - 1) \cos(r_n) + r_n^2 \sin(r_n)}, \]  

(5.57)

where \( \{r_n, n = 1, 2, \ldots\} \), are the sequence of roots of

\[ r_n = \beta \tan(r_n). \]  

(5.58)

Now, \( \tilde{\psi}_2(\xi, z) \) has simple poles where \( M(z) = 0 \), and where \( G(z) = 0 \). The zeroes of \( M(z) \) and \( G(z) \) occur at \( z = ir_n \) and \( z = i\rho_n \), which are the roots of Equations (5.58) and (5.49) respectively. Residues at \( z = i\rho_n \) are given by

\[ \text{Res}_{21} = \frac{-N(\xi, i\rho_n)}{i\rho_n^3 M(i\rho_n) G'(i\rho_n)} = A_{21}(\rho_n) \sin(\xi \rho_n) e^{-r_n^2 t}, \]  

(5.59)

where

\[ A_{21}(\rho_n) = \frac{\alpha A_{11}(\rho_n) \sin(\nu_1 \rho_n)}{\rho_n \cos(\rho_n) - \beta \sin(\rho_n)}. \]  

(5.60)

Similarly, residues at \( z = -r_n^2 \) are given by

\[ \text{Res}_{22} = \frac{-N(\xi, i\rho_n)}{i\rho_n^3 M'(i\rho_n) G(i\rho_n)} = A_{22}(r_n) \sin(\xi r_n) e^{-r_n^2 t}, \]  

(5.61)

where

\[ A_{22}(r_n) = \frac{2\alpha r_n^{-1} A^{-1}(r_n) \left[ r_n(\gamma - 1) \cos(r_n) + \beta \sin(r_n) \right] \sin(\nu_1 r_n) - 2\gamma}{r_n(\beta - 1) \cos(r_n) + r_n^2 \sin(r_n)}. \]  

(5.62)
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\[ \Lambda(r_n) = \left[ \frac{\nu_1}{\mu} [r_n \cos(r_n) - \beta \sin(r_n)] \cos(\nu_1 r_n) + \alpha \cos(r_n) \sin(\nu_1 r_n) \right]. \quad (5.63) \]

Summing Equations (5.56), (5.57), (5.59), and (5.61), and substituting back for \( x \), we have

\[
\theta_2^{(1)}(x, t) = A_{20}(x) + \sum_{n=0}^{\infty} \left[ A_{21}(\rho_n) \sin(\rho_n(1 - x)) e^{\rho_n t} + A_{22}(\tau_n) \sin(\tau_n(1 - x)) e^{-\tau_n t} \right].
\]

Finally, substituting Equations (5.52) and (5.64) into Equation (5.42), the electrode overvoltage, \( \eta(t) \), is given by

\[
\eta^{(1)}(t) = \left[ \zeta^*(1 + A_{20}'(0)) + \frac{\epsilon}{\omega} A_{10}(0) \right] - \zeta^* \sum_{n=0}^{\infty} r_n A_{22}(r_n) \cos(r_n) e^{-\rho_n^2 t}
+ \sum_{n=0}^{\infty} \left[ \frac{\epsilon}{\omega} A_{11}(\rho_n) \sin(\nu_1 \rho_n) - \zeta^* \rho_n A_{21}(\rho_n) \cos(\rho_n) \right] e^{-\rho_n^2 t}.
\]

The above equation is an approximate expression for the potential transient response to a galvanostatic step in the presence of mixed charge-transfer and diffusion control, including the metal-ion deposition partial reaction. This equation can be used in curve-fitting routines to calculate corrosion parameters in a galvanostatic experiment where the potential transient response is recorded. It is interesting to note that the coupling at the boundary conditions arises in the equations which govern the solution poles in the Laplace domain. In this case, the poles given by Equation (5.49), are affected by the coupling, and thus the final solutions are inherently coupled. This is unlike the boundary value problems given in Section 5.3.1, where there was no such coupling, the poles being given by an equation analogous to Equation (5.58).
5.4 Numerical Algorithm

In this section, we present a numerical algorithm for solving the boundary value problems given by Equations (5.5)-(5.7), (5.10) and the nonlinear coupled boundary condition (5.12). Equation (5.12) is a nonlinear algebraic equation which must be inverted in order to express the flux of the $H^+$ ions, at $x = 0$, as a function of $C_1(0,t)$ and $C_2(0,t)$. Substituting $C_{2x}^n = \partial C_2(0,t)/\partial x$, and using the fixed point iteration method, Equation (5.12) can be rearranged so that $C_{2x}^n$ is the limit of the map given by,

$$C_{2x,k+1}^n = g_l(C_{2x,k}^n), \quad l = 1, 2, \text{ or } 3 \text{ and } k = 0, 1, 2, \cdots,$$  \hspace{1cm} (5.66)

where $k$ is the number of iterations, $n$ is the time level and

$$g_1(C_{2x,k}^n) = i_k \zeta \left[ \left( \frac{hC_{2x,k}^n}{C_2(0,t)} \right)^{-\gamma_1} - \epsilon C_1(0,t) \left( \frac{hC_{2x,k}^n}{C_2(0,t)} \right)^{\gamma_2} \right] - I,$$  \hspace{1cm} (5.67)

$$g_2(C_{2x,k}^n) = h^{-1} C_2(0,t) \left[ \left( \frac{C_{2x,k}^n + I}{i_k \zeta} \right) + \epsilon C_1(0,t) \left( \frac{hC_{2x,k}^n}{C_2(0,t)} \right)^{\gamma_2} \right]^{-1/\gamma_1},$$  \hspace{1cm} (5.68)

$$g_3(C_{2x,k}^n) = h^{-1} C_2(0,t) \left[ \left( \frac{hC_{2x,k}^n}{C_2(0,t)} \right)^{-\gamma_1} \left( \frac{C_{2x,k}^n + I}{i_k \zeta} \right)^{1/\gamma_2} \right].$$  \hspace{1cm} (5.69)

Note that if the metal-ion deposition reaction is neglected (i.e. $\epsilon = 0$), then only $g_1$ and $g_2$ are to be used. There are many ways of expressing the solution of equation (5.12) as the fixed point of a nonlinear function $g_l$. However, $g_l$ needs to be chosen so that the convergence condition,

$$|g'_l(C_{2x,0}^n)| < 1,$$ \hspace{1cm} (5.70)
is satisfied. This may be achieved by choosing either of $g_1$, $g_2$ or $g_3$ given above. Here, $C_{2x,0}^n$ is the initial guess at time level $n$. For small time increments, it is reasonable to set this equal to the value calculated at the previous time level, i.e. $C_{2x,0}^n = C_{2x}^{n-1}$.

In practice, we have found that an adequate approximation is achieved after 10 iterations of Equation (5.66),

$$C_{2x,K}^n = g_1(g_1(\cdots g_1(C_{2x}^{n-1})))) \quad (K = 10). \quad (5.71)$$

The approach here is to reformulate the solution of a nonlinear equation (5.12) as a stable fixed point of a nonlinear map (see for example Fulford et al. [31]). The iteration (5.71) converges exponentially to the fixed point.

Equation (5.71) then represents, in explicit form, the nonlinearly coupled boundary condition, given by Equation (5.12), for $C_2(0, t)$. Substitution into Equation (5.10) then yields the analogous boundary condition for $C_1(0, t)$. These are then used in a numerical nonlinear partial differential equation solver, which is based on the method of lines [58], where a semidiscrete approximation of the original system of partial differential equations is developed. The original system of partial differential equations thus reduces to a system of time dependent ordinary differential equations, which can be solved using an ordinary differential equation integrator [58]. Finally, having calculated values for the concentrations at time level $n$, the overvoltage of the electrode, $\eta(t)$ can be calculated by inverting the equation

$$I = i_k \left( \zeta e^{\eta(t)/b_{a_1}} - \epsilon C_1(0, t)e^{-\eta(t)/b_{a_1}} - \frac{C_2(0, t)}{C_2(0, 0)} e^{-\eta(t)/b_{a_2}} \right), \quad (5.72)$$

which is obtained by combining Equations (2.17)-(2.19). This equation is solved using Newton’s method [33].
The above numerical algorithm was used to evaluate the nonlinearly coupled boundary condition given by Equation (5.12) and hence solve the original system of boundary value problems given by Equations (5.5)-(5.10). It should be noted that alternatively, a splitting method, similar to that used in Section 6.4, can be used to decouple the calculations of concentrations and the potential overvoltage at each time level. In the next section, we compare numerical solutions to the leading order perturbation (approximate analytical) solutions obtained in the previous section.

5.5 Results and Discussion

Parameters used in all calculations are as follows; \( D_1 = 0.72 \times 10^{-5} \text{ cm}^2\text{s}^{-1}, \) \( D_2 = 9.13 \times 10^{-5} \text{ cm}^2\text{s}^{-1}, \) \( b_{a_1} = 36 \text{ mV}, \) \( b_{c_1} = 20 \text{ mV}, \) \( b_{c_2} = 120 \text{ mV} \) (which are typical values for \( \text{Zn}^{2+} \) and \( \text{H}^+ \) ions respectively) [69] and \( C_{1b}^0 = C_{2b}^0 = 1 \times 10^{-5} \text{ mol cm}^{-3}. \) The equilibrium potential of the metal, \( E_{01} \) was calculated using the bulk concentration, \( C_i^0 \) in the Nernst equation (given by Equation (2.19)).

Using the above physical values for all the parameters, it was found that there was excellent agreement between the approximate analytical solution and the numerical solution. Typical potential transient responses are shown in Figure 5.1 while typical surface concentration responses of metal and hydrogen ions are shown in Figure 5.2. It was found that errors increased linearly with increasing the applied current step, with maximum errors at \( I = 5 \times 10^{-1}, \) being less than 5% for all of \( C_1(0, t), \) \( C_2(0, t) \) and \( \eta(t). \)

Furthermore, these solutions are in qualitative agreement with experimentally observed transients, where an initial fast rise (kinetic) response, is followed by a slow
approach to steady state due to diffusion of the reactive ions (as reported by Walter [98, 99]). This is due to the diffusion of metal and hydrogen ions away from and towards the electrode surface, respectively. In the absence of metal-ion deposition (i.e. diffusion of metal ions not considered) the typical time to steady state is given by $\tau_2 = \delta^2 / D_2$, which is approximately 10 sec. This is relatively slow compared to the case of charge-transfer kinetics, where the time to steady state is given by the time constant of the equivalent circuit in Figure 2.2 (which is approximately 200 msec). If metal-ion deposition is included, then the time to steady state will be even larger (approximately 100 sec) due to the lower diffusivity of the metal ions compared to the hydrogen ions. This is demonstrated in Figures 5.3 and 5.4, where it can be seen that as the metal-ion deposition becomes more significant (i.e. for lower values of $\Delta E_{1k} = E_k - E_{01}$) the time to steady state increases.

This experiment is very similar, in principle, to the potentiostatic experiment, and can also be used as part of a curve-fitting routine where potential transients are analysed to evaluate the corrosion rate. It is believed that this would provide greater accuracy compared to the equivalent circuit representation, wherein mass transport effects are assumed negligible, or under conditions of semi-infinite diffusion (the limitations of the equivalent circuit representation and transport due to semi-infinite diffusion have been discussed earlier in Section 2.2.3). In particular, when conducting nondestructive tests (where small amplitude currents are applied to avoid sample destruction), the approximate analytical solutions can be used instead of the numerical solutions with acceptable accuracy levels. The discrepancy between numerical and approximate analytical solutions is smaller than typical experimental
Figure 5.1: Comparison between potential transients calculated numerically (---) and from leading order perturbation solutions (----); \( i_k = 0.5i_L \), \( E_k - E_{01} = 60 \text{ mV} \), \( b_{a1} = 35 \text{ mV} \), \( b_{c2} = 120 \text{ mV} \); (a) \( I = 1 \times 10^{-1} \) and (b) \( I = 5 \times 10^{-1} \).
Figure 5.2: Comparison between surface concentrations $C_1(0,t)$ and $C_2(0,t)$ obtained numerically (—) and from leading order perturbation solutions (---); $I = 5 \times 10^{-1}$; $i_k = 0.5i_{L_2}$, $E_k - E_{01} = 60$ mV, $b_{a_1} = 35$ mV, $b_{c_2} = 120$ mV.
Figure 5.3: Effect of metal-ion deposition (back reaction) on potential transients. 
\( i_k = 0.5i_L, b_{a1} = 35 \text{ mV}, b_{c2} = 120 \text{ mV}; \) (a) \( I = 1 \times 10^{-2}, \) and (b) \( I = -1 \times 10^{-2}; \)
back reaction not included (---), back reaction included with, \( E_k - E_{01} = 60\text{ mV} \) (-----) and \( E_k - E_{01} = 90\text{ mV} \) (- - - )
Figure 5.4: Effect of metal-ion deposition (back reaction) on potential transients. 

\[ i_k = 0.5i_{\text{L2}}, \quad b_{a1} = 35 \text{ mV}, \quad b_{c2} = 120 \text{ mV}; \]

(a) \( I = 3 \times 10^{-1} \), and (b) \( I = -3 \times 10^{-1} \); back reaction not included (---), back reaction included with, \( E_k - E_{0i} = 60 \text{ mV} \) (-----) and \( E_k - E_{0i} = 90 \text{ mV} \) (-----)
errors. In practice, only the first three (the fourth term having virtually no noticeable
effect) terms are required in the series solutions obtained in the previous section, in
order to replicate the relatively smooth transient curves displayed in Figures 5.1-
5.4. This opens the possibility of measuring corrosion parameters merely by fitting
a class of elementary functions to experimental potential transients, leading to a
significant reduction in the number of computations required for the curve fitting,
and hence increasing the overall efficiency of the measurement process compared to
the conventional steady state methods.
Chapter 6

Modelling Diffusion-Migration

Transport Processes

6.1 Introduction

In the previous chapters, it was assumed that the electrolytic solution consisted of an excess of inert ions (i.e. concentration of inert ions is much larger than that of the reactive ions). In this case, the concentrations of the inert ions and the solution potential are assumed to be constant throughout the solution, and mass transport of the reactive ions is due to diffusion only. However, most natural waters (except seawater and marine environment), for example, are of low conductivity, where excess of supporting electrolyte is absent and consequently transport processes due to diffusion and migration need to be considered. In this chapter, the more general problem of electrochemical mass transport by migration and diffusion is considered. Here, the term “migration” is given to the transport of charged ions under the
influence of an electrical field, present in the solution. The governing equations describing such transport constitute a set of coupled nonlinear equations, which in general must be solved numerically.

In the next section, the one-dimensional transport equations in dilute solutions will be presented. In Section 6.3, analytical solutions for the steady state case will be presented. In Section 6.4 a numerical algorithm is presented for the simulation of transient processes. In the next section, the governing equations are presented for one-dimensional transport in dilute solutions (i.e. where an ionic species does not interact with other species).

6.2 1-D Transport in Dilute Solutions

6.2.1 Transport equations

Consider a dilute electrolytic solution consisting of an unionized solvent and ionized electrolyte, which contains both inert and reactive ions. It is assumed that transport of all ions due to diffusion and migration occurs inside a Nernstian layer, where fluid motion is negligible owing to finite viscous forces, and outside of which convective motion takes place. As before, we consider a planar electrode which is large compared to the Nernstian layer thickness, such that the transport equations become one-dimensional. Then the flux of ionic species $j$, where the bulk solution is stagnant, is given by the Nernst-Planck equation [65, 66]

$$N_j = -D_j \frac{\partial C_j}{\partial x} - z_j u J C_j \frac{\partial \phi}{\partial x},$$  

(6.1)
where $N_j$, $z_j$, $u_j$, $C_j$, are the flux, charge, mobility and concentration of the $j$th ionic species, respectively, and $\phi$ is the electrostatic potential (the gradient of which is the negative of the electrical field). The mobility, $u_j$, is defined as the average velocity of a charged particle in solution when acted upon by a force of 1 N mol$^{-1}$, and thus has units of mol N$^{-1}$m s$^{-1}$ [73]. The first term of Equation (6.1) represents molecular diffusion due to a concentration gradient, while the second term represents the motion of charged ions in an electrical field (migration). This migration term can be understood as follows, the term $z_jF$ gives the charge on one mole of species $j$. Multiplying this by the electric field (i.e. $-\partial\phi/\partial x$), we obtain the force exerted on the ions due to the electrical field. It is assumed that rather than causing uniform acceleration, a constant electrostatic force is soon balanced by a mechanical resistance (friction), so that a terminal particle velocity is soon attained. This model is analogous to Ohm's law. Multiplying by the mobility, $u_j$, gives the velocity of these ions relative to the solution. Finally, multiplying by the ionic concentration, $C_j$, gives the contribution to the net flux $N_j$ due to migration in an electrical field [65, 66].

The flux equation given by Equation (6.1), is only strictly valid for dilute solutions. This is because firstly, Equation (6.1) considers interactions between an ionic species and the solvent while essentially neglecting interactions with other species. Secondly, the driving force for diffusion should be an activity gradient, and activity gradients can be replaced by concentration gradients only in highly dilute solutions [66]. Despite its apparent limitations, Equation (6.1) is widely used in the electrochemical literature because it provides a good approximation of the physical
processes involved while avoiding extra complications [66]. The current density in the solution can be expressed in terms of the ionic fluxes as

\[ i = F \sum_j z_j N_j. \quad (6.2) \]

The above equation merely states that the flux of charged ions produces an electric current. Finally, the governing (material balance) equation for each ionic species, in the absence of any production/depletion due to chemical reactions in the bulk of the solution, is given by

\[ \frac{\partial C_j}{\partial t} = -\frac{\partial N_j}{\partial x}, \quad (6.3) \]

which upon using Equation (6.1), yields the nonlinear system of equations given by

\[ \frac{\partial C_j}{\partial t} = D_j \frac{\partial^2 C_j}{\partial x^2} + z_j u_j F \frac{\partial}{\partial x} \left( C_j \frac{\partial \phi}{\partial x} \right), \quad (6.4) \]

### 6.2.2 The Nernst-Einstein relation

The Nernst-Einstein equation provides a relationship between the mobility and the diffusion coefficient of an ionic species, and is given by

\[ D_j = RT u_j, \quad (6.5) \]

where \( R \) is the universal gas constant and \( T \) is the absolute temperature. This relationship originates from the fact that the electrochemical potential is the actual driving force for both diffusion and migration processes. The equation is strictly applicable at infinite dilution (i.e. when it is assumed that there are no interactions between the different species), and this restriction is related to the approximate nature of Equation (6.1) as discussed earlier. Equation (6.5) is commonly used in
the electrochemical literature to simplify the analysis of electrochemical systems [65]. However, it is not necessary to use this if an independent way of determining \( u_j \) is available.

### 6.2.3 The electroneutrality condition

In order to solve the system of equations given by Equation (6.4), a governing equation for the solution potential, \( \phi \), is required. This is given by Poisson’s equation which relates the spatial variation in the electrical field to the charge distribution.

For a medium of uniform dielectric constant, \( \epsilon \), this is given by

\[
\frac{\partial^2 \phi}{\partial x^2} = -\frac{F}{\epsilon} \sum_j z_j C_j. \tag{6.6}
\]

However, in the electrochemical literature, it is common to replace the above equation with the electroneutrality condition,

\[
\sum_j z_j C_j = 0. \tag{6.7}
\]

The above equation states that there is no local accumulation of charge in the solution (which can be easily shown to correspond to \( \partial i / \partial x = 0 \)). This is only an approximation in electrolytic solutions, and the more correct statement would be that \( \sum_j z_j C_j \), is not zero but that its absolute value is small compared with the maximum absolute value of \( z_j C_j \) [73].

The assumption of electroneutrality (or absence of charge separation) holds closely in aqueous electrolytic solutions everywhere, except at thin regions near charged boundaries. These regions are called double layers or Debye sheaths and have a thickness of the order of 1 to 10 nm. These regions are important when
the interactions of very small charged particles and charged surface phenomena are considered, but are otherwise unimportant with respect to bulk transport characteristics [44, 65, 66, 73]. It is for this reason, as well as the resulting mathematical simplification in the treatment of electrochemical problems, that the electroneutrality condition is widely used instead of Poisson's equation. Finally, it should be noted that the assumption of electroneutrality does not imply that Laplace's equation holds for the solution potential. This incorrect deduction would result if the Poisson equation and the electroneutrality condition were adopted simultaneously.

In fact using both the electroneutrality condition and Poisson's equation could lead to inconsistencies, as this would overspecify the problem. To illustrate this point, let us assume that Poisson's equation reduces to Laplace's equation due to electroneutrality, then we have

\[ \frac{\partial^2 \phi}{\partial x^2} = 0. \]  

(6.8)

Now, we also know that electroneutrality implies that \( \partial i / \partial x = 0 \), which upon using Equations (6.2) and (6.1) yields,

\[ \sum_j \left[ z_j D_j \frac{\partial^2 C_j}{\partial x^2} + z_j^2 u_j F \frac{\partial}{\partial x} \left( C_j \frac{\partial \phi}{\partial x} \right) \right] = 0, \]  

(6.9)

which seems to be a contradiction. In fact this is not so, and one should use either Poisson's equation or the electroneutrality condition.

### 6.2.4 Boundary conditions

As well as the governing system of equations (Equation (6.4)) and the electroneutrality condition (Equation (6.7)), appropriate boundary conditions are required for the unique specification of a well-posed system. At the electrode/solution interface,
the flux of each ionic species will be matched by the corresponding partial current
density, \( i_j \). Thus
\[
D_j \frac{\partial C_j}{\partial x} \bigg|_{x=0} + z_j u_j F C_j \frac{\partial \phi}{\partial x} \bigg|_{x=0} = -\frac{i_j}{z_j F},
\]
where, in general
\[
i_j = f_j(C_j(0, t), \phi(0, t), E),
\]
where \( E \) is the electrode potential, and is measured relative to a reference potential, \( \phi^* \) (given below in Equation (6.14)), and \( f_j \) represents Butler-Volmer kinetics of the corresponding reaction. Note that for inert ions, \( i_j = 0 \), which corresponds to no flux boundary conditions. Using a similar approach to that in Section 2.2.1, and noting that the driving force for the reactions to occur is given by the difference in potential between the metal electrode and the solution adjacent to the electrode (i.e. \( E - \phi(0, t) \)), it can easily be shown that for an electrochemical reaction given by,
\[
R_j \Leftrightarrow O_j + z_j e^-, \quad \text{(6.12)}
\]
the current density, \( i_j \) is given by
\[
i_j = i_{0j} \left[ \frac{C_{R_j}(0, t)}{C_{R_j}^0} e^{(\Delta E - \Delta \phi(0, t))/b_a} - \frac{C_{O_j}(0, t)}{C_{O_j}^0} e^{-(\Delta E - \Delta \phi(0, t))/b_c} \right],
\]
where \( \Delta E = E - E_0 \) and \( \Delta \phi(0, t) = \phi(0, t) - \phi(0, 0) \). Here \( E_0 \) is the equilibrium potential, and \( \phi(0, 0) \) is the solution potential at equilibrium.

At the edge of the Nernstian layer, we have constant concentration boundary conditions as before, and we take the potential at that point as the reference potential (since experimentally only differences in potential between two points can be measured). Thus,
\[
C_j(\delta, t) = C_j^0, \quad \phi(\delta, t) = \phi^*, \quad \text{(6.14)}
\]
where $\phi^*$ is the reference potential. It should be noted that the coupled boundary conditions at the electrode surface, are highly nonlinear and their treatment will require special attention.

In this chapter, we consider the problem of electroysis, where the electrode potential is varied from an initial steady state value to a constant value, measured relative to an appropriately positioned reference electrode (i.e. potentiostatic conditions as in Chapter 4), such that $\Delta E$ in Equation (6.13) is constant.

### 6.2.5 Nondimensional variables

To facilitate the analysis, the following nondimensional variables are introduced,

$$
\tilde{C}_j = \frac{C_j}{C_j^0}, \quad \tilde{t} = \frac{t}{\tau_2}, \quad \tilde{x} = \frac{x}{\delta}, \quad \tilde{i}_j = \frac{i_j}{i_{L_2}}, \quad \tilde{\phi} = \frac{z_2 F \phi}{R T} = e_2 \phi,
$$

where as before, $\tau_2 = \delta^2 / D_2$ and $i_{L_2} = n_2 F D_2 C_j^0 / \delta$. Using the Nernst-Einstein relation for the mobility, $u_j$, and substituting the above nondimensional variables, Equation (6.4) can be rewritten in nondimensional form as

$$
\frac{\partial \tilde{C}_j}{\partial \tilde{t}} = D_j^* \left[ \frac{\partial^2 \tilde{C}_j}{\partial \tilde{x}^2} + \mu_j \frac{\partial}{\partial \tilde{x}} \left( \tilde{C}_j \frac{\partial \tilde{\phi}}{\partial \tilde{x}} \right) \right], \quad (6.15)
$$

where $\mu_j = z_j / z_2$ and $D_j^* = D_j / D_2$. Note that the overbars have been dropped for convenience. Similarly the boundary conditions become

$$
\left. \frac{\partial \tilde{C}_j}{\partial \tilde{x}} \right|_{\tilde{x}=0} + \mu_j \tilde{C}_j \frac{\partial \tilde{\phi}}{\partial \tilde{x}} \bigg|_{\tilde{x}=0} = -g_j(\tilde{C}_j(0, \tilde{t}), \tilde{\phi}(0, \tilde{t}), E), \quad (6.16)
$$

where

$$
g_j(\tilde{C}_j(0, t), \tilde{\phi}(0, t), E) = \left( \frac{C_j^0}{C_j} \right) \frac{i_j}{\mu_j D_j^*},
$$

and

$$
C_j(1, t) = 1, \quad \tilde{\phi}(1, t) = \phi^*. \quad (6.17)
$$
6.3 Analytical solutions for steady state model

6.3.1 Introduction

The equations describing steady electrochemical transport due to diffusion and migration constitute a set of coupled ordinary differential equations for which analytical solutions are difficult to obtain without making any simplifying assumptions. From a mathematical point of view, the most common type of approximation is linearization of the reaction kinetics [6, 47, 65, 94], which is valid at low current densities (i.e. when potential steps of a small amplitude are applied to the electrode). The other commonly used approximation is that transport of ions is the dominant rate-limiting process, such that the concentrations of the reacting ions is zero at the electrode surface (i.e. limiting current conditions) [40, 44, 85]. An excellent review of this work can be found in [84].

In 1990, Pritzker [72] presented a general analytical solution for diffusion-migration transport in a Nernstian layer, without making any assumptions about the reaction kinetics, or approximating the governing equations. He considered the case of only one reactive ion with any number of inert ions, where the electrode was subjected to a constant potential. His solution procedure resulted in a system of four nonlinear algebraic equations, which had to be solved numerically. In addition to numerical results, he presented some explicit solutions for cases of small current densities and for current densities that are close to the limiting current density. Other analytical solutions for the case of one reactive ion were also presented in [84, 15], where a two electrode model was considered, and [4, 5] where a transformation was intro-
duced which reduced the governing equations to Laplace’s equation with nonlinear boundary conditions.

An extension to the above works for more than one reactive ion was finally presented by Borfels et al. in 1997 [14]. They presented an analytical solution for the case of two reactive ions and any number of inert ions, and a general extension towards systems containing any number of reacting ions. For the case of two reacting ions, their solution procedure results in seven nonlinear algebraic equations which need to be solved numerically. In this section, we present this analytical solution with two reactive ions, for the sake of completeness.

6.3.2 Analytical solution

Consider the system of coupled differential equations, representing a one-dimensional steady diffusion-migration electrochemical model containing \( m \) ions, two of which are reactive. The nondimensional governing equations are given by

\[
\begin{align*}
\frac{dC_1}{dx} + \mu_1 C_1 \frac{d\phi}{dx} &= -N_1, \\
\frac{dC_2}{dx} + \mu_2 C_2 \frac{d\phi}{dx} &= -N_2, \\
\frac{dC_j}{dx} + \mu_j C_j \frac{d\phi}{dx} &= 0, \quad j = 3, \ldots, m,
\end{align*}
\]

(6.18) (6.19) (6.20)

where

\[ N_1 = \left( \frac{C_2}{C_1} \right) \frac{i_1}{\mu_1 D_1^*}, \quad N_2 = -i_2, \]

and the boundary conditions are given by

\[ C_j(1) = 1, \quad j = 1, 2, \ldots, m, \quad \phi(1) = \phi^*. \]

(6.21)
We also have the electroneutrality condition which is given by Equation (6.7). The transport Equations (6.18)-(6.20) and the electroneutrality condition constitute a complex set of equations which must first be decoupled in order for a solution to be obtained. This can be achieved by obtaining explicit expressions for $C_1, C_2, \ldots, C_m$ in terms of $\phi$ and then using these to derive a single differential equation for $\phi$.

Therefore, Equations (6.18) and (6.19) can be rewritten as

$$\frac{dC_1}{d\phi} = \frac{dC_1}{dx} \frac{dx}{d\phi} = -\mu_1 C_1 - N_1 \frac{dx}{d\phi}, \quad (6.22)$$

$$\frac{dC_2}{d\phi} = \frac{dC_2}{dx} \frac{dx}{d\phi} = -\mu_2 C_2 - N_2 \frac{dx}{d\phi}. \quad (6.23)$$

Now, on multiplying each of (6.18), (6.19) and (6.20) by $z_1$, $z_2$ and $z_j$, respectively and applying electroneutrality we can show that

$$z_1 \mu_1 C_1 + z_2 \mu_2 C_2 + \sum_{j=3}^{m} z_j \mu_j C_j \frac{d\phi}{dx} = -z_1 N_1 - z_2 N_2, \quad (6.24)$$

and on rearranging (6.24) we have

$$\frac{dx}{d\phi} = -\frac{1}{N} \left\{ z_1 \mu_1 C_1 + z_2 \mu_2 C_2 + \sum_{j=3}^{m} z_j \mu_j C_j \right\}, \quad (6.25)$$

where $N = z_1 N_1 + z_2 N_2$. Now, using the electroneutrality condition, we may rewrite $C_2$ as

$$C_2 = -\frac{1}{z_2} \left(z_1 C_1 + \sum_{j=3}^{m} z_j C_j \right), \quad (6.26)$$

which on substitution into (6.25) gives

$$\frac{dx}{d\phi} = -\frac{1}{N} \left\{ z_1 (\mu_1 - \mu_2) C_1 + \sum_{j=3}^{m} z_j (\mu_j - \mu_2) C_j \right\}. \quad (6.27)$$

We next substitute (6.27) into (6.22) such that

$$N \frac{dC_1}{d\phi} = -N \mu_1 C_1 + N_1 \left\{ z_1 (\mu_1 - \mu_2) C_1 + \sum_{j=3}^{m} z_j (\mu_j - \mu_2) C_j \right\}. \quad (6.28)$$
Now, on integration of (6.20) for the inert ions, we may deduce that

$$C_j = A_j e^{-\mu_j \phi}, \quad j = 3, \ldots, m, \tag{6.29}$$

where $A_j$ is an integration constant, which upon applying boundary condition (6.21) may be shown to be given by

$$A_j = e^{\mu_j \phi^*}, \quad j = 3, \ldots, m. \tag{6.30}$$

Now, on using (6.29), (6.28) can be shown to become

$$N \frac{dC_m}{d\phi} + \left[ N \mu_1 - z_1 N_1 (\mu_1 - \mu_2) \right] C_1 = N_1 \sum_{j=3}^{m} z_j (\mu_j - \mu_2) A_j e^{-\mu_j \phi}, \tag{6.31}$$

and from the definition of $N$ and the identity $z_1 \mu_2 = z_2 \mu_1$ we may eventually deduce

$$N \frac{dC_1}{d\phi} + z_1 \mu_2 (N_1 + N_2) C_1 = N_1 \sum_{j=3}^{m} z_j (\mu_j - \mu_2) A_j e^{-\mu_j \phi}. \tag{6.32}$$

We note that equation (6.32) is a first order non-homogeneous differential equation for $C_1$, whose general solution is given by the sum of a homogeneous and particular solution. Moreover, the homogeneous solution is given by

$$C_{1h} = \rho_1 e^{\lambda_1 \phi}, \tag{6.33}$$

where $\rho_1$ is an unknown constant and $\lambda_1$ is given by

$$\lambda_1 = -\frac{1}{N} \left[ z_1 \mu_2 (N_1 + N_2) \right], \tag{6.34}$$

while the particular solution is given by

$$C_{1p} = \sum_{j=3}^{m} \rho_j e^{-\mu_j \phi}, \tag{6.35}$$

where $\rho_j$ is defined by

$$\rho_j = \frac{z_j N_1 (\mu_j - \mu_2) A_j}{z_1 N_1 (\mu_2 - \mu_j) + z_2 N_2 (\mu_1 - \mu_j)}. \tag{6.36}$$
Thus, the general solution is

\[ C_1 = \rho_1 e^{\lambda_1 \phi} + \sum_{j=3}^{m} \rho_j e^{-\mu_j \phi}. \]  
\[ (6.37) \]

Now, on using equations (6.26), (6.29) and (6.37) we may readily deduce the following expression for \( C_2 \)

\[ C_2 = -\frac{1}{z_2} \left\{ z_2 \rho_1 e^{\lambda_1 \phi} + \sum_{j=3}^{m} \left( z_1 \rho_j + z_j A_j \right) e^{-\mu_j \phi} \right\}, \]
\[ (6.38) \]

which on differentiation yields

\[ \frac{dC_2}{d\phi} = -\frac{1}{z_2} \left\{ \lambda_1 z_2 \rho_1 e^{\lambda_1 \phi} - \sum_{j=3}^{m} \mu_j \left( z_1 \rho_j + z_j A_j \right) e^{-\mu_j \phi} \right\}. \]
\[ (6.39) \]

Now, on substitution of (6.38) and (6.39) into (6.23) we obtain an ordinary differential equation of the following form

\[ z_2 N_2 \frac{dx}{d\phi} = z_1 \rho_1 (\lambda_1 + \mu_2) e^{\lambda_1 \phi} + \sum_{j=3}^{m} \left( z_1 \rho_j + z_j A_j \right) (\mu_2 - \mu_j) e^{-\mu_j \phi}. \]
\[ (6.40) \]

The above is a differential equation for \( x \) in terms of \( \phi \), which can be integrated immediately to give

\[ z_2 N_2 x = M_1 e^{\lambda_1 \phi} + \sum_{j=3}^{m} M_j e^{-\mu_j \phi} + \rho_2, \]
\[ (6.41) \]

where \( \rho_2 \) is an integration constant and \( M_1 \) and \( M_j \) are given respectively by

\[ M_1 = z_1 \rho_1 (\lambda_1 + \mu_2)/\lambda_1, \]
\[ (6.42) \]

\[ M_j = (z_1 \rho_j + z_j A_j)(\mu_2 - \mu_j)/\mu_j, \quad j = 3, \ldots, m. \]
\[ (6.43) \]

Thus, the unknown variables are \( \rho_1, \rho_2, N_1 \) and \( N_2 \). Now, by substituting \( x=0, 1 \) into (6.41) we obtain two new relations between the unknowns

\[ M_1 e^{\lambda_1 \phi_0} + \sum_{j=3}^{m} M_j e^{-\mu_j \phi_0} + \rho_2 = 0, \]
\[ (6.44) \]

\[ M_1 e^{\lambda_1 \phi^*} + \sum_{j=3}^{m} M_j e^{-\mu_j \phi^*} + \rho_2 = z_2 N_2, \]
\[ (6.45) \]
where the subscript 0 denotes surface values (i.e. \( x = 0 \)), and we also have from the reaction kinetics at the electrode/solution interface

\[
N_1 = f(C_{10}, \phi_0, E) ,
\]

(6.46)

\[
N_2 = g(C_{20}, \phi_0, E) .
\]

(6.47)

Now by substitution of \( x=0, 1 \) into (6.37) for \( C_x \) we have

\[
m C_{10} = \pi e^{x} + y P e^{-x} ,
\]

(6.48)

\[
l = \pi e^{x} + y P e^{-x} .
\]

(6.49)

Furthermore, by evaluating (6.29) at \( x=0 \) for the inert ions we may show

\[
z_1 C_{10} + z_2 C_{20} + \sum_{j=3}^{m} z_j e^{\mu_j (\phi - \phi_0)} = 0 .
\]

(6.50)

Thus, we have obtained a set of 7 nonlinear algebraic equations, (6.44)-(6.50) for the unknown variables \( N_1, N_2, C_{10}, C_{20}, \phi_0, \rho_1 \) and \( \rho_2 \), which can be solved using a standard Newton-Raphson method [33]. Once these unknowns have been determined, \( \rho_2 \) and \( N_2 \) can then be substituted into (6.41) to obtain an implicit solution for \( \phi \) in terms of the variable \( x \). It is then straightforward to obtain \( C_1(x), C_2(x) \) and \( C_j(x) \) for \( j = 3, \ldots, m \), from equations (6.29), (6.37) and (6.38), respectively.

6.4 Numerical simulation of transient model

6.4.1 Introduction

Unlike the steady state case, analytical solutions for transient models cannot be found, due to the complexity of the governing equations and the strongly nonlinear
boundary conditions. To the knowledge of the author, the only analytical solution that exists is that derived by Choi and Chan [19] for a binary inert electrolyte (i.e. transport of two ions with zero flux boundary conditions). In general one must resort to numerical methods for the solution of transient electrochemical processes. A survey of numerical methods for calculating primary current distributions (i.e. solving Laplace’s equation for the potential when diffusion is assumed to be negligible) has been presented by Prentice and Tobias [70]. More recently, numerical methods for such problems have been presented in [32, 59, 86, 101] and [36, 48], the latter dealing with currents produced in a lead-acid battery. There also exists a large number of papers dealing with the numerical solution of parallel plate electrochemical reactor models (see paper by Edwards and Newman [28] for a review of these models). However, these models usually contain restrictive assumptions, such as migration of the reactive species is negligible (not necessarily so for inert species).

In 1992, Choi and Chan [20] proposed a fractional step (or operator splitting) algorithm [89, 104] for the numerical simulation of diffusion-migration transport processes, using finite difference methods. The fractional step method is one of the most cost-efficient methods in dealing with multi-dimensional phenomena. Another further advantage of this method is that if the initial concentration data are positive, then the algorithm will always preserve such positivity in the computations, which is a physical requirement. This approach led to decoupling the nonlinear interactions between ions (note that different ionic species are coupled through the solution potential, $\phi(x, t)$). Their algorithm consisted of a diffusion step, where only diffusion took place, followed by a step for applying the electroneutrality constraint and finally
a step for migration to take place. However, their algorithm was limited to transport of inert ions, i.e. zero flux boundary conditions. Furthermore, their algorithm exhibited only first order spatial and temporal accuracy. Using a splitting algorithm similar to that in [20], Kwok and Wu [45] developed a finite difference numerical scheme for modelling diffusion-migration processes with reactions at the electrodes (their model was set up for a two electrode model where metal dissolution occurs at the anode and metal-ion deposition occurs at the cathode). Their algorithm was more accurate, exhibiting second order spatial and temporal accuracy. However, the algorithm was limited for a number of reasons. Firstly, it was assumed that only one ion took part in an electrochemical reaction at each of the electrodes (i.e. only one reactive ion). Secondly, it was assumed that the concentrations of the inert ions were much larger than that of the reactive ion. This allowed them to expand the concentrations of ions and the potential as a perturbation series, where to the zeroth-order, only inert ions were present in the electrolytic solution. This led to decoupling the leading order equations governing the concentration evolution of inert and reactive ions and simplifying the boundary conditions. Finally, they only consider linearized reaction kinetics, which is valid at low current densities only.

In this section, a general finite difference scheme, with second-order spatial and temporal accuracy, is developed for examining the transient physical behaviour of electrolytes containing any number of reacting and inert ions. Furthermore, we present an alternative way of linearizing the reaction kinetics which, we believe, is more accurate and reliable than the conventional linearization found in the literature.
6.4.2 Numerical scheme for multiple reacting ions

Consider the nondimensional transport equations given by Equations (6.15) and (6.7), subject to the boundary conditions given by Equations (6.16) and (6.17). Let the number of reactive and inert ions be denoted by \( r \) and \( m \), respectively. These equations constitute a system of nonlinear algebraic-differential equations. A review of numerical algorithms for solving these systems was presented by Hairer et al. [38]. The added difficulties in the present model are due to the nonlinear nature of the boundary conditions (at \( x = 0 \)), which arise from the reaction kinetics.

**Governing equations for** \( C_j(x, t) \)

If values of \( \phi(x, t) \) are known, then Equation (6.15), is a parabolic partial differential equation governing the evolution of the concentrations, \( C_j(x, t) \). Thus the boundary value problems governing the evolution of \( C_j(x, t) \) are given by

\[
\frac{\partial C_j}{\partial t} = D_j^* \left[ \frac{\partial^2 C_j}{\partial x^2} + \mu_j \frac{\partial}{\partial x} \left( C_j \frac{\partial \phi}{\partial x} \right) \right], \quad j = 1, \ldots, r + m, \tag{6.51}
\]

\[
\frac{\partial C_j}{\partial x} \bigg|_{x=0} + \mu_j C_j \frac{\partial \phi}{\partial x} \bigg|_{x=0} = -g_j(C_j(0, t), \phi(0, t), E), \tag{6.52}
\]

\[
C_j(1, t) = 1. \tag{6.53}
\]

Note that for the inert ions \( (j = r + 1, \ldots, m) \), we have \( g_i = 0 \).

**Governing equations for** \( \phi(x, t) \)

If values of \( C_j(x, t) \) are known, then using the electroneutrality condition (Equation (6.7)), we can derive an elliptic differential equation for \( \phi(x, t) \), which is given by

\[
\sum_{j=1}^{r+m} D_j^* z_j \left[ \frac{\partial^2 C_j}{\partial x^2} + \mu_j \frac{\partial}{\partial x} \left( C_j \frac{\partial \phi}{\partial x} \right) \right] = 0. \tag{6.54}
\]
Similarly, we can obtain the boundary condition for \( \phi(x, t) \) at \( x = 0 \),

\[
\left[ r + m \right] \sum_{j=1}^{r} z_j \mu_j C_j \left. \frac{\partial \phi}{\partial x} \right|_{x=0} = - \sum_{j=1}^{r} z_j g_j(C_j(0, t), \phi(0, t), E). 
\] (6.55)

Finally, we also have

\[
\phi(1, t) = \phi^*. 
\] (6.56)

We now develop a finite difference algorithm for solving the coupled systems given by Equations (6.51)-(6.53) and (6.54)-(6.56). The calculations for \( C_j(x, t) \) and \( \phi(x, t) \) are decoupled at every time step, and an iterative approach is utilised to achieve convergence. Let \( \Delta x \) and \( \Delta t \) denote the stepwidth and time step respectively, such that \( x = i \Delta x, i = 0, 1, \ldots, N \), \( N \Delta x = 1 \), and \( t = n \Delta t, n = 0, 1, 2, \ldots \). Furthermore, let \( C_{j,i}^{n,k} \) and \( \phi_{i}^{n,k} \) denote the finite difference approximation to \( C_j(i \Delta x, n \Delta t) \) and \( \phi(i \Delta x, n \Delta t) \) at the \( k \)th iteration, respectively. Before the numerical algorithm is presented, we linearize the function \( g_j \), which is of the form given in Equation (6.13). Unlike the conventional approach, where the exponential terms are linearized about \( \phi(0, t) = 0 \) (note that the applied potential, \( E \) is constant, thus there is no need to linearize that term), we linearize \( e^{\phi(t+1)} \) about \( \phi^0 \), such that the function \( g_j \), at time step \( n + 1 \), can be expressed in linearized form as

\[
\hat{g}_j(C_{j,i}^{n+1}, \phi_{i}^{n+1}, E) = a_j^{(1)} + a_j^{(2)} C_j(0, t) + a_j^{(3)} C_j(0, t) \phi_{i}^{n+1} + a_j^{(4)} \phi_{i}^{n+1}, 
\] (6.57)

where \( \hat{g}_j \) is the linearized version of \( g_j \), and the coefficients \( a_j^{(l)}, l = 1, \ldots, 4 \), are functions of \( \phi^0 \). This approach to linearizing the reaction kinetics is more reliable than the conventional approach, since the errors produced can be controlled by choosing an appropriate value of \( \Delta t \), and no assumptions are made about the size of \( \phi(0, t) \). Given values of \( C_{j,i}^{n} \) and \( \phi_{i}^{n} \), the following algorithm is proposed for
determining $C_{j,i}^{n+1}$ and $\phi_i^{n+1}$.

1. **Predictor values for concentrations ($k = 0$)**

We begin by discretizing Equation (6.51). Because values for $\phi_i^{n+1}$ are not known, the second order time accurate Crank-Nicholson scheme [33] cannot be adopted directly. Therefore, we use an explicit forward-time centered-space (FTCS) scheme [33] to obtain predictor values for the concentrations, $C_{j,i}^{n+1,0}$. Applying the FTCS scheme to Equation (6.51), yields

$$\frac{C_{j,i}^{n+1,0} - C_{j,i}^n}{\Delta t} = D_j \left[ \mu_j \left( \frac{C_{j,i+1}^n + C_{j,i-1}^n}{2} - \frac{C_{j,i+1}^n - C_{j,i-1}^n}{2 \Delta x^2} \right) \right], \quad i = 0, 1, 2, \ldots, N - 1, \quad (6.58)$$

Note that the migration term of Equation (6.51) was discretized as follows

$$\frac{\partial}{\partial x} \left( C_j \frac{\partial}{\partial x} \right)_{x = i \Delta x} = \frac{(C_j \phi_x)_{i+1/2} - (C_j \phi_x)_{i-1/2}}{\Delta x},$$

where we have applied a centre difference discretization using half steps, i.e. we use values at the node points $i - 1/2$ and $i + 1/2$ to approximate the derivative at the node $i$. Now applying the same treatment to $\phi_x$ and taking $C_{j,i+1/2}$ and $C_{j,i-1/2}$ as the average values of $C_{j,i+1}$, $C_{j,i}$ and $C_{j,i}$, $C_{j,i-1}$, respectively, we may deduce that

$$\frac{\partial}{\partial x} \left( C_j \frac{\partial}{\partial x} \right)_{x = i \Delta x} = \left( \frac{C_{j,i+1} + C_{j,i}}{2} \right) \left( \frac{\phi_{i+1} - \phi_i}{\Delta x^2} \right) - \left( \frac{C_{j,i} + C_{j,i-1}}{2} \right) \left( \frac{\phi_i - \phi_{i-1}}{\Delta x^2} \right),$$

which is second order accurate in $\Delta x$. Now, the fictitious values $C_{j,1}^n$ are obtained from the discretized version of the boundary condition (6.52),

$$\frac{C_{j,1}^n - C_{j,-1}^n}{2 \Delta x} + \mu_j C_{j,0}^n \left( \frac{\phi_1^n - \phi_{-1}^n}{2 \Delta x} \right) = -g_j(C_{j,0}^n, \phi_0^n, E), \quad (6.59)$$
where \( \hat{g}_j(C_{j,0}^n, \phi^n_0, E) \) is given by Equation (6.57). Similarly, the fictitious values \( \phi^n_{-1} \) are obtained from the discretized version of the boundary condition (6.55),

\[
\left[ \sum_{j=1}^{r+m} z_j \mu_j C_{j,0}^n \right] \left( \frac{\phi^n_1 - \phi^n_{-1}}{2\Delta x} \right) = -\sum_{j=1}^{r} \mu_j \hat{g}_j(C_{j,0}^m, \phi^n_0, E). \tag{6.60}
\]

Also at \( x = N\Delta x \), Equation (6.53) implies that

\[
C_{j,N}^n = 1. \tag{6.61}
\]

2. Predictor values for potential \((k = 0)\)

Having calculated values for \( C_{j,i}^{n+1,0} \), we use these to calculate \( \phi_i^{n+1,0} \). We discretize the elliptic equation (6.54) with second order spatial accuracy. Therefore, we obtain

\[
\sum_{j=1}^{r+m} D_j z_j \left\{ 2(C_{j,i-1}^{n+1,0} - 2C_{j,i}^{n+1,0} + C_{j,i+1}^{n+1,0}) + \mu_j \left[ \left( C_{j,i+1}^{n+1,0} + C_{j,i}^{n+1,0} \right) \left( \phi_{i+1}^{n+1,0} - \phi_i^{n+1,0} \right) - \left( C_{j,i}^{n+1,0} + C_{j,i-1}^{n+1,0} \right) \left( \phi_i^{n+1,0} - \phi_{i-1}^{n+1,0} \right) \right] \right\} = 0, \quad i = 0, \ldots, N - 1. \tag{6.62}
\]

The above discretization leads to a tridiagonal system for the unknown vectors \( \{\phi_0^{n+1,0}, \ldots, \phi_{N-1}^{n+1,0}\} \). The fictitious values \( \phi_{-1}^{n+1,0} \) are given by

\[
\left[ \sum_{j=1}^{r+m} z_j \mu_j C_{j,0}^{n+1,0} \right] \left( \frac{\phi_{1}^{n+1,0} - \phi_{-1}^{n+1,0}}{2\Delta x} \right) = -\sum_{j=1}^{r} \mu_j \hat{g}_j(C_{j,0}^{n+1,0}, \phi_0^{n+1,0}, E), \tag{6.63}
\]

and at \( x = N\Delta x \), we have

\[
\phi_N^{n+1,0} = \phi^*. \tag{6.64}
\]

3. Corrector values for concentrations \((k = 1)\)

Now, that we have an approximate value for \( \phi_i^{n+1} \) (i.e. \( \phi_i^{n+1,0} \)), we return to Equation (6.51) and apply the Crank-Nicholson scheme in order to achieve second order spatial
and temporal accuracy. Therefore,

\[
\frac{C_{j,i}^{n+1,1} - C_{j,i}^n}{D_j^* \Delta t} = \frac{1}{2} \left[ \frac{C_{j,i+1}^{n+1,1} - 2C_{j,i}^{n+1,1} + C_{j,i-1}^{n+1,1}}{\Delta x^2} \right]
+ \frac{\mu_j}{2} \left[ \frac{(\phi_{i-1}^{n+1,0} - \phi_{i+1}^{n+1,0})C_{j,i-1}^{n+1,1} + (\phi_{i+1}^{n+1,0} - 2\phi_i^{n+1,0} + \phi_{i-1}^{n+1,0})C_{j,i}^{n+1,1}}{2\Delta x^2} \right]
+ \frac{(\phi_{i-1}^{n} - \phi_i^{n})C_{j,i-1}^{n} + (\phi_{i+1}^{n} - 2\phi_i^{n} + \phi_{i-1}^{n})C_{j,i}^{n}}{2\Delta x^2}, \quad i = 0, \ldots, N - 1. \tag{6.65}
\]

The boundary condition (6.52) becomes

\[
\frac{C_{j,1}^{n+1,1} - C_{j,0}^{n+1,1}}{2\Delta x} + \mu_j C_{j,1}^{n+1,1} \left( \frac{\phi_1^{n+1,0} - \phi_{-1}^{n+1,0}}{2\Delta x} \right) = -\hat{g}_j(C_{j,0}^{n+1,1}, \phi_0^{n+1,0}, E), \tag{6.66}
\]

where \(\phi_{-1}^{n+1,0}\) is available from Equation (6.63).

4. **Corrector values for potential \((k = 1)\)**

We now calculate \(\phi_i^{n+1,1}\) as in step 2 above, using \(C_{j,i}^{n+1,1}\) instead of \(C_{j,i}^{n+1,0}\). Thus, upon discretizing Equation (6.54) we get

\[
\sum_{j=1}^{r+m} D_j^* z_j \left\{ 2(C_{j,i-1}^{n+1,1} - 2C_{j,i}^{n+1,1} + C_{j,i+1}^{n+1,1}) + \mu_j \left[ (C_{j,i+1}^{n+1,1} + C_{j,i}^{n+1,1}) (\phi_i^{n+1,1} - \phi_i^{n+1,1}) 
- (C_{j,i}^{n+1,1} + C_{j,i-1}^{n+1,1}) (\phi_i^{n+1,1} - \phi_i^{n+1,1}) \right] \right\} = 0, \quad i = 0, \ldots, N - 1. \tag{6.67}
\]

As before, the fictitious values \(\phi_{-1}^{n+1,1}\) are given by

\[
\left[ \sum_{j=1}^{r+m} z_j \mu_j C_{j,0}^{n+1,1} \right] \left( \frac{\phi_1^{n+1,1} - \phi_{-1}^{n+1,1}}{2\Delta x} \right) = -\sum_{j=1}^{r} \mu_j \hat{g}_j(C_{j,0}^{n+1,1}, \phi_0^{n+1,1}, E), \tag{6.68}
\]

which is analogous to Equation (6.63).

5. **Corrector values for concentration and potential \((k \geq 2)\)**

Having calculated \(\phi_j^{n+1,k}\), we now return to Step 3 above to calculate \(C_{i,j}^{n+1,k+1}\). These are then used to calculate \(\phi_j^{n+1,k+1}\), as in Step 4. This process is repeated until the
convergence condition

\[ \left| \phi_j^{n+1,k+1} - \phi_j^{n+1,k} \right|_{\text{max}} \leq \epsilon, \]  

(6.69)
is satisfied, at which point we proceed to the next time step. The above marching procedure, given by steps 1-5, allows us to calculate the solution potential and the concentrations of ions at each subsequent time step. It should be noted that the FTCS explicit scheme (step 1) is only used to start the calculations at each time step (i.e. for \( k = 0 \)). From then on, the subsequent iterations for the concentrations are calculated using the Crank-Nicholson scheme, which is second order accurate in space and time.

### 6.5 Results and Discussion

In this section, we apply the above numerical algorithm to simulate an electrochemical model, involving a corrosion reaction, given by

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-, \]  

(6.70)

\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2, \]  

(6.71)

where a zinc electrode corrodes in an acidic sodium sulphate electrolyte containing zinc ions (added in as zinc sulphate). We let \( C_j, j = 1, \ldots, 4 \) denote the concentrations of \( \text{Zn}^{2+}, \text{H}^+, \text{Na}^+ \) and \( \text{SO}_4^{2-} \) ions, respectively. Here, \( \text{Zn}^{2+} \) and \( \text{H}^+ \), are the reactive ions, while \( \text{Na}^+ \) and \( \text{SO}_4^{2-} \) are the inert ions. Using a similar treatment as in Section 2.1.2 and Equation (6.13) above, it is straightforward to obtain the following expressions for the partial current densities,

\[ i_1 = i_ke^{(E-E_k)/b_{a1}}e^{-(\phi(0,t)-\phi(0,0))/b_{a1}}, \]  

(6.72)
Before applying the above numerical algorithm, initial concentration and potential profiles must be specified. The initial conditions were obtained by solving the steady system of equations (6.18)-(6.20), with the condition $i_1 = |i_2| = i_k$ (which is the physical requirement that the net current is zero before applying a potential step). This leads to simpler problem, where there is no system of algebraic equations to be solved as in Section 6.3.2. It is also necessary to select the bulk concentrations of all ions such that the electroneutrality condition is satisfied. This can be easily achieved by selecting physical values of the concentrations as follows. If the concentrations of $\text{H}_2\text{SO}_4$, $\text{ZnSO}_4$ and $\text{Na}_2\text{SO}_4$ are given by $M_1$, $M_2$ and $M_3$ respectively, then we have $C_1 = M_2$, $C_2 = 2M_1$, $C_3 = 2M_3$ and $C_4 = M_1 + M_2 + M_3$, which satisfies the electroneutrality condition. In our simulations, which are discussed below, $M_1$ and $M_2$ were held constant (0.5 and 1.0 Mol cm$^{-3}$ respectively), while the concentration of the supporting electrolyte, $M_3$, was varied to investigate its effect on the concentrations of the reactive ions, the solution potential and the current density transients. Of course, it is expected that as the value of $M_3$ increases, migration of the reactive ions becomes less significant, and the results should approach those obtained under conditions of diffusive transport only. The following values for the diffusivities were used [69], $D_1 = 0.72 \times 10^{-5} \text{cm}^2\text{s}^{-1}$, $D_2 = 9.43 \times 10^{-5} \text{cm}^2\text{s}^{-1}$, $D_3 = 1.35 \times 10^{-5} \text{cm}^2\text{s}^{-1}$ and $D_4 = 1.08 \times 10^{-5} \text{cm}^2\text{s}^{-1}$. In all the calculations, we fixed the Tafel slopes $b_{o_1} = 35\text{mV}$ and $b_{c_2} = 120\text{mV}$, since we are only interested in the effect of migration.

In Figure 6.1, 6.2 and 6.3 the steady state profiles for $C_1$, $C_2$ and $\phi$, respectively,
are shown for the case of diffusion-migration transport ($M_3 = 1.0$ and 10.0), and for
the case of diffusive transport only. From these, it is clear that as $M_3$ (concentration of supporting electrolyte) increases, the concentration profiles of the reactive ions approach those obtained in the absence of migration transport, and that the solution potential approaches a uniform value (i.e. electric field approaches zero), as expected. Another interesting observation, is that the presence of less supporting electrolyte, i.e. as migration becomes more significant, the rate of metal dissolution decreases, while the rate of hydrogen evolution increases. In other words, the presence of large concentrations of the supporting electrolyte (compared to the reactive ions) increases the rate of corrosion of the metal, or the presence of large electric fields in the solution reduces the rate of corrosion. This is not surprising, since the rate of metal dissolution is proportional to the negative exponential of the solution potential at $x = 0$ (as given by Equation (6.72)), and thus an increase in the solution potential reduces (i.e. decrease of supporting electrolyte concentration) the rate of metal dissolution. Similarly, from Equation (6.73), it can be seen that the rate of hydrogen evolution increases as the solution potential increases.

In Figure 6.4, a comparison between the numerical solution, as $t \to \infty$, and the exact steady state analytical solution is presented. It can be seen that there is excellent agreement between the two, and that the numerical solution converges to the exact steady state values. Figures 6.5-6.9 show typical profiles, obtained numerically, of the concentration of all ions and the solution potential, at different times. It can be seen from Figure 6.5 that the concentration of the metal ions increases at the electrode surface with time, while Figure 6.6 shows that there is
Figure 6.1: Effect of migration on the nondimensional steady state metal-ion concentration response to a potential step, $\Delta E$. Here $b_{a_1} = 35$ mV, $b_{c_2} = 120$ mV, $i_k = 0.5 i_L$, $C^b_1 = C^b_2 = 1$. (-----) diffusive transport only; (- - - - ) diffusion-migration with $C^b_3 = 2.0$, and $C^b_4 = 2.5$; (· · · · · ·) diffusion-migration with $C^b_3 = 20.0$, and $C^b_4 = 11.5$. 

$\Delta E = 60$ mV

$\Delta E = 90$ mV
Figure 6.2: Effect of migration on the nondimensional steady state hydrogen ion concentration response to a potential step, \( \Delta E \). Here \( b_a = 35 \text{mV}, b_c = 120 \text{mV}, i_k = 0.5i_{L_2}, C_1^b = C_2^b = 1 \). (———) diffusive transport only; (- - - -) diffusion-migration with \( C_3^b = 2.0 \), and \( C_4^b = 2.5 \); (· · · · · ·) diffusion-migration with \( C_3^b = 20.0 \), and \( C_4^b = 11.5 \).
Figure 6.3: Effect of migration on the nondimensional steady state potential distribution due to a potential step, $\Delta E$. Here $b_{a_1} = 35\text{mV}$, $b_{c_2} = 120\text{mV}$, $i_k = 0.5i_L$, $C^b_1 = C^b_2 = 1$. (---) diffusion-migration with $C^b_3 = 2.0$, and $C^b_4 = 2.5$; (-----) diffusion-migration with $C^b_3 = 20.0$, and $C^b_4 = 11.5$. 
Figure 6.4: Comparison between numerical and steady state analytical solutions. Here $b_{a_1} = 35\text{mV}$, $b_{c_2} = 120\text{mV}$, $i_k = 0.5i_{L_2}$, $\Delta E = 60\text{mV}$, $C_1^b = C_2^b = 1$ $C_3^b = 20.0$, and $C_4^b = 11.5$
Figure 6.5: Evolution of concentration profiles for $C_1$ (metal ions). Here $b_{a_1} = 35\text{mV}$, $b_{c_2} = 120\text{mV}$, $i_k = 0.7i_{L_2}$, $\Delta E = 90\text{mV}$, $C_1^b = C_2^b = 1$, $C_3^b = 2.0$, and $C_4^b = 2.5$
Figure 6.6: Evolution of concentration profiles for $C_2$ (hydrogen ions). Here $b_{a_1} = 35\text{mV}$, $b_{c_2} = 120\text{mV}$, $i_k = 0.7i_{I_2}$, $\Delta E = 90\text{mV}$, $C_1^b = C_2^b = 1$, $C_3^b = 2.0$, and $C_4^b = 2.5$
Figure 6.7: Evolution of concentration profiles for $C_3$ (sodium ions). Here $a_1 = 35\, \text{mV}$, $b_2 = 120\, \text{mV}$, $i_i = 0.7 i_{L_2}$, $\Delta E = 90\, \text{mV}$, $C_1^b = C_2^b = 1, C_3^b = 2.0$, and $C_4^b = 2.5$
Figure 6.8: Evolution of concentration profiles for $C_4$ (sulphate ions). Here $b_{a_1} = 35 \text{mV}$, $b_{c_2} = 120 \text{mV}$, $i_k = 0.7i_{L_2}$, $\Delta E = 90 \text{mV}$, $C_1^b = C_2^b = 1$, $C_3^b = 2.0$, and $C_4^b = 2.5$
Figure 6.9: Evolution of concentration profiles for $\phi(x)$. Here $b_{a_1} = 35\text{mV}$, $b_{c_2} = 120\text{mV}$, $i_k = 0.7i_{L_2}$, $\Delta E = 90\text{mV}$, $C_1^b = C_2^b = 1$, $C_3^b = 2.0$, and $C_4^b = 2.5$
a depletion of hydrogen ions at the electrode surface, as expected. The evolution of the sodium and sulphate ions, shown in Figures 6.7 and 6.8, respectively, are a consequence of the electroneutrality condition. In particular there is a significant increase in the surface concentration of the sulphate ions, seen in Figures 6.8 and 6.10, which offsets the large build up of the (positively charges) metal ions. Evolution of surface concentrations and the solution potential, are shown in Figure 6.10. It is interesting to note that, for $C_2(0,t)$ and $C_3(0,t)$, there is an initial decrease, followed by an increase in values. This is a result of the behaviour of $\phi(0,t)$. This behaviour is not observed for the case of diffusive transport only, where the surface concentrations of the reacting ions are either monotonic increasing or decreasing (depending on the applied potential).

Finally, in Figures 6.11 and 6.12, typical current transients obtained, by summing Equations (6.72) and (6.73), for different concentrations of the supporting electrolyte, and for the case of diffusive transport only, are shown. It can be seen that these transients can be significantly different depending on the concentrations of the supporting electrolyte, with higher values observed as the effect of migration becomes more significant. It was also observed that as the effect of migration increased (i.e. lower concentrations of the supporting electrolyte), the times to steady state were considerably larger than that obtained when migration was neglected. For example, attainment of steady state conditions was observed at $t=20$ ($\approx 200$ sec) for low supporting electrolyte concentrations (Figures 6.11 and 6.12 a and b), and at $t=2$ ($\approx 20$ sec) for larger concentrations of supporting electrolyte (Figures 6.11 and 6.12 c and d). The reason for this is very simple. In the absence of migra-
Figure 6.10: Surface concentrations and solution potential as a function of time. Here $b_{c_1} = 35\text{mV}$, $b_{c_2} = 120\text{mV}$, $i_k = 0.7i_{L_2}$, $\Delta E = 90\text{mV}$, $C_1^b = C_2^b = 1$, $C_3^b = 2.0$, and $C_4^b = 2.5$.
Figure 6.11: Nondimensional current density transients. Here $b_a = 35 \text{mV}$, $b_c = 120 \text{mV}$, $i_k = 0.5 i_{L_2}$, $\Delta E = 60 \text{mV}$, $C_1^b = C_2^b = 1$; (a) $C_3^b = 2.0$, and $C_4^b = 2.5$; (b) $C_3^b = 10.0$, $C_4^b = 10.5$; (c) $C_3^b = 200.0$, $C_4^b = 101.5$; and (d) diffusion of reactive ions only (migration not included).
Figure 6.12: Nondimensional current density transients. Here $b_{a_1} = 35\text{mV}$, $b_{c_2} = 120\text{mV}$, $i_k = 0.7i_{L_2}$, $\Delta E = 100\text{mV}$, $C_1^b = C_2^b = 1$; (a) $C_3^b = 2.0$, and $C_4^b = 2.5$; (b) $C_3^b = 10.0$, and $C_4^b = 10.5$; (c) $C_3^b = 200.0$, $C_4^b = 101.5$; and (d) diffusion of reactive ions only (migration not included).
tion, the rate of metal dissolution is independent of the metal ion concentration, and hence diffusion of these ions away from the electrode does not influence the current (note that we are not including metal-ion deposition). Thus, in this case the time to steady state is controlled by the diffusion of hydrogen ions towards the surface (with diffusivity, $D_2 = 9.43 \times 10^{-5} \text{cm}^2\text{s}^{-1}$). Now, in the presence of migration, even though the current does not explicitly depend on the zinc ion concentration, the concentration of the hydrogen ions, and the solution potential are coupled to the concentration of the zinc ions (with diffusivity, $D_1 = 0.72 \times 10^{-5} \text{cm}^2\text{s}^{-1}$). Therefore, the time to steady state is now also controlled by the transport of metal ions, which are considerably slower than the hydrogen ions. It is also interesting to note the presence of a peak in the current transient response for low supporting electrolyte concentrations, seen in Figures 6.11 and 6.12 a and b, which is a result of the solution potential response adjacent to electrode surface (i.e. at $x=0$), seen in Figure 6.10. A similar effect occurs in galvanostatic experiments, where a peak in the potential transients, known as superpolarization, has been reported by Walter [96, 99]. It is possible that this effect may be explained in terms of the supporting electrolyte concentration (i.e. migration effects).
Chapter 7

Conclusion

In this thesis we have developed appropriate mathematical models, representing typical electrochemical experiments used for corrosion rate measurements of metals, particularly zinc and steel in slightly acidic deaerated stagnant solutions, at BHP Research Laboratories and elsewhere. These models are well known fundamental electrochemical kinetic-diffusion problems, for which few antecedent approximate analytical solutions are known.

A new steady state polarization equation, based on mixed charge-transfer and diffusion control, and including the metal-ion deposition partial reaction, has been presented. We have shown that use of the conventional (charge-transfer) polarization equation, which is the case for most of the currently available corrosion measurement software, can produce significant errors in the measured parameters under conditions of mixed charge-transfer and diffusion control. This new equation can easily be incorporated into the existing corrosion software available to analyse polarization curves, resulting in greater accuracy and reliability of the corrosion rates
and Tafel slopes calculated over a wider range of experimental conditions. A number of transient electrochemical methods, which are commonly used for corrosion testing were also modelled. New exact solutions for the potentiostatic method were presented. Numerical and approximate analytical solutions for the potentiodynamic and galvanostatic methods were also presented.

The existence of exact and approximate analytical solutions for these transient electrochemical methods means that these methods can be readily used for rapid corrosion rate measurements instead of the much slower steady state methods (which are the standard methods used frequently at most industrial research laboratories). Also, extensive use can be made of the approximate analytical solutions, especially when conducting nondestructive tests, where the magnitude of a given perturbation is relatively small. Most importantly, these solutions make possible the calculation of corrosion parameters by merely fitting an elementary class of functions to transient experimental data. This would not only lead to more accurate results, but an increased efficiency compared to steady state methods, which are the standard methods for corrosion measurements.

A general numerical scheme for the simulation of electrochemical diffusion-migration processes was also developed. This is in contrast to the currently available algorithms in the literature, which are limited in their application or make restrictive simplifying assumptions. Migration effects can be important in practical situations because, for example, most natural waters are of low conductivity, where excess of supporting electrolyte is absent and consequently transport processes due to diffusion and migration need to be considered. Using this algorithm, the effects of
migration on metallic corrosion were examined, and it is shown that this leads to a lower predicted rate of metal dissolution compared to that obtained when diffusion is the sole mechanism for transport.

**Future Work**

An obvious extension to the present work, would be to include the oxygen reduction partial reaction and coupled chemical reactions, which are usually associated with corrosion reactions. This involves more complicated models, where surface coverage of the metallic electrode and passivation, where a protective layer covers the metal surface, would need to be considered. These models can also exhibit some very interesting dynamic behaviour, which has been investigated in the literature (see for example [103]). Also of importance are AC electrochemical methods and the corrosion of painted metals. AC methods, which have not been considered here, are also commonly used for corrosion testing, especially for painted or coated metals. These are still predominantly based on equivalent circuit models. A more rigorous mathematical approach, based on widely applicable boundary value problems related to those considered here, would have obvious advantages.

The work on diffusion-migration processes in Chapter 6 could be extended in a number of ways. First of all, this work has been based on dilute solution theory, where no interactions exist between the different ionic species. An extension to concentrated solutions, where ionic species interact with each other (through electrostatic forces, multicomponent diffusion and friction) could reveal some interesting results. A closer study of the electrified double layer (across the metal/solution inter-
face) could also be undertaken. In particular, understanding the double layer would be of value if we calculate the potential distribution using the Poisson equation, rather than the (approximate) electroneutrality condition. Also, the phenomenon of superpolarization, which was mentioned in Chapter 6, is worth investigating. It is possible that this phenomenon could be explained in terms of diffusion-migration transport.

Corrosion modelling is a very rich and diverse field, in which there is great potential for future research. In particular, there exists a wide range of mathematical techniques which could be utilised for investigating very interesting and complicated problems, for which few solutions exist in the literature.
Appendix A

Derivation of Equations (5.44) and (5.45)

Consider the boundary value problems given by Equations (5.16)-(5.18), (5.41) and (5.43), which are given by

\[ \frac{d\theta_j^{(1)}}{dt} = D_j \frac{\partial^2 \theta_j^{(1)}}{\partial \xi^2}, \]  
\[ \theta_j^{(1)}(\xi, 0) = 0, \]  
\[ \theta_j^{(1)}(0, t) = 0, \]  
\[ \frac{\partial \theta_1^{(1)}}{\partial \xi}(1, t) = \mu \left( 1 - \frac{\partial \theta_2^{(1)}}{\partial \xi}(1, t) \right), \]  
\[ \frac{\partial \theta_2^{(1)}}{\partial \xi}(1, t) = \alpha \theta_1^{(1)}(1, t) + \beta \theta_2^{(1)}(1, t) + \gamma. \]

Taking the Laplace transform of Equation (A.1) and using Equations (A.2) and (A.3) yields

\[ \tilde{\theta}_j^{(1)}(\xi, s) = A_j(s) \sinh \left( \nu_j \xi \sqrt{s} \right), \]

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where \( \nu_j = (D_j^*)^{-1/2} \) and \( \tilde{\theta}_j^{(1)}(\xi, s) \) is the Laplace transform of \( \theta_j^{(1)}(\xi, t) \). Substituting (A.6) into (A.4) yields

\[
\frac{1}{\mu} \nu_1 \sqrt{s} A_1(s) \cosh(\nu_1 \sqrt{s}) = \frac{1}{s} - \sqrt{s} A_2(s) \cosh(\sqrt{s}). \tag{A.7}
\]

Similarly, substituting (A.6) into (A.5) yields

\[
A_2(s) = \frac{\alpha A_1(s) \sinh(\nu_1 \sqrt{s}) + \gamma / s}{\sqrt{s} \cosh(\sqrt{s}) - \beta \sinh(\sqrt{s})}. \tag{A.8}
\]

Equations (A.7) and (A.8) are two linear algebraic equations in \( A_1(s) \) and \( A_2(s) \).

Substituting (A.8) into (A.7) yields

\[
\frac{\nu_1}{\mu} \sqrt{s} A_1(s) \cosh(\nu_1 \sqrt{s}) = \frac{1}{s} - \frac{\sqrt{s} \cosh(\sqrt{s}) (\alpha A_1(s) \sinh(\nu_1 \sqrt{s}) + \gamma / s)}{\sqrt{s} \cosh(\sqrt{s}) - \beta \sinh(\sqrt{s})}, \tag{A.9}
\]

and by rearranging (A.9) we may deduce the following expression for \( A_1(s) \)

\[
A_1(s) = \frac{s^{-3/2} \sqrt{s} (1 - \gamma) \cosh(\sqrt{s}) - \beta \sinh(\sqrt{s})}{\nu_1 \mu^{-1} \cosh(\nu_1 \sqrt{s}) \sqrt{s} \cosh(\sqrt{s}) - \beta \sinh(\sqrt{s}) + \alpha \cosh(\sqrt{s}) \sinh(\nu_1 \sqrt{s})}. \tag{A.10}
\]

Hence, using Equation (A.6), we have

\[
\tilde{\theta}_1^{(1)}(\xi, s) = \frac{s^{-3/2} \sqrt{s} (1 - \gamma) \cosh(\sqrt{s}) - \beta \sinh(\sqrt{s}) \sinh(\nu_1 \xi \sqrt{s})}{\nu_1 \mu^{-1} \cosh(\nu_1 \sqrt{s}) \sqrt{s} \cosh(\sqrt{s}) - \beta \sinh(\sqrt{s}) + \alpha \cosh(\sqrt{s}) \sinh(\nu_1 \sqrt{s})}. \tag{A.11}
\]

Now \( A_2(s) \) may readily be obtained using Equations (A.8) and (A.10), and hence \( \tilde{\theta}_2^{(1)}(\xi, s) \) can easily be shown to be given by

\[
\tilde{\theta}_2^{(1)}(\xi, s) = \frac{\alpha [\sqrt{s}(1 - \gamma) \cosh(\sqrt{s}) - \beta \sinh(\sqrt{s})] \sinh(\nu_1 \sqrt{s}) \sinh(\xi \sqrt{s})}{\mu^{-1} \nu_1 \cosh(\nu_1 \sqrt{s}) \sqrt{s} \cosh(\sqrt{s}) - \beta \sinh(\sqrt{s}) + \alpha \sinh(\nu_1 \sqrt{s}) \cosh(\sqrt{s})} \times \frac{s^{-3/2}}{\sqrt{s} \cosh(\sqrt{s}) - \beta \sinh(\sqrt{s})} + \frac{\gamma}{s} \frac{\sinh(\xi \sqrt{s})}{\sqrt{s} \cosh(\sqrt{s}) - \beta \sinh(\sqrt{s})}. \tag{A.12}
\]
Appendix B

Program for simulating the 1-D diffusion-migration model

The program given below was used for simulating diffusion-migration transport processes, discussed in Chapter 6. This specific program was used to simulate the corrosion reaction described in Section 6.4.2. However, the program was written in a way to facilitate modelling electrochemical systems involving any number of reactive and inert ions, as well as any type of reaction kinetics (as long as these are linear in the concentrations of the reactive ions).

Program Diffusion-Migration

c This program solves the transient electrochemical diffusion-migration transport equations. The model considered is one where a metal electrode corrodes in an acidic sodium sulphate electrolyte. The electrochemical reactions occurring at the electrode/solution interface are: anodic metal dissolution and cathodic hydrogen evolution. Thus, there are two reactive and two inert ions. This program can, however, be easily modified to handle any number of reactive and inert ions.
c We consider a transport in a finite diffusion layer, with a constant potential applied (Eapp) to the electrode surface (however we can use
Appendix

c any controlled potential conditions, i.e. \( E_{\text{app}}(t) = g(t) \).

c Note: We take ionic species 2 to be the H\(^+\) ions.

c We scale all variables as follows (\([\text{ ]}\) indicates dimensional variables):

c Note: We take ionic species 2 to be the H\(^+\) ions.

c We scale all variables as follows (\([\text{ ]}\) indicates dimensional variables):

\[
x = \frac{x}{\delta}; \quad C(i) = \frac{[C(i)]}{C_b(2)}; \quad t = \frac{[t]}{\tau_2}; \quad \Phi = e(2) \cdot \Phi, \quad i = \frac{[i]}{i_{L2}},
\]

\[
\tau_2 = \delta^2 / D(2); \quad \text{and} \quad i_{L2} = z(2) D(2) C_b(2) / \delta.
\]

\[
\begin{align*}
N &= \text{number of mesh points, } j = 0, \ldots, N. \\
M &= \text{number of ionic species, } i = 1, \ldots, M. \\
z(i) &= \text{charge of ion } i \\
e(i) &= \frac{z(i) F}{R T} \\
F &= \text{Faraday's constant} \\
R &= \text{Universal gas constant} \\
T &= \text{temperature (K)} \\
D(i) &= \text{diffusivity of ion } i \\
C_b(i) &= \text{bulk concentration of ion } i \text{ (outside diffusion layer)} \\
E_{\text{app}} &= \text{applied potential step} \\
E_k &= \text{corrosion potential (electrode potential at } t = 0) \\
i_k &= \text{corrosion current density} \\
i_t &= \text{current response to } E_{\text{app}} \\
\text{ba}_1 &= \text{anodic Tafel slope of metal} \\
\text{bc}_2 &= \text{cathodic Tafel slope of hydrogen} \\
\Phi_{\text{ref}} &= \text{solution potential outside diffusion layer} \\
\Phi_{o}(j) &= \text{initial potential} \\
C_{o}(i,j) &= \text{initial concentrations} \\
dx &= \text{grid size} \\
dt &= \text{time step size}
\end{align*}
\]

---

Variable declarations:

```fortran
table
integer N,M,i,j,k,KMAX
Parameter (M=4)
Parameter (N=20)
Parameter (KMAX=100)
double precision R,T,F,ba1,bc2,it,i1,i2
double precision D(M),z(M),e(M),Cb(M),Phi_ref,Eapp,Ek,ik
double precision dx,x(0:N),t,dt
```
double precision Phi_dif(0:N), C_pr(M,0:N), Phi_pr(0:N)
double precision C_cr(M,0:N), Phi_cr(0:N)
double precision lam1, lam2, mu1, mu2, alpha1, alpha2
double precision Phi_o(0:N), C_o(M,0:N)
double precision Net_charge, max_norm, TOL
double precision Cnl_pr(M), Cnl_o(M), Phinl_o
double precision Cnl_cr(M)

Common/Data1/ Phi_ref, Cb, z, e, D, ik
Common/Data2/ Eapp, Ek, ba1, bc2
Common/Data3/ lam1, lam2, mu1, mu2, alpha1, alpha2

open(unit=1, file='input.dat', status='old')
open(unit=2, file='Surface_poten.dat', status='unknown')
open(unit=3, file='Surface_conc.dat', status='unknown')
open(unit=4, file='Current.dat', status='unknown')
open(unit=7, file='Conc_prof.dat', status='unknown')
open(unit=8, file='Potentiaprof.dat', status='unknown')

C ** Read input data

R=8.31
T=298.0
F=96480.0

read(1,*) Phi_ref, Eapp, Ek, ik, ba1, bc2

do i=1,M
read(1,*) Cb(i), z(i), D(i)
enddo

C ** Check electroneutrality of bulk concentrations

Net_charge=0.0d0
do i=1,M
Net_charge = Net_charge + z(i)*Cb(i)
enddo

if (Net_charge.eq.0.0d0) then
write(*,*) 'Electroneutrality OK'
else
    write(*,*) 'ERROR : Bulk solution NOT neutral'
    STOP
endif

c ** Calculate step size, and coordinate of each node

dx=1.0d0/(1.0d0*N)
do j=0,N
    x(j) = j*dx
endo
c ** Calculate initial concentration and potential distributions

call Initial(x,C_o, Phi_o)

c Write out initial potential

t=0.0d0

write(2,'(F9.5,A1,F9.5)') t, ',', Phi_o(0)
c Write out initial concentrations

    # t, ',', C_o(1,0)/Cb(1), ',', C_o(2,0)/Cb(2),
    # ',', C_o(3,0)/Cb(3), ',', C_o(4,0)/Cb(4)
c These will be used in the current density function

alpha1 = (e(2)*ba1)**(-1)
alpha2 = (e(2)*bc2)**(-1)

lam1 = dexp((Eapp-Ek)/ba1)
lam2 = dexp(-(Eapp-Ek)/bc2)/C_o(2,0)

mu1 = z(2)/z(1)*D(2)*lam1*ik*dexp(Phi_o(0)/(e(2)*ba1))
mu2 = D(2)*lam2*ik*dexp(-Phi_o(0)/(e(2)*bc2))

i1 = ik*dexp((Eapp-Ek)/ba1)
i2 = -ik*dexp(-(Eapp-Ek)/bc2)

it = i1 + i2
write(4,'(F9.5,1X,F9.5)') t, ',', it

c ** Calculate time step, dt.

dt = 1.0d0*dx**2

t = 0.0d0

do 1150 k=1,KMAX

t = k*dt

c ** Calculate Predictor Values for Concentrations

call C_predictor(dx,x,t,dt,Phi_o,C_o,C_pr,Cnl_o,
    # Phinl_o,Cnl_pr)

c ** Calculate Predictor Values for Potential

call Phi_solver(dx,x,C_pr,Phi_o,Phi_pr,Cnl_pr)

c ** Calculate Corrector values for concentrations.

101 call C_corrector(dx,t,dt,x,Phi_o,C_o,Phi_pr,Phinl_o,C_pr,
    # Cnl_o,C_cr,Cnl_cr)

c ** Calculate corrector values for potential

call Phi_solver(dx,x,C_cr,Phi_o,Phi_cr,Cnl_cr)

c ** Check for convergence : Compare Phi_cr and Phi_pr

TOL = 5.0d-1*dx**2

do j=0,N

    Phi_dif(j) = Phi_cr(j)-Phi_pr(j)

enddo

max_norm=Phi_dif(0)

do j=0,N-1

    if (abs(Phi_dif(j)).ge.abs(max_norm)) then

        max_norm=Phi_dif(j)

    endif

enddo
IF (dabs(max_norm).ge.TOL) THEN
  do i=1,M
    do j=0,N
      C_pr(i,j) = C_cr(i,j)
    enddo
  enddo
  do j=0,N
    Phi_pr(j) = Phi_cr(j)
  enddo
  GOTO 101
ENDIF

WRITE OUT SURFACE CONCENTRATIONS AND POTENTIAL

IF (MOD(k,20).eq.0) THEN
  write(3,'(F9.5,A1,F9.5,A1,F9.5,A1,F9.5,A1,F9.5)')
    # t, ',', C_cr(1,0)/Cb(1), ',', C_cr(2,0)/Cb(2),
    # ',', C_cr(3,0)/Cb(3), ',', C_cr(4,0)/Cb(4)
  write(2,'(F9.5)') t, ',', Phi_cr(0)
ENDIF

WRITE OUT CONCENTRATION AND POTENTIAL PROFILES

IF ( (K.eq.1).OR.(K.eq.6).OR.(K.eq.64)
    # .OR.(K.eq.320).OR.(K.eq.640).OR.
    # (K.eq.3200).OR.(K.eq.6400).OR.(K.eq.12800)
    # .OR.(K.eq.32000) ) THEN
  write(7,*), 'T = ', t
    do j=0,N
      write(7,'(F5.3,A1,F9.5,A1,F9.5,A1,F9.5,A1,F9.5)')
        # x(j), ',', C_cr(1,j)/Cb(1), ',', C_cr(2,j)/Cb(2),
        # ',', C_cr(3,j)/Cb(3), ',', C_cr(4,j)/Cb(4)
    enddo
  write(8,*), 'T = ', t
    do j=0,N
      write(8,'(F5.3,A1,F9.5)') x(j), ',', Phi_cr(j)
    enddo
ENDIF
Appendix

ENDIF

c** Calculate partial currents and total current response

il = ik*lam1*dexp(-alpha1*(Phi_cr(0)-Phi_o(0)))
i2 = -ik*lam2*C_cr(2,0)*dexp(alpha2*(Phi_cr(0)-Phi_o(0)))
it = il + i2

IF (MOD(k,20).eq.O) THEN
write(4,'(F9.5,Al,F9.5)') t, ', ', it
ENDIF

c** Now we set the solution given by C_cr(i,j) and Phi_cr(j) to
C_o(i,j) and Phi_o(j), and repeat the procedure

do i=1,M
  do j=0,N
    C_o(i,j)=C_cr(i,j)
  enddo
endo

do j=0,N
  Phi_o(j)=Phi_cr(j)
enddo

c**************************************************************************
Subroutine C_corrector(dx,t,dt,x,Phi_o,C_o,Phi_pr,Phinl_o, 
# C_pr,Cnl_o,C_cr,Cnl_cr)

This subroutine calculates corrector values of concentration
at time level n+1, using C(i,j) and Phi(j) at time level n,
and predictor values for Phi at time level n+1.
Note: Predictor values for C are not needed here.
We need Phinl_o, Phi1_pr, and Cn1_o, which are passed through.

implicit none

integer M,N,i,j,kk
Parameter(M=4)
Parameter(N=20)
double precision \( z(M), e(M), D(M), C_b(M), a_k, \Phi_{\text{ref}}, x(0:N) \)

double precision \( C_o(M,0:N), C_{\text{cr}}(M,0:N), C_{\text{pr}}(M,0:N) \)

double precision \( \Phi_o(0:N), \Phi_{\text{pr}}(0:N) \)

double precision \( \Phi_{\text{ref}}, a_1(M), a_2(M), a_3(M), a_4(M) \)

double precision \( t, dt, dx, \rho(M), \varepsilon(M), S_5, S_6, S_7 \)

double precision \( C_{\text{n1}_o}(M), \Phi_{\text{n1}_o}, \Phi_{\text{n1}_pr}, C_{\text{n1}_cr}(M) \)

double precision \( \Phi_{B_o}(0:N-1), \Phi_{C_o}(0:N-1), \Phi_{F_o}(0:N-1) \)

double precision \( \Phi_{B_{pr}}(0:N-1), \Phi_{C_{pr}}(0:N-1), \Phi_{F_{pr}}(0:N-1) \)

double precision \( \alpha_o(0:N-1), \beta_o(0:N-1), \gamma_o(0:N-1) \)

double precision \( \alpha_{pr}(0:N-1), \beta_{pr}(0:N-1), \gamma_{pr}(0:N-1) \)

double precision \( \Phi_{B_o}(0:N-1), \Phi_{C_o}(0:N-1), \Phi_{F_o}(0:N-1) \)

double precision \( \Phi_{B_{pr}}(0:N-1), \Phi_{C_{pr}}(0:N-1), \Phi_{F_{pr}}(0:N-1) \)

double precision \( \alpha_{pr}(0:N-1), \beta_{pr}(0:N-1), \gamma_{pr}(0:N-1) \)

double precision \( \Psi(0:N-1), \omega(M), \eta(M), L(M), K(M) \)

double precision \( A_{cr}(0:N-1,0:N-1), b_{cr}(0:N-1) \)

double precision \( A_{cr}(0:N-1,0:N-1), det \)

Common/Data1/ \( \Phi_{\text{ref}}, C_b, z, e, D, a_k \)

Common/Data3/ \( \lambda_1, \lambda_2, \mu_1, \mu_2, \alpha_1, \alpha_2 \)

do i=1,M
\[ \rho(i) = \frac{(dt/dx^2) \cdot D(i)}{D(2)} \]
\[ \varepsilon(i) = 0.5d0 \cdot e(i)/e(2) \]
enddo

c---------------------------------------------------------------------
do i=3,M
\[ a_1(i) = 0.0d0 \]
\[ a_2(i) = 0.0d0 \]
\[ a_3(i) = 0.0d0 \]
\[ a_4(i) = 0.0d0 \]
enddo

\[ a_1(1) = \mu_1 \cdot (1.0d0 + \alpha_1 \cdot \Phi_o(0)) \cdot \text{dexp}(-\alpha_1 \cdot \Phi_o(0)) \]
\[ a_2(1) = 0.0d0 \]
\[ a_3(1) = 0.0d0 \]
\[ a_4(1) = -\alpha_1 \cdot \mu_1 \cdot \text{dexp}(-\alpha_1 \cdot \Phi_o(0)) \]

\[ a_1(2) = 0.0d0 \]
\[ a_2(2) = -\mu_2 \cdot (1.0d0 - \alpha_2 \cdot \Phi_o(0)) \cdot \text{dexp}(\alpha_2 \cdot \Phi_o(0)) \]
\[ a_3(2) = -\mu_2 \cdot \alpha_2 \cdot \text{dexp}(\alpha_2 \cdot \Phi_o(0)) \]
\[ a_4(2) = 0.0d0 \]

S5=0.0d0
S6=0.0d0
S7=0.0d0
do i=1,M  
S5 = S5 + e(i)**2*C_pr(i,0)  
  S6 = S6 + 2.0d0*e(2)*dx*(e(i)/D(i))*(a1(i)+a2(i)*C_pr(i,0))  
  S7 = S7 + 2.0d0*e(2)*dx*(e(i)/D(i))*(a3(i)*C_pr(i,0)+a4(i))  
enddo  

Phinl_pr = Phi_pr(1) + (S7/S5)*Phi_pr(0) + (S6/S5)  
c----------------------------------

c We rewrite the current density functions as :  
c f(i) = omega(i) + eta(i)*C(i,o)  

omega(1) = mu1*dexp(-alpha1*Phi_pr(0))  
eta(1) = 0.0d0  

omega(2) = 0.0d0  
eta(2) = -mu2*dexp(alpha2*Phi_pr(0))  

do i=3,M  
omega(i) = 0.0d0  
eta(i) = 0.0d0  
enddo  

c-----------------------------

doi=1,M  
K(i) = 2.0d0*dx*omega(i)/D(i)  
L(i) = 2.0d0*( eps(i)*(Phi_pr(1)-Phinl_pr)+dx*eta(i)/D(i) )  
enddo  

c-----------------------------

PhiB_o(0) = Phinl_o-Phi_o(0)  
PhiB_pr(0) = Phinl_pr-Phi_pr(0)  

PhiC_o(0) = Phi_o(l)-2.0d0*Phi_o(0)+Phinl_o  
PhiC_pr(0) = Phi_pr(l)-2.0d0*Phi_pr(0)+Phinl_pr  

PhiF_o(0) = Phi_o(l)-Phi_o(0)  
PhiF_pr(0) = Phi_pr(l)-Phi_pr(0)  

do j=1,N-1  
  PhiB_o(j) = Phi_o(j-1)-Phi_o(j)  
  PhiC_o(j) = Phi_o(j+1)-2.0d0*Phi_o(j)+Phi_o(j-1)  
  PhiF_o(j) = Phi_o(j+1)-Phi_o(j)  
  PhiB_pr(j) = Phi_pr(j-1)-Phi_pr(j)  
  PhiC_pr(j) = Phi_pr(j+1)-2.0d0*Phi_pr(j)+Phi_pr(j-1)  
  PhiF_pr(j) = Phi_pr(j+1)-Phi_pr(j)
The approach used here is to setup the matrix system for each ionic species separately.

\[
\begin{align*}
\text{do } i & = 0, \ldots, M, \\
\alpha_0(j) & = \rho(i) \times (1.0 + \epsilon(i) \times \Phi_{B_0}(j)), \\
\beta_0(j) & = \rho(i) \times (2.0 - \epsilon(i) \times \Phi_{C_0}(j)), \\
\gamma_0(j) & = \rho(i) \times (1.0 + \epsilon(i) \times \Phi_{F_0}(j)), \\
\alpha_{pr}(j) & = \rho(i) \times (1.0 + \epsilon(i) \times \Phi_{B_{pr}}(j)), \\
\beta_{pr}(j) & = \rho(i) \times (2.0 - \epsilon(i) \times \Phi_{C_{pr}}(j)), \\
\gamma_{pr}(j) & = \rho(i) \times (1.0 + \epsilon(i) \times \Phi_{F_{pr}}(j)),
\end{align*}
\]

\[
\begin{align*}
\Psi(0) & = \alpha_0(0) \times C_{nl_0}(i) + (2.0 - \beta_0(0)) \times C_{o}(i,0) \\
& \quad + \gamma_0(0) \times C_{o}(i,1) \\
\text{do } j & = 1, \ldots, N-1, \\
\Psi(j) & = \alpha_0(j) \times C_{o}(i,j-1) + (2.0 - \beta_0(j)) \times C_{o}(i,j) \\
& \quad + \gamma_0(j) \times C_{o}(i,j+1)
\end{align*}
\]

\[
\begin{align*}
\text{c Setup the matrices } A_{cr} \text{ and } b_{cr} \text{ such that: } A_{cr} \times C_{cr} = b_{cr}
\end{align*}
\]

\[
\begin{align*}
A_{cr}(0,0) & = 2.0 + \beta_{pr}(0) - \alpha_{pr}(0) \times L(i), \\
A_{cr}(0,1) & = -(\gamma_{pr}(0) + \alpha_{pr}(0)), \\
A_{cr}(N-1,N-2) & = -\alpha_{pr}(N-1), \\
A_{cr}(N-1,N-1) & = 2.0 + \beta_{pr}(N-1)
\end{align*}
\]

\[
\begin{align*}
b_{cr}(0) & = \Psi(0) + \alpha_{pr}(0) \times K(i), \\
b_{cr}(N-1) & = \Psi(N-1) + \gamma_{pr}(N-1) \times C_{b}(i)
\end{align*}
\]

\[
\begin{align*}
\text{do } j & = 1, \ldots, N-2, \\
A_{cr}(j,j-1) & = -\alpha_{pr}(j), \\
A_{cr}(j,j) & = 2.0 + \beta_{pr}(j), \\
A_{cr}(j,j+1) & = -\gamma_{pr}(j), \\
b_{cr}(j) & = \Psi(j)
\end{align*}
\]

\[
\begin{align*}
\text{c Call subroutine to solve linear system above}
\end{align*}
\]

\[
\begin{align*}
\text{do } kk & = 1, N
\end{align*}
\]
do j=1,N+1
    AA(kk,j)=0.0d0
enddo
enddo

do kk=0,N-1
    do j=0,N-1
        AA(kk+1,j+1) = A_cr(kk,j)
    enddo
enddo

do j=0,N-1
    AA(j+1,N+1) = b_cr(j)
enddo

call DSID(AA,1,N,N,N+1, det)

do j=0,N-1
    C_cr(i,j) = AA(j+1,N+1)
enddo

C_cr(i,N) = Cb(i)

Cn1_cr(i) = C_cr(i,1)+L(i)*C_cr(i,0)+K(i)

1010 continue
RETURN
END

**************************************************************************

Subroutine Phi_solver(dx,x,C_pr,Phi_o,Phi_pr, # Cnl_pr)

This subroutine calculates predictor values for Phi given predictor values for concentrations.

implicit none

integer M,N,i,j

Parameter(M=4)
Parameter(N=20)

double precision z(M),e(M),D(M),Cb(M),ik,Phi_ref,x(0:N)
double precision Phi_o(0:N),C_pr(M,0:N), Phi_pr(0:N),dx
double precision Phi_ref,ik,lam1,lam2,mu1,mu2,alpha1,alpha2
double precision a1(M),a2(M),a3(M),a4(M)
double precision mu(M),lam(M),Cn1_pr(M),Phin1_pr
double precision A_pr(0:N-1,0:N-1),b_pr(0:N-1)
double precision S1(0:N-1),S2(0:N-1),S3(0:N-1),S4(0:N-1)
double precision S5,S6,S7,AA(N,N+1),det

Common/Data1/ Phi_ref,Cb,z,e,D,ik
Common/Data3/ lam1,lam2,mu1,mu2,alpha1,alpha2

doi=1,M
mu(i) = (D(i)/D(2))*(e(i)/e(2))
lam(i) = 0.5d0*(D(i)/D(2))*(e(i)**2/e(2)**2)
enddo

c Current density functions are given by:
c f1 = mu1*dexp(-alpha1*Phi(0,t))
c f2 = -mu2*C2(0,t)*dexp(alpha2*Phi(0,t))
c Note: Here we linearize f1 and f2, about the potential at the
c previous time level; i.e. about Phi_o. Thus we have:
c f(i) = a1(i) + a2(i)*C(i,0) + a3(i)*C(i,0)*Phi(0) + a4(i)*Phi(0)

doi=3,M
a1(i)=0.0d0
a2(i)=0.0d0
a3(i)=0.0d0
a4(i)=0.0d0
enddo

a1(1) = mu1*(1.0d0+alpha1*Phi_o(0))*dexp(-alpha1*Phi_o(0))
a2(1) = 0.0d0
a3(1) = 0.0d0
a4(1) = -alpha1*mu1*dexp(-alpha1*Phi_o(0))

a1(2) = 0.0d0
a2(2) = -mu2*(1.0d0-alpha2*Phi_o(0))*dexp(alpha2*Phi_o(0))
a3(2) = -mu2*alpha2*dexp(alpha2*Phi_o(0))
a4(2) = 0.0d0

do j=0,N-1
S1(j) = 0.0d0
S2(j) = 0.0d0
S3(j) = 0.0d0
S4(j) = 0.0d0
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S5 = 0.0d0
S6 = 0.0d0
S7 = 0.0d0

do i=1,M
S1(0) = S1(0) + lam(i)*(Cnl_pr(i) + C_pr(i,0))
S2(0) = S2(0) + lam(i)*(Cnl_pr(i) + 2.0d0*C_pr(i,0) # + C_pr(i,1))
S3(0) = S3(0) + lam(i)*(C_pr(i,1)+C_pr(i,0))
S4(0) = S4(0) + mu(i)*(Cnl_pr(i)-2.0d0*C_pr(i,0)+C_pr(i,1))
S5 = S5 + e(i)**2*C_pr(i,0)
S6 = S6 + 2.0d0*e(2)*dx*(e(i)/D(i))*(al(i)+a2(i)*C_pr(i,0))
S7 = S7 + 2.0d0*e(2)*dx*(e(i)/D(i))*(a3(i)*C_pr(i,0)+a4(i))
endo

do 160 j=1,N-1
   do i=1,M
      S1(j)=S1(j)+lam(i)*(C_pr(i,j)+C_pr(i,j-1))
      S2(j)=S2(j)+lam(i)*(C_pr(i,j-1)+2.0d0*C_pr(i,j) # +C_pr(i,j+1))
      S3(j)=S3(j)+lam(i)*(C_pr(i,j+1)+C_pr(i,j))
      S4(j)=S4(j)+mu(i)*(C_pr(i,j-1)-2.0d0*C_pr(i,j)) # +C_pr(i,j+1))
   enddo
160 continue

c Set up the system : A_pr(N-1xN-1)*Phi=b_pr(N-1x1)

A_pr(0,0) = S1(0)*(S7/S5)-S2(0)
A_pr(0,1) = S1(0)+S3(0)
A_pr(N-1,N-2) = S1(N-1)
A_pr(N-1,N-1) = -S2(N-1)
b_pr(0) = -S4(0)-S1(0)*S6/S5
b_pr(N-1) = -S3(N-1)*Phi_ref-S4(N-1)

do j=1,N-2
   A_pr(j,j) = -S2(j)
   A_pr(j,j+1) = S3(j)
   A_pr(j,j-1) = S1(j)
b_pr(j) = -S4(j)
endo
Call subroutine to solve linear system above

do i=1,N
  do j=1,N+1
    AA(i,j)=0.0d0
  enddo
enddo

do i=0,N-1
  do j=0,N-1
    AA(i+1,j+1) = A_pr(i,j)
  enddo
enddo

do i=0,N-1
  AA(i+1,N+1) = b_pr(i)
enddo

call DSID(AA,1,N,N,N+1,det)

do j=0,N-1
  Phi_pr(j) = AA(j+1,N+1)
enddo

Phi_pr(N) = Phi_ref

Phinl_pr = Phi_pr(1) + (S7/S5)*Phi_pr(0) + (S6/S5)

RETURN
END

Subroutine C_predictor(dx,x,t,dt,Phi_o,C_o,C_pr,Cnl_o,
# Phinl_o,Cnl_pr)

c This subroutine calculates predictor values of concentration
at time level n+1, using C(i,j) and Phi(j) at time level n,
using an dexplicit scheme.

implicit none

integer M,N,i,j

Parameter(M=4)
Parameter(N=20)

double precision z(M),e(M),D(M),Cb(M),ik,Phi_ref,x(0:N)
double precision C_o(M,0:N), Phi_o(0:N), C_pr(M,0:N)
double precision Phi_ref,ik,lambda1,lambda2,mu1,mu2,alpha1,alpha2
double precision Cnl_o(M), Cnl_pr(M), Phinl_o

double precision t,dt,dx,S1,S2, Peclet,dPhidx(0:N-1),max
double precision f(M), f_pr(M), rho(M),eps(M)
double precision b1(M,0:N-1),b2(M,0:N-1),b3(M,0:N-1)

Common/Data1/ Phi_ref,Cb,z,e,D,ik
Common/Data3/ lambda1,lambda2,mu1,mu2,alpha1,alpha2

do i=1,M
rho(i) = (dt/dx**2)*D(i)/D(2)
eps(i) = 0.5d0*e(i)/e(2)
enddo

C Current density functions are given by :
f1 = mu1*dexp(-alpha1*Phi(0,t))
f2 = -mu2*C2(0,t)*dexp(alpha2*Phi(0,t))

Note: Here we do not use a linearized form for f1 and f2.

f(1) = mu1*dexp(-alpha1*Phi_o(0))
f(2) = -mu2*C_o(2,0)*dexp(alpha2*Phi_o(0))
f(3) = 0.0d0
f(4) = 0.0d0

C Define ghost cell values for C_o and Phi_o : Cnl(i), Phinl

S1 = e(1)*f(1)/D(1) + e(2)*f(2)/D(2)
S2 = 0.0d0
do i=1,M
S2 = S2 + e(i)**2*C_o(i,0)
enddo

Phinl_o = Phi_o(1) + 2.0d0*e(2)*dx*S1/S2

do i=1,M
Cnl_o(i)=C_o(i,1)+2.0d0*eps(i)*C_o(i,0)*(Phi_o(i)-Phinl_o)
    # + 2.0d0*dx*f(i)/D(i)
enddo

C ** Calculate Peclet number. First, we need to calculate the derivative
of $\Phi$ wrt $x$ at each node, and find the maximum value.

$$d\Phi_{idx}(0)=0.5d0*(\Phi_o(1)-\Phi_{inl_o})/dx$$
$$d\Phi_{idx}(N-1)=0.5d0*(\Phi_{ref}-\Phi_o(N-2))/dx$$

do $j=1,N-2$
$$d\Phi_{idx}(j)=0.5d0*(\Phi_o(j+1)-\Phi_o(j-1))/dx$$
enddo

$$\text{max}=d\Phi_{idx}(0)$$

do $j=0,N-1$
if $(\text{abs}(d\Phi_{idx}(j)).ge.\text{abs}(\text{max}))$ then
$$\text{max}=d\Phi_{idx}(j)$$
endif
enddo

$$\text{Peclet}=2.0d0*\text{max}*dx$$

if ($\text{Peclet}.ge.2.0d0$) then
$$\text{write}(*,*)'\text{Peclet number exceeds 2.0'}$$
$$\text{write}(*,*)'\text{Peclet=}','\text{Peclet}$$
stop
endif

c--

do $i=1,M$
$$b1(i,0) = \rho(i)*(1.0d0 - \epsilon(i)*(\Phi_o(0)-\Phi_{inl_o}) )$$
$$b2(i,0) = 1.0d0 - 2.0d0*\rho(i) + \rho(i)*\epsilon(i)*$$
  # ( $\Phi_o(1) - 2.0d0*\Phi_o(0) + \Phi_{inl_o} )$
$$b3(i,0) = \rho(i)*(1.0d0 + \epsilon(i)*(\Phi_o(i)-\Phi_o(0)) )$$
enddo

do 120 $i=1,M$
  do 130 $j=1,N-1$
$$b1(i,j) = \rho(i)*(1.0d0 - \epsilon(i)*(\Phi_o(j)-\Phi_o(j-1)))$$
$$b2(i,j) = 1.0d0 - 2.0d0*\rho(i) + \rho(i)*\epsilon(i)*$$
  # ( $\Phi_o(j+1) - 2.0d0*\Phi_o(j) + \Phi_o(j-1) )$
$$b3(i,j) = \rho(i)*(1.0d0 + \epsilon(i)*(\Phi_o(j+1) - \Phi_o(j))$$
130 continue
120 continue

do $i=1,M$
$$C_{pr}(i,N) = C_{b}(i)$$
$$C_{pr}(i,0)=b1(i,0)*C_{nl_o}(i)+b2(i,0)*C_{o}(i,0)+$$
```fortran
Appendix

# b3(i,0)*C_o(i,1)
enddo

do 140 i=1,M
   do 150 j=1,N-1
      C_pr(i,j) = b1(i,j)*C_o(i,j-1) + b2(i,j)*C_o(i,j) +
      # b3(i,j)*C_o(i,j+1)
   150 continue
140 continue

RETURN
END

c**********************************************************************
Subroutine Initial(x,C_o, Phi_o)

c This subroutine calculates the initial concentrations and
potential distributions, given the value of ik.

implicit none

integer M,N,i,j

Parameter(M=4)
Parameter(N=20)

double precision z(M),e(M),D(M),Cb(M),ik,Phi_ref,x(0:N)
double precision C_o(M,0:N), Phi_o(0:N)
double precision eps(M),diff(M), N1, N2, Nt, alpha, rho,K, A1
```
**Appendix**

```fortran
double precision beta(3:M), lam(3:M), A(3:M), sigma(3:M)
double precision S1,S2,c1,c2

Common/Data1/ Phi_ref,Cb,z,e,D,ik

do i=1,M
   eps(i)=e(i)/e(2)
   diff(i)=D(i)/D(2)
enddo

N1 = -z(2)/z(1)*ik/diff(1)
N2 = ik/diff(2)
Nt = eps(1)*N1+eps(2)*N2
alpha = eps(1)*(1.0d0 - (N1/Nt)*(eps(1)-eps(2))

do i=3,M
   beta(i) = eps(i)*(eps(i)-eps(2))*Cb(i)*dexp(eps(i)*Phi_ref)
   lam(i) = (N1/Nt)*beta(i)*(alpha-eps(i))**(-1.0d0)
   A(i) = Cb(i)*dexp(eps(i)*Phi_ref)
   sigma(i) = (1.0d0/Nt)*(lam(i)*eps(1)*(eps(1)-eps(2)) + eps(i)*A(i)
#  *(eps(i)-eps(2)))
enddo

S1=0.0d0
do i=3,M
   S1= S1 + lam(i)*dexp((alpha-eps(i))*Phi_ref)
enddo

A1 = Cb(1)*dexp(alpha*Phi_ref) - S1
rho = (A1/Nt)*(eps(1)**2-eps(2))

S2 =0.0d0
do i=3,M
   S2 = S2 + (sigma(i)/eps(i))*dexp(-eps(i)*Phi_ref)
enddo

K = -(1.0d0 + (rho/alpha)*dexp(-alpha*Phi_ref) + S2)
c---------------------------------------------------------------
c Calculate the potential distribution, Phi_o(0:N)

do j=0,N
call Newt(M,x(j),eps,sigma,rho,alpha,K,Phi_o(j))
enddo
```

---

*Appendix* continues...
We now calculate the initial concentration distributions, using the potential distribution found above.

\[
\begin{align*}
\text{do } & 100 \ j = 0, N \\
\text{do } & i = 3, M \\
C_o(i, j) & = A(i) \cdot \exp(-\varepsilon(i) \cdot \Phi_o(j)) \\
\text{enddo} \\
cl & = 0.0d0 \\
\text{do } & i = 3, M \\
c1 & = c1 + \lambda(i) \cdot \exp(-\varepsilon(i) \cdot \Phi_o(j)) \\
\text{enddo} \\
C_o(1, j) & = A1 \cdot \exp(-\alpha \cdot \Phi_o(j)) + c1 \\
c2 & = 0.0d0 \\
\text{do } & i = 3, M \\
c2 & = c2 + \varepsilon(i) \cdot C_o(i, j) \\
\text{enddo} \\
C_o(2, j) & = -(1.0d0/\varepsilon(2)) \cdot (\varepsilon(1) \cdot C_o(1, j) + c2) \\
100 & \text{ continue} \\
\text{RETURN} \\
\text{END}
\end{align*}
\]

Subroutine Newt(M, y, eps, sigma, rho, alpha, K, Phi)

** implicit none

integer M, j
do double precision y, eps(M), sigma(3:M), rho, alpha, K, Phi, S1, S2

INTEGER i, IMAX
Parameter(IMAX=500)
do double precision x, xo, f, df, ddf, TOL, root, Conv
DIMENSION x(IMAX)

TOL=1.0D-4

C Initial guess obtained by linearizing the dexponential terms.
Appendix

S1 = 0.0d0
S2 = 0.0d0
do j=3,M
  S1 = S1 + sigma(j)/eps(j)
  S2 = S2 + sigma(j)
enddo

xo = (rho+S2)**(-1.0d0)*(y + rho/alpha + K + S1)

do 101 i=1,IMAX
  CALL FUNCD(M,y,rho,alpha,sigma,eps,K,xo,f,df,ddf)
  Conv = f*ddf/(df)**2
  if (dabs(Conv).ge.1.0d0) then
    Write(*,*),'Newtons Method Diverges'
    STOP
  endif
  x(i) = xo - (f/df)
  IF (dabs(xo-x(i)).lt.TOL) THEN
    root=x(i)
    GOTO 105
  ELSE
    xo=x(i)
  ENDIF
105 continue
101 continue

Phi=root
RETURN

END

c***********************************************************************
Subroutine FUNCD(M,y,rho,alpha,sigma,eps,K,xo,f,df,ddf)
implicit none
integer M,i
double precision g1,g2,g3,x,f,df,ddf
double precision eps(M), sigma(3:M)
double precision y,rho,alpha,K

g1=0.0d0
g2=0.0d0
g3=0.0d0
do i=3,M
  g1 = g1 + (sigma(i)/eps(i))*dexp(-eps(i)*x)
g2 = g2 + sigma(i)*dexp(-eps(i)*x)
\[ g_3 = g_3 + \varepsilon(i) \sigma(i) \exp(-\varepsilon(i)x) \]

\[ \text{endo} \]

\[ f = y + (\rho/\alpha) \exp(-\alpha x) + K + g_1 \]
\[ df = -\rho \exp(-\alpha x) - g_2 \]
\[ ddf = \alpha \rho \exp(-\alpha x) + g_3 \]

\[ \text{RETURN} \]
\[ \text{END} \]

```
SUBROUTINE DSID(SIDW,LSID,NROW,MSID,NSID,SIDET)
IMPLICIT DOUBLE PRECISION (A-H,0-Z)
DIMENSION SIDW(NROW,NSID),IFSID(1000),IGSID(1000),ILSID(1000)
SIDET=1.0D0
ISID1=MSID-1
ISIDR=NSID-MSID
IF(ISIDR.LT.0) GO TO 16
DO 1 KSID=1,MSID
   ILSID(KSID)=0
   IGSID(KSID)=KSID
   KSID1=1
   DO 8 KSID=1,MSID
      IF(LSID.GE.0) KSID1=KSID+1
      RSID=0.0D+0
      DO 2 ISID=1,MSID
         IF(ILSID(ISID).NE.0) GO TO 2
         WSID=SIDW(ISID,KSID)
         XSID=ABS(WSID)
         IF(RSID.GT.XSID) GO TO 2
         RSID=XSID
         KSID=KSID
      CONTINUE
      IFSID(KSID)=KSID
      ILSID(KSID)=KSID
      SIDET=SIDET*PSID
      IF(SIDET.EQ.0) GO TO 16
      XSID=1.0D+0/PSID
      DO 4 ISID=1,MSID
         IF(ISID.EQ.KSID) GO TO 3
         SIDW(ISID,KSID)=XSID
      CONTINUE
      3 SIDW(ISID,KSID)=-SIDW(ISID,KSID)*XSID
      4 CONTINUE
   8 CONTINUE
1 IFSID(KSID)=KSID
   KSID1=1
   DO 8 KSID=1,MSID
      IF(LSID.GE.0) KSID1=KSID+1
      RSID=0.0D+0
      DO 2 ISID=1,MSID
         IF(ILSID(ISID).NE.0) GO TO 2
         WSID=SIDW(ISID,KSID)
         XSID=ABS(WSID)
         IF(RSID.GT.XSID) GO TO 2
         RSID=XSID
         PSID=WSID
         KFSID=ISID
      CONTINUE
      IFSID(KSID)=KFSID
      ILSID(KSID)=KFSID
      SIDET=SIDET*PSID
      IF(SIDET.EQ.0) GO TO 16
      XSID=1.0D+0/PSID
      DO 4 ISID=1,MSID
         IF(ISID.EQ.KSID) GO TO 3
         SIDW(ISID,KSID)=XSID
      CONTINUE
      3 SIDW(ISID,KSID)=-SIDW(ISID,KSID)*XSID
      4 CONTINUE
```
Appendix

IF(KSID.LT.NSID) GO TO 8
DO 7 JSID=KSID1,NSID
IF(JSID.EQ.KSID) GO TO 7
WSID=SIDW(KFSID,JSID)
IF(WSID.EQ.0.0D+0) GO TO 7
DO 6 ISID=1,MSID
IF(ISID.NE.KFSID) GO TO 5
SIDW(ISID,JSID)=WSID*XSID
GO TO 6
5 SIDW(ISID,JSID)=SIDW(ISID,JSID)+WSID*SIDW(ISID,KSID)
6 CONTINUE
7 CONTINUE
8 CONTINUE
   DO 15 KSID=1,ISID1
   KFSID=IFSID(KSID)
   KLSID=ILSID(KFSID)
   KGSID=IGSID(KSID)
   IF(KFSID.EQ.KGSID) GO TO 15
   IF(LSID) 10,14,9
9 IF(ISIDR) 16,14,12
10 DO 11 ISID=1,MSID
   WSID=SIDW(ISID,KGSID)
   SIDW(ISID,KGSID)=SIDW(ISID,KFSID)
11 SIDW(ISID,KFSID)=WSID
12 DO 13 JSID=1,NSID
   WSID=SIDW(KLSID,JSID)
   SIDW(KLSID,JSID)=SIDW(KSID,JSID)
13 SIDW(KSID,JSID)=WSID
14 ILSID(KFSID)=KSID
   ILSID(KGSID)=KLSID
   IGSID(KLSID)=IGSID(KSID)
   IGSID(KSID)=KFSID
   SIDET=-SIDET
15 CONTINUE
16 RETURN
END
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