LIBRARY
University of Bahrain

MORPHOLOGICAL INSTABILITY IN ELECTRODEPOSITION

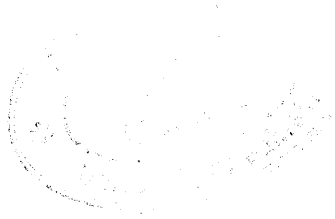
By

QAIS ABDULLATIF BUALI

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2004



Copyright 2004

by

QAIS ABDULLATIF BUALI

جامعة البحرين
المكتبة
LIBRARY
University of Bahrain

To my beloved family.

ACKNOWLEDGMENTS

The successful completion of this dissertation would have been impossible if not for the assistance and help I received from numerous people. First, I wish to express my gratefulness and deep gratitude to my advisors, Dr. Lewis E. Johns and Dr. Ranga Narayanan. Dr. Johns and Dr. Narayanan with their strong background and extensive knowledge in this field were always there to guide me through this work. I will always remember the inspiring and motivating discussions I have had with them. Their professional demeanor and sense of humor have made my graduate studies both highly educational and enjoyable.

I am thankful to the other members of my supervisory committee, Dr. Oscar Crisalle and Dr. Peter Zory, for their time and effort, and to the Chemical Engineering Department at the University of Florida for the excellent education they provided me throughout my graduate studies.

My family in Bahrain have been very supportive to me in all of my work and decisions, and I know I will never be able to repay everything that they have done to me.

This work was made possible by the heartfelt love and support of my wife, and the peaceful serenity of our son, Salman.

I would also like to thank my friend Mohamed for being a true brother that made me feel at home while studying in the United States. I would also like to thank my many friends in Bahrain for always being in touch for the years of my study.

Finally I gratefully acknowledge the University of Bahrain for its financial support in allowing me to pursue my educational goals within the United States of America.

TABLE OF CONTENTS

page

ACKNOWLEDGMENTS iv

LIST OF TABLES x

LIST OF FIGURES xii

LIST OF SYMBOLS xiv

ABSTRACT xvii

CHAPTER

1 INTRODUCTION AND PHYSICS OF THE PROBLEM 1

1.1 Introduction 1
1.2 Physics of Electrodeposition 2
1.3 Physics of the Instability 4

2 MATHEMATICAL MODELLING 13

2.1 The Nonlinear Equations 13
2.1.1 The Domain Equations 14
2.1.2 The Equations at the Electrode Surface: Boundary Conditions 17
2.1.3 Electrode Kinetics 23
2.2 The Nonlinear Equations Simplified by Local Electrical Neutrality 29
2.3 The Effect of Convection 34
2.4 Main Assumptions and Limitations 35

3 LINEAR STABILITY ANALYSIS OF THE CHEMICAL REACTION EQUILIBRIUM (CRE) MODEL 37

3.1 The Base Solution 39
3.1.1 Getting the Base Solution Using the B-V Equation 39
3.1.2 Getting the Base Solution Using the CRE Approximation 44
3.1.3 The Signs of $\frac{dc}{dy}$ and $\frac{d\phi}{dy}$ 47
3.2 The Perturbation Problem 47

3.2.1 The Input Variables to the Electrodeposition Problem 51
3.2.2 The Perturbation Equations at Fixed Values of L_0, $\bar{c}$ and $V^A - V^C$ 51
3.3 The Stability of the Base Solution when Current Passes Through the Cell 56
3.4 Putting the Solution in Terms of the Limiting Current $U_{\lim}$ 60
3.5 Results, Discussion and Comparison with Previous Work 62
3.5.1 Main Results and Discussion 64
3.5.2 Comparison with Previous Work 69
3.5.3 The Reason Why the CRE Turns to be a Good Approximation 74

4 CALCULATION OF THE GROWTH CONSTANT AND ITS APPROXIMATIONS 79

4.1 The Nonlinear Equations Obtained by Setting $c = \bar{c}$ in the Migration Term 81
4.2 The Base Solution 83
4.3 The Perturbation Problem 85
4.4 Solving the Eigenvalue Problem 88
4.5 Results and Discussion 93
4.5.1 The Effect of the Current on the σ vs. k^2 Relation 95
4.5.2 The Effect of the Distance Between the Electrodes on the σ vs. k^2 Relation 97
4.5.3 The Effect of the Average Ionic Concentration on the σ vs. k^2 Relation 100
4.6 The Effect of Dropping σ from the Domain Equation 103
4.6.1 Scaling the Electrodeposition Problem to Study the Importance of the Different Growth Constants 105
4.6.2 Getting σ Explicitly in Terms of k^2 by Setting $\sigma = 0$ on the Domain 109
4.6.3 Comparison Between the Results Obtained by Dropping and Keeping σ on the Domain 114
4.6.4 Explaining the Behavior of the σ vs. k^2 Relation 122

5 THE SOLUTION FOR THE GROWTH CONSTANT 130

5.1 The Nonlinear Equations 131
5.2 The Base Solution 132
5.3 The Perturbation Problem 134
5.4 The Stability of the Base Solution 136
5.5 Results and Discussion 146
5.5.1 Comparison of the Results in Chapters 4 and 5 147
5.5.1.1 The Comparison for Different Values of $U/U_{\lim}$ 147
5.5.1.2 The Comparison at Different Values of L_0 152
5.5.1.3 The Comparison for Different $\bar{c}$ 155
5.5.2 Comparison with Previous Work by S&B 158

6 WEAKLY NONLINEAR CALCULATIONS 164

6.1 The Nonlinear Equations 168
6.2 The Scaled Nonlinear Equations 170
6.3 The Weakly Nonlinear Calculations 172
6.3.1 The Base Solution 175
6.3.2 The Steady First Order Solution 177
6.3.3 The Second Order Problem 185
6.4 Drawing Inferences from the U vs. $V^A - V^C$ Relationship 195
6.5 Getting the Relation Between D_1 and U_2 198
6.6 Predicting the Behavior of the Total Current After Passing the Critical Voltage 200

7 THE DESIGN VARIABLES IN AN ELECTRODEPOSITION EXPERIMENT AND SOME CONCLUDING REMARKS ON THIS DISSERTATION 208

APPENDIX

A ANNOTATED BIBLIOGRAPHY 216

B DOMAIN PERTURBATIONS 229

B.1 The Expansion of a Domain Variable and Its Derivatives Along the Mapping 233
B.2 An Example on How to Use the Expansions of u and Its Derivatives 242
B.3 The Rule 244

C A SIMPLER PROBLEM TO SUPPORT THE (CRE) RESULTS 246

D HEAT FLUX THROUGH A ROD 250

E THE EXPANSION OF THE CURVATURE TO SECOND ORDER 257

F THE EXPANSION OF THE INTEGRAL CONDITIONS TO SECOND ORDER 260

G CALCULATING THE DETERMINANT FROM THE NONLINEAR PROBLEM 264

H WEAKLY NONLINEAR CALCULATIONS WITHOUT THE APPLICATION OF THE MIGRATION TERM APPROXIMATION 266

H.1 The Nonlinear Equations 266
H.2 The Scaled Nonlinear Equations 267
H.3 The Base Solution 268

H.4 The First Order Problem 269
H.5 The Second Order Problem 271

LIST OF REFERENCES 277

BIOGRAPHICAL SKETCH 279

LIST OF TABLES

Table page

3-1. Data for the copper/copper sulphate system. 63

7-1. Calculated critical voltages and critical output currents at different input conditions. 210

D-1. The effect of dropping the decay constant from the domain equation for the rod problem. 255

LIST OF FIGURES

Figure page

1-1. Schematic of an electrochemical cell. 2

1-2. Fingerlike deposits on the cathode after a long time of unstable operation of electrodeposition process. 4

1-3. The potential and the concentration gradients after a voltage drop is applied across the anode and the cathode. 5

1-4. The potential and the concentration gradients after introducing bumps to the anode and the cathode surfaces. 6

1-5. Physics of the instability. 7

2-1. Important variables and formulas associated with the surfaces. 19

2-2. Explaining the contribution of different terms in equation (2.20) for the total current. 22

2-3. The effect of the electrical potential on the extent of the oxidation and reduction reactions. 25

2-4. The effect of surface curvature on the reaction rates at both electrodes. 26

2-5. Explaining the equilibrium situation. 27

3-1. The Perturbed Surface. 49

3-2. As $V^A - V^C$ or U/U_{lim} increases, the critical wave number increases and the stable region is reduced. 65

3-3. The effect of U/U_{lim} on the critical wave number for different electrode spacing. 66

3-4. The effect of U/U_{lim} on the critical wave number for different average ionic concentrations. 68

3-5. Comparison of the (CRE) model with the model by Sundström and Bark. 70

3-6. The agreement of the (CRE) model with the results by Johns and Narayanan for large electrode spacing, L_0 72

3-7. Excellent agreement with Johns and Narayanan for higher L_0 and lower average electrolytic concentration. 73

4-1. σ vs. k^2 relation for small values of U/U_{lim} 96

4-2. σ vs. k^2 relation for larger values of U/U_{lim} 98

4-3. σ vs. k^2 relation for different values of electrode spacing. 99

4-4. σ vs. k^2 relation for smaller values of electrode spacing. 101

4-5. σ vs. k^2 relation for different values of average ionic concentration. 102

4-6. σ vs. k^2 relation for larger values of average ionic concentration. 104

4-7. Effect of dropping σ from the domain at $U/U_{\text{lim}} = 0.3$ 115

4-8. Effect of dropping σ from the domain at $U/U_{\text{lim}} = 0.5$ 116

4-9. Effect of dropping σ from the domain at $U/U_{\text{lim}} = 0.9$ 117

4-10. Effect of dropping σ from the domain for smaller electrode spacing. 118

4-11. Effect of dropping σ from the domain for $\overline{c} = 0.1$ kg-mole/m^3 119

4-12. Effect of dropping σ from the domain for $\overline{c} = 1.0$ kg-mole/m^3 120

4-13. Effect of dropping σ from the domain for $\overline{c} = 10$ kg-mole/m^3 121

4-14. The relation between σ and k^2 from equations (4.53), (4.61) and (4.62). 127

5-1. Evaluation of the approximation at $U/U_{\text{lim}} = 0.1$. 148

5-2. Evaluation of the approximation at $U/U_{\text{lim}} = 0.3$ 149

5-3. Evaluation of the approximation at $U/U_{\text{lim}} = 0.5$ 150

5-4. Evaluation of the approximation at $L_0 = 0.005$ m. 153

5-5. Evaluation of the approximation at $L_0 = 0.002$ m. 154

5-6. Evaluation of the approximation at $\overline{c} = 0.01$ kg-mole/m^3. 156

5-7. Evaluation of the approximation at $\overline{c} = 0.005$ kg-mole/m^3. 157

5-8. Contours of the non-dimensional growth constant given by S&B. 159

5-9. Results obtained by our approach for three different values of the scaled growth constant. 161

6-1. The effect of changing L_0 on U. 205

6-2. The expected current vs. voltage relation in an experiment. 206

7-1. Schematic of an electrodeposition cell. 213

B-1. The mapping of D_0 into D_ε. 231

C-1. Configuration of the simpler problem where the reaction $A \rightleftarrows B$ takes place on the right, fed by a reservoir of pure A through a film of thickness l. 246

D-1. Configuration of the heat flux through a rod problem. 250

LIST OF SYMBOLS

c Concentration, kg-mole/m^3.

$\bar{c}$ Average concentration of the electrolytic solution, kg-mole/m^3.

c_M Molar density of the metal, kg-mole/m^3.

D_1 Diffusion coefficient of species 1, m^2/sec.

D_2 Diffusion coefficient of species 2, m^2/sec.

e^- Electronic charge, A$\cdot$sec.

F Faraday constant, A$\cdot$sec/kg-mole.

$2H$ Curvature of the surface, 1/m.

$\vec{i}$ Electrical current density in the solution, A/m^2.

i_0 Exchange current density, A/m^2.

I Total current in the electrochemical cell, A.

k Wave number, 1/m.

$\vec{k}$ Forward chemical rate constant.

$\overleftarrow{k}$ Backward chemical rate constant.

L_0 Distance between electrodes, m.

M Metal atom.

M^{z_1+} Metal ion.

$\vec{N}_1$ Molar current density of species 1, kg-mole/m$^2\cdot$sec.

$\vec{N}_2$ Molar current density of species 2, kg-mole/$m^2 \cdot$ sec.

R Gas constant, J/kg-mol $\cdot$ K.

S Surface, m^2.

t Time, sec.

T Temperature, K.

u Local velocity of electrode surfaces, m/sec.

u_i Mobility of ionic species, $m^2 \cdot$ kg-mole / J $\cdot$ sec.

U Velocity of electrode surfaces, m/sec.

U_{lim} Limiting velocity of electrode surface, m/sec.

$\vec{v}$ Fluid molar average velocity, m/sec.

V Electrical potential at an electrode, V.

W Wronskian.

W_0 Width of the electrochemical cell, m.

z_1 Charge number of species 1.

z_2 Charge number of species 2.

Greek Symbols

β Factor describing the activation step.

γ Surface tension, J/m^2.

ρ Density, kg/m^3.

ρ_M Mass density of the metal, kg/m^3.

σ Eigenvalue or growth constant, 1/sec.

ϕ Electrical potential at a point in the electrolytic solution, V.

$\Delta\phi$ Difference between electrical potential at metal and solution, V.

$\Delta\phi_{EQ}$ Equilibrium electrical potential difference, V.

Subscripts

c Critical.

EQ Equilibrium.

lim Limiting.

M Metal.

Superscripts

A Anode.

C Cathode.

Abbreviations

B-V Butler-Volmer.

CRE Chemical reaction equilibrium.

J&N Johns and Narayanan.

P&F Pritzker and Fahidy.

S&B Sundström and Bark.

Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

MORPHOLOGICAL INSTABILITY IN ELECTRODEPOSITION

By

Qais Abdullatif Buali

December 2004

Chair: Lewis E. Johns
Major Department: Chemical Engineering

This work focuses on the morphological instability of moving fronts. The stability of electrode surfaces during an electrodeposition process has been considered as an example. We have shown that the physics of the instability is due to reinforced concentration and electrical potential gradients at the cathode generating the instability there. The anode, on the other hand, retains a stable planar morphology.

It has been found that increasing the voltage drop between the electrodes or the average ionic concentration will shift the electrolytic cell more towards the instability. Conversely, increasing the distance between the electrodes will work in favor of stabilizing the electrodeposition process.

We have also shown theoretically that once the electrodes lose their planar shape, the velocity of the surfaces and consequently the measured current will drop in relation to the predicted base value. It should not have been possible to obtain this conclusion without the application of two important restrictions, namely constant volume and constant average concentration of electrolytic solution.

Through this dissertation three main approximations were introduced. The first approximation is one of chemical reaction equilibrium which implies that reactions are assumed to take place fast compared to the transport processes of diffusion and migration. The second important approximation was to assume that the concentration is the same as the average ionic concentration as far as the migration is concerned. The last approximation was that the dynamic change of concentration is subservient to the dynamic change due to transport arising from the movement of the boundary. These approximations simplify the model greatly and proved to be valid under reasonable conditions.

The design parameters of an electrodeposition cell are also calculated where the dimensions of the cell are suggested in addition to the predicted values of the voltage drop and the current at which the instability might take place.

It is recommended that the findings of this work be linked to other moving front instabilities such as those that take place in solidification, precipitation and viscous fingering and to see what these instabilities have in common and in what aspects they might differ.

CHAPTER 1
INTRODUCTION AND PHYSICS OF THE PROBLEM

1.1 Introduction

This dissertation is concerned with patterns that occur during the motion of phase boundaries. Electrodeposition is one process where patterns often form on electrode surfaces and it will be the focus of our attention.

During electrodeposition, metal ions are released from a metal surface, the anode- in contact with an ionic solution, and are deposited at a second metal surface also in contact with the solution-the cathode. The release and the deposition of the ions are caused by chemical reactions involving the transfer of electrons. Hence the direction of these electron transfer reactions is determined in part by the electrostatic potential difference between the metal and the nearby solution. To cause the ions to leave a metal surface and enter the solution, a positive potential difference is required. To make an electrodeposition process take place, an overall electrical potential difference must be imposed between the two metal surfaces, the anode and the cathode.

The problems of interest to us in electrodeposition have to do with the reactions at the electrodes, the geometry of the surfaces of the anode and the cathode and the process by which charged species are transported from one place to another. It is important to emphasize here that the main objective of this work is to study what happens at electrodes as it relates to transport phenomena and reaction kinetics. Electrodeposition was picked as a nice example in which these effects on the stability of the system can be

visualized. The purpose of this work is not to study electrochemistry, but to use it as a tool to understand important issues related to interfacial instability.

Understanding how the electrodeposition process occurs is an important task and it is to this that we now turn.

1.2 Physics of Electrodeposition

Electrodeposition takes place in what is known as an electrochemical cell which is shown in Figure 1-1. In its simplest configuration, an electrochemical cell ordinarily consists of two metals (electrodes) held at different voltages dipped into a common electrolytic solution. One of these electrodes dissolves in the solution producing metal ions that cross the electrolytic solution. These ions then plate out on the other electrode which, therefore, grows.

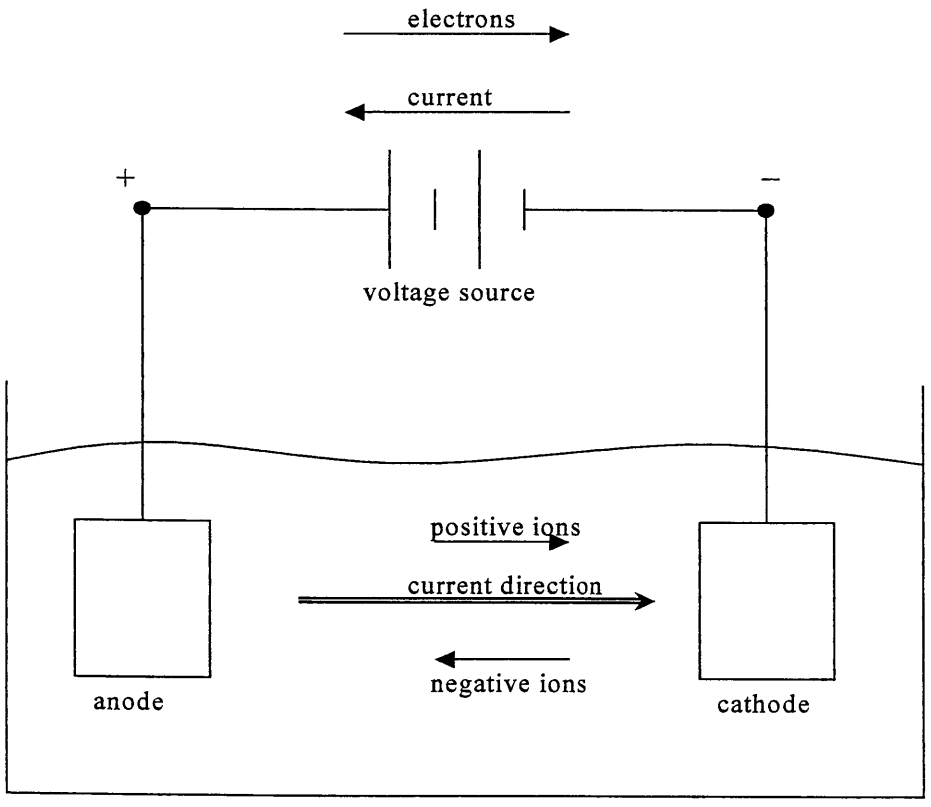


Figure 1-1. Schematic of an electrochemical cell.

Now metal ions are released at the anode on account of an oxidation reaction there. The reaction causes the release of electrons. It is depicted by

$$M \rightarrow M^{z_1+} + z_1 e^-$$

The electrons move through the connecting wires from the dissolving anode to the growing cathode. Meanwhile, the ions traverse the solution by way of diffusion and migration and combine with the electrons at the cathode to become "plated metal" via the reduction reaction

$$M^{z_1+} + z_1 e^- \rightarrow M$$

The current passing through the electrolytic solution is carried by the ions moving from the anode to the cathode and the counter ions moving in the other direction. To complete the circuit, the current passes through the wires, from the cathode to the anode.

It has been observed that the electrodes, namely the anode and the cathode, typically do not always remain planar during an electrodeposition process; instead there is a certain voltage drop at which the growth of the cathode is not uniform across its width. This voltage drop and the wavelength of the wiggly surface that corresponds to it are called respectively the critical voltage and the critical wavelength.

Now we are interested in such problems because the wavy shapes are not desired in most applications where smooth film surfaces are required. Moreover, these wavy shapes can grow to the point that dendrites result and these dendrites can then cause the cathode and the anode to touch each other; this will cause a short-circuit. Figure 1-2 shows the shape of such deposits obtained after a long period of time. If our aim is to avoid this situation, we need to understand this problem better. So one of our objectives will be to find the critical conditions at which the growth of the deposits goes from being uniform

and steady to non-uniform either steady or unsteady. The reasons for getting non-planar surfaces, as the electrodeposition process advances with time, are explained in the next section where the physics of the instability is discussed.

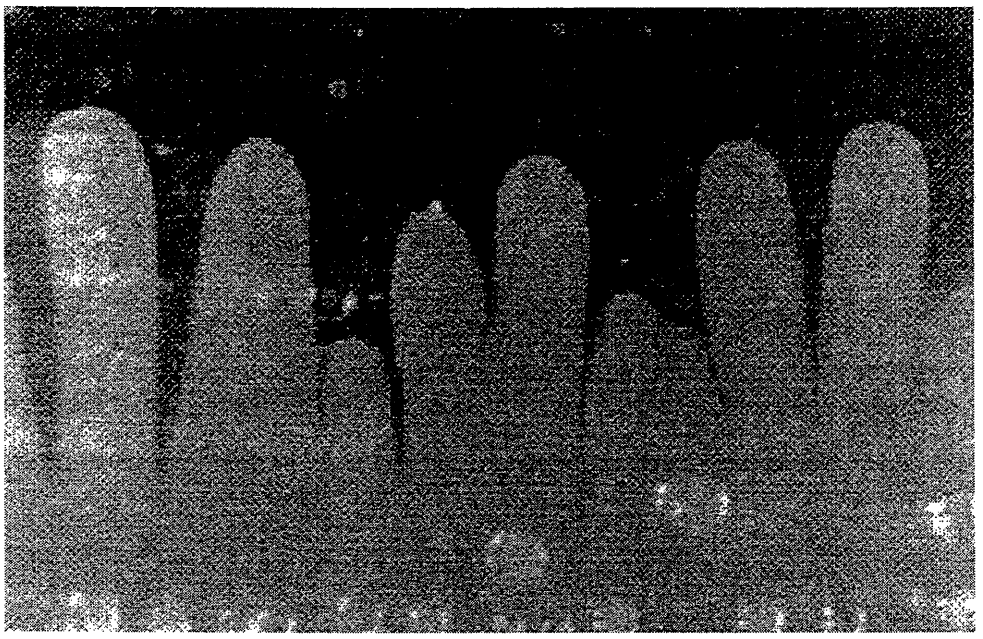


Figure 1-2. Fingerlike deposits on the cathode after a long time of unstable operation of electrodeposition process (López-Salvans *et al.*, 1996).

1.3 Physics of the Instability

When an electrochemical cell is in equilibrium and is not connected to a voltage source, there will be no oxidation or reduction reactions taking place, and the voltage at the electrodes will be the same but the voltage in the solution, while uniform, may differ. When a voltage source is connected, the voltage at the anode and at the cathode will differ and a voltage drop will take place across the solution.

Once a voltage drop is imposed across the electrodes leading to a voltage gradient in the electrolytic solution, there is going to be a metal ion gradient in the solution as well, as the ions traverse the solution from one electrode to the other. Now both oxidation and reduction take place at both electrodes but which reaction is favored depends on the

potential drop between the metal and the solution. Figure 1-3 depicts the cell after a voltage drop is applied across the anode and the cathode. In Figure 1-3, the electrical potential at the anode, V^A, is higher than the electrical potential at the cathode, V^C, which causes a potential gradient through the solution. In the solution, ϕ and $c_{M^{z_1+}}$ is used to represent the electrical potential and the concentration of the metal ion respectively. Their gradients help to move the metallic ions from the anode, where they are supplied, to the cathode, where they are plated out.

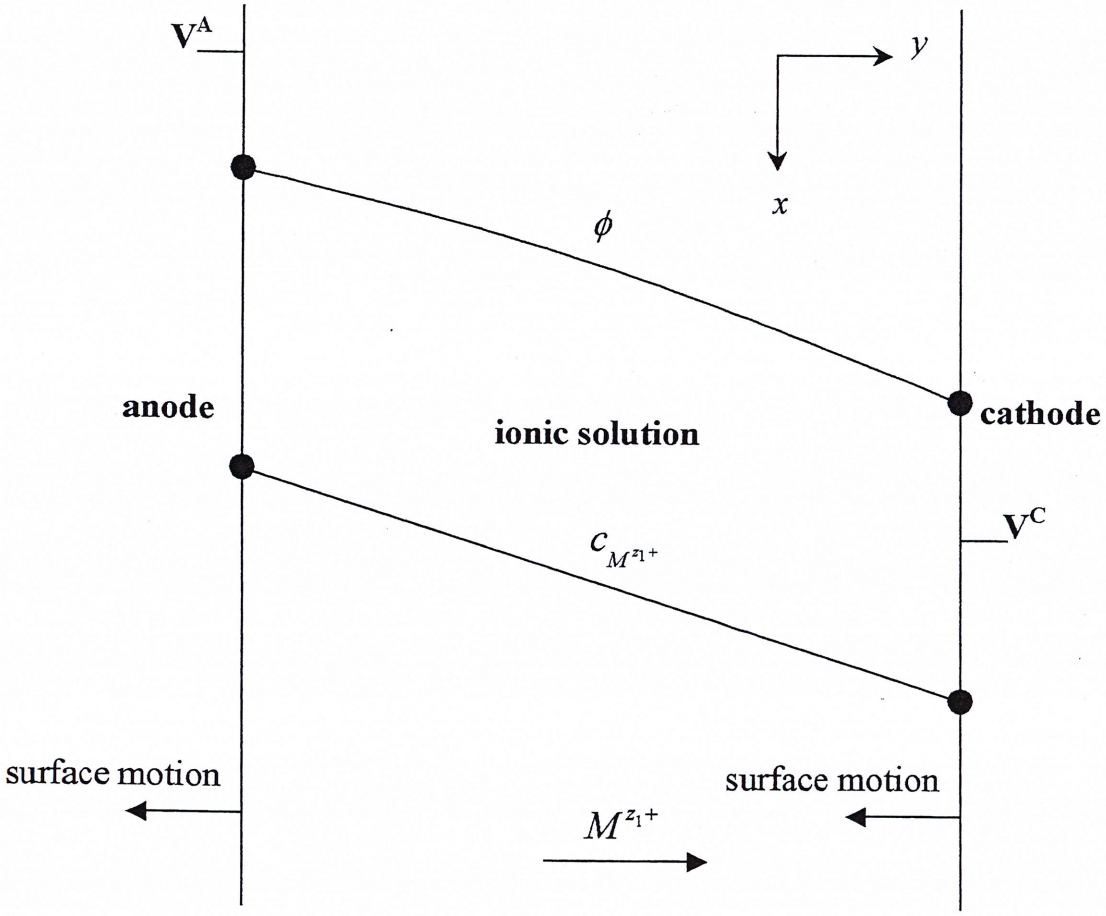


Figure 1-3. The potential and the concentration gradients after a voltage drop is applied across the anode and the cathode.

To decide whether a planar electrode ought to remain planar after a voltage drop is applied across the cell, introduce a bump, a small displacement, and try to determine if a

displacement is reinforced. If so, the planar surface is unstable. Figure 1-4 depicts the two electrodes when such bumps are introduced. Let us now consider the following argument which leads to the conclusion that under all conditions the cathode is a source of instability to at least some disturbances.

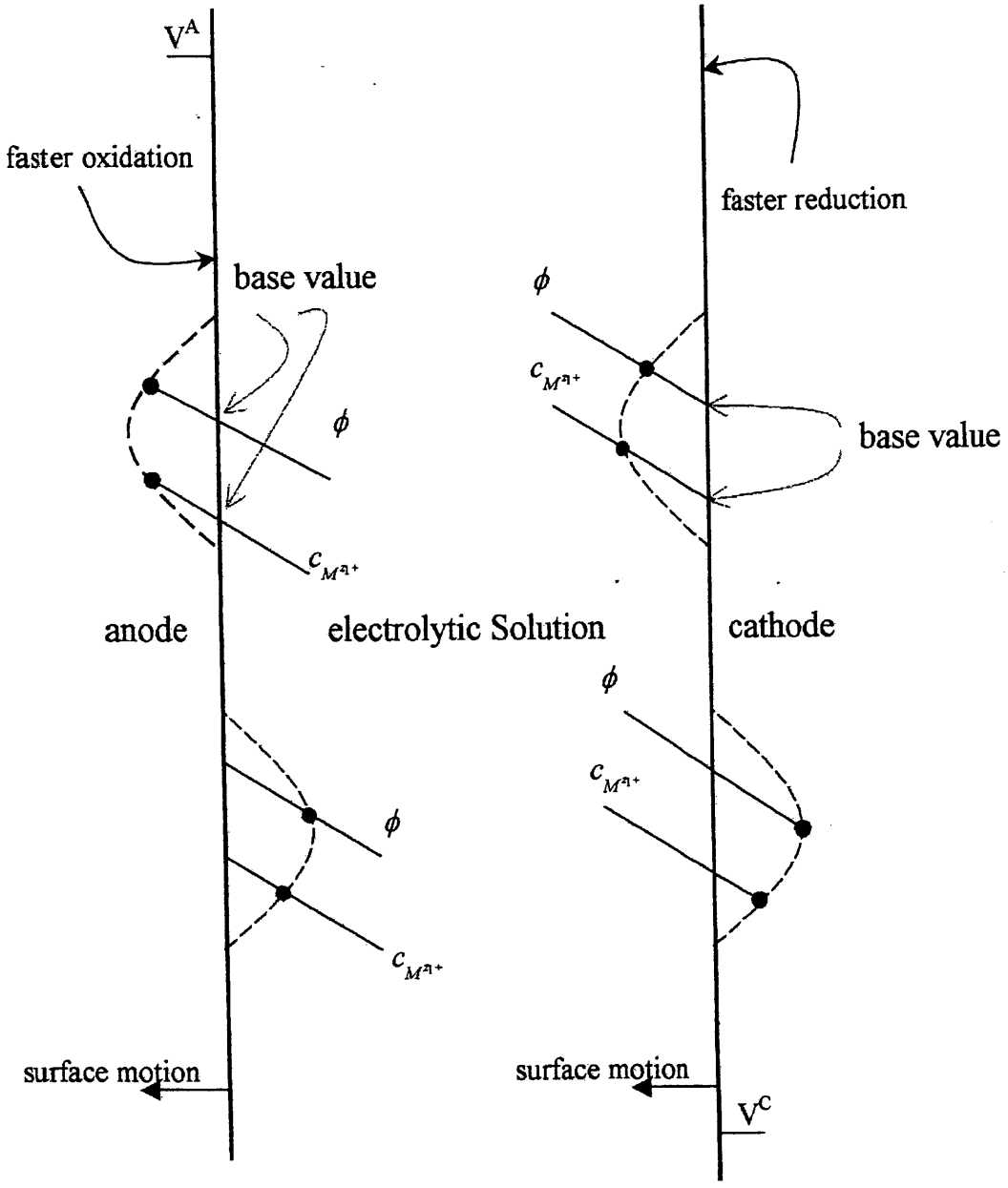


Figure 1-4. The potential and the concentration gradients after introducing bumps to the anode and the cathode surfaces.

Refer to Figure 1-4 and notice that both oxidation and reduction reactions take place at the anode and at the cathode. However, the oxidation reaction is predominant at the anode while the reduction reaction is predominant at the cathode. By these reactions, the surfaces of the two electrodes will appear to move in the same direction, to the left; however, the anode dissolves while the cathode grows.

Now Figure 1-5 is an excerpt from Figure 1-4 that shows a trough at the anode and a crest at the cathode with a potential gradient through the solution. Crests are defined as projections into the solution, troughs as projections into the solid. We will limit our discussion in this figure and consider the effect of the electrical potential on the rates of the oxidation-reduction reaction; however, similar arguments concerning ion concentration gradients will lead to the same conclusion and will do so even if a crest at the anode and a trough at the cathode are considered.

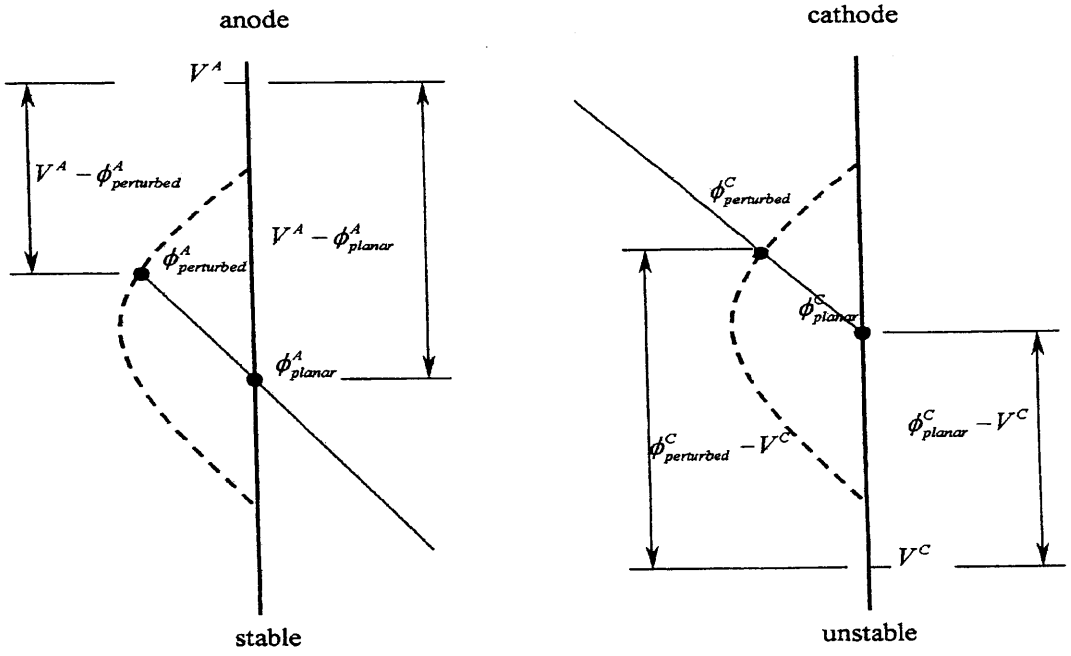


Figure 1-5. Physics of the instability.

In Figure 1-5, ϕ^A_{planar} is the potential at the solution adjacent to the anode before a bump is given, $\phi^A_{perturbed}$ is the potential at the solution adjacent to the anode after perturbing the surface (i.e., giving a bump to the anode) ϕ^C_{planar} is the potential at the solution adjacent to the cathode before a bump is given and $\phi^C_{perturbed}$ is the potential at the solution adjacent to the cathode after perturbing the surface (i.e., giving a bump to the cathode).

By looking at the anode in Figure 1-5, our sketch indicates that the perturbation causes the voltage difference, $V^A - \phi^A_{planar}$, at the planar surface to be reduced (i.e., to the voltage difference, $V^A - \phi^A_{perturbed}$) at the perturbed surface. This means that the electrical force causing ions to leave the planar surface is greater than that at the wavy one. As a result, the oxidation reaction will run slower at the perturbed surface than at the flat surface; hence the planar surface will dissolve faster and finally it will catch-up with the perturbed surface whence the bump disappears and the anode would appear to be stable to surface displacements.

Let us now draw our attention to the cathode to see if something interesting happens there. By looking at Figure 1-5 again, it is clear that $\phi^C_{perturbed} - V^C$ is larger than $\phi^C_{planar} - V^C$. This implies that the reduction reaction is faster at the perturbed surface than it is at the flat surface, building up the crest more and more. Consequently, the flat surface will always lag the perturbed surface with the bump growing larger and the cathode losing its planarity and becoming unstable and what is also important, these arguments based on the rates of the chemical reactions hold no matter what the lateral extent of the perturbations and hence the wavelengths.

In conclusion, the picture argument tells us that surface perturbations to the anode ought to die out, preserving for the anode its planar surface. The anode is therefore considered to be stable to small perturbations. On the other hand, the cathode would appear to be unstable to small surface disturbances. In fact surface tension is stabilizing but its strength depends on the wavelength of the displacement. As will be seen later, the role of surface curvature is to stabilize the interfaces. It reinforces the stability of the anode but opposes the instability of the cathode.

We are interested in what makes the electrodeposition process unstable. There are a number of researchers who have tried to determine when the electrodes will lose their planar surfaces. These people became interested in this problem after the work of Mullins and Sekerka (1963, 1964) on solidification and most of them will refer to Mullins and Sekerka and claim that they are following their approach in determining the instability and the shapes of the surfaces. There are a lot of researchers who have done their calculations with one electrode such as Aogaki *et al.* (1980), Aogaki and Makino (1981), Landau (1982), Barkey *et al.* (1989b), Chen and Jorne (1991) and Pritzker and Fahidy (1992). We will discuss Pritzker and Fahidy in more detail in Appendix A because their work is related to ours. Sundström and Bark (1995) used two electrodes in their model and this has the advantage of introducing the constant volume condition to the problem, an assumption which is not available in the model with one electrode. One objective of this work will be to design a sensible experiment and see what a person might detect once the instability takes place. Researchers have done experiments and some of the experimental results seem to confirm our predictions. For more information regarding the

work in this area, the reader can check the annotated bibliography given in Appendix A where we discuss these papers in some detail.

The organization of this dissertation will be as follows. Chapter 2 will set the foundations for the rest of the work by presenting a model for the electrodeposition problem along with some important assumptions that are going to be applied all through this work. Following that will be chapter 3 where a base solution for the model will be found, then an approximation called chemical reaction equilibrium (CRE) will be utilized to simplify the equation that models the electrode reactions. This approximation will serve two purposes. First, it will simplify the base solution of the problem. Second, it will simplify the algebra of the model for the subsequent calculations. In this chapter critical conditions will be found and results obtained using the CRE approximation will be validated by comparison with previous work.

In chapter 4 a new approximation that will simplify the modeling of the transport processes will be introduced. Using this approximation will enable us to calculate the growth constants of the perturbations analytically. In addition, the effect of neglecting the growth constants in the domain will be studied and it will be shown that domain perturbations can be ignored without affecting the precision of the results. Even with these two approximations, the effect of different variables of the problem cannot be traced due to the complexity of the results. So the approximations introduced in this chapter will be coupled with the CRE approximation in order to simplify the problem even more so we can then understand the behavior of the results.

Chapter 5 will serve two main purposes. First, the results of the approximation in chapter 4 will be validated by comparison with the results of chapter 5, where the

problem is solved without any approximations. Second, previous results obtained numerically by Sundström and Bark (1995) will also be checked out.

All the approximations introduced earlier, which will be proven to be good, will be applied in chapter 6. This chapter is concerned with what we might see when running an experiment. While the calculations in chapter 3 were done to decide what is the critical wavelength for any value of the control variable, chapter 6 calculations will show, in a physical cell, how to find the critical value of the control variable.

Whatever we decide our control variable is, we are going to find its critical value; then we are going to worry about increasing the control variable beyond the critical point. So when running an electrodeposition experiment and if we choose the voltage drop to be the control variable and its value is set, then the easiest thing to measure will be the total current passing through an ammeter. Then we will try to decide what we ought to see beyond the critical point when the electrodes lose their planarity.

It is very important to indicate that all the approximations introduced earlier in chapters 3 and 4 were mainly introduced to simplify the model so we can go with our calculations beyond the critical point where every bit of simplification of the equations is needed due to the complexity of the calculations. Stating that, one will know the real purpose of introducing such approximations instead of wondering why we keep on presenting one approximation after another, then showing that we are able to find the solution without utilizing the approximations introduced as was done in chapter 5.

While this dissertation does not have to do with running an experiment, it does have a lot to do with the design of an experiment. We will conclude in the last chapter,

chapter 7, by designing an electrochemical cell where a person will be able to predict when the instability might occur.

So our first job is to present a model for the electrodeposition problem and to show what are the main assumptions that this model is based on. This will be the topic of chapter 2.

CHAPTER 2
MATHEMATICAL MODELLING

This chapter will lay down the foundation for a model describing an electrodeposition process. The following chapters will refer to this one as additional approximations are introduced. The equations describing different processes occurring either in the electrolytic solution or at the electrode-solution interface will be given. These equations will be simplified by applying an approximation called local electrical neutrality. The electrode kinetics will then be discussed in detail. Finally, the limitations and main assumptions of the model for the electrodeposition process will be presented.

It is of great importance at this stage to draw the reader's attention to the fact that the problem we are focusing on is one with only two ions and no supporting electrolyte. We begin our work by presenting the nonlinear equations describing the physics.

2.1 The Nonlinear Equations

In this dissertation, we are interested mainly in the transition that occurs when a control variable is changed and a planar surface turns non planar. Now there may be many control variables in this problem. One possible control variable might be the distance between the electrodes. Another control variable might be the average ionic concentration of the solution. But a more suitable control variable is the voltage drop across the cell and we hypothesize that as this control variable (i.e., the voltage difference) is changed, holding the distance and the average concentration fixed, the system acquires the possibility that it can exist in more than one state. The first state is the flat state; the second state is a wavy state.

A steady state movement of the anode and the cathode cannot be achieved unless the electrodes are moving at the same constant velocity and in the same direction and viewed by an observer participating in this uniform motion. Hence all the work in this dissertation will be carried in a moving frame in uniform translation, at a velocity denoted $\vec{U}$, vis-à-vis a laboratory observer. The moving observer sets the origin of the coordinate system on the surface of the anode; the cathode is at a distance L_0 from the anode.

The nonlinear equations can be classified into two types. First, the equations that describe the phenomena occurring in the bulk of the electrolytic solution (i.e., the domain equations) and second, the boundary equations, which are valid at the electrode-electrolytic solution interface. The example that we will use for purposes of discussion throughout the dissertation is that of two copper electrodes in a solution of copper sulphate dissolved in water. Then species 1 refers to copper ions, species 2 refers to sulphate ions and the solvent will be water. We start by discussing the domain equations.

2.1.1 The Domain Equations

Throughout the ionic solution, salt dissociates completely into ions and no reactions take place there. We will only consider two ionic species in our model. The first equation that is valid on the domain is

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \vec{N}_i = 0 \ , \quad i = 1,2 \tag{2.1}$$

where c_i, $i = 1,\ 2$ denote the molar densities of the metal ion and the non-metallic ion and $\vec{N}_i$ denotes the molar current density of species i in the solution.

The molar current density of the dissolved species in the electrolytic solution is given by

$$\vec{N}_i = -D_i \nabla c_i - z_i F u_i c_i \nabla \phi + c_i \vec{v} \tag{2.2}$$

where D_i stands for the diffusion coefficient, $|z_i|$ denotes the number of equivalents per mole, F denotes Faraday's constant, u_i is the mobility of ionic species and $\vec{v}$ is the fluid molar average velocity.

The first term on the right hand side of equation (2.2) represents the diffusion effect, the second stands for migration and the last represents the effect of convection. Diffusion occurs under the influence of a concentration gradient. Migration occurs under the influence of an electric field (a gradient of electrical potential). And convection occurs in the presence of density gradients or density differences at a phase boundary, as in the electrodeposition problem.

The work in this dissertation is done on the basis that the electrolytic solution is dilute. In dilute solutions, the mobility of ionic species is related to the diffusion coefficient by the Nernst-Einstein relation (i.e., $u_i = \frac{D_i}{RT}$) where R and T stand for the gas constant and the temperature of the solution respectively and D_i is to be taken independent of ion concentration. Making use of the dilute solution assumption will turn equation (2.2) into

$$\vec{N}_i = -D_i \nabla c_i - \frac{z_i F}{RT} D_i c_i \nabla \phi + c_i \vec{v} \tag{2.3}$$

It is interesting to notice that when steady state is achieved inside the electrochemical cell, there is no transport of sulphate ions, as only the cupric ions react at the electrodes. Migration will drive the negative sulphate ions towards the left to the

positive electrode (anode). This tendency of migration will be opposed by the tendency of diffusion towards the right. As a result a balance between the effect of migration and diffusion will be achieved for the sulphate ions. On the other hand, migration will move the positive cupric ions towards the right (i.e., towards the cathode). In addition to the migration effect, the diffusion tendency is also towards the right; thus both migration and diffusion move cupric ions in the same direction and these ions will carry all the current from the anode to the cathode (Newman, 1991).

Another equation that is valid on the domain is the conservation of mass equation which can be expressed as

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \vec{v}) \tag{2.4}$$

and for constant density, equation (2.4) simplifies to

$$\nabla \cdot \vec{v} = 0 \tag{2.5}$$

The last equation tells us that the electrical current density is due to the motion of charged species (i.e., it is the sum of the flux of charged species multiplied by its charge per mole) and is denoted by $\vec{i}$, where

$$\vec{i} = \sum F z_i \vec{N}_i \tag{2.6}$$

and where the absolute value of z_i tells us, for species i, the number of equivalents per mole and hence $z_i F$ is the charge per mole carried by species i and where $\vec{N}_i$ denotes the mole current density of species i in the solution as was mentioned above.

The above equations, (2.1)-(2.6), are the domain equations that hold in the electrolytic solution. Let us now turn to the second type of equations governing the

electrodeposition process, namely the equations at the electrode-electrolytic solution interface or the boundary conditions.

2.1.2 The Equations at the Electrode Surface: Boundary Conditions

This section will be concerned with the boundary conditions that are valid on both electrodes. But before writing the equations at the boundary let us define the main variables that are associated with the surface conditions. For simplicity, a two-dimensional problem is considered. The main variables that describe the surface are the surface normal, the surface local velocity and the curvature of the surface. It is important to define these surface variables early along as they will appear in most of the equations to come. A surface will be denoted by $y = f(x,t)$. The normals will always be taken to point out of the metal into the solution, and at the anode the expression for the normal is

$$\vec{n}^A = \frac{-f_x^A \vec{i} + \vec{j}}{\left[\left(f_x^A\right)^2 + 1\right]^{1/2}} \tag{2.7}$$

while at the cathode it is

$$\vec{n}^C = \frac{f_x^C \vec{i} - \vec{j}}{\left[\left(f_x^C\right)^2 + 1\right]^{1/2}} \tag{2.8}$$

where the superscripts A and C in the above equations and all the equations to come stand for anode and cathode respectively. Moreover, $\vec{j}$ always points from the anode to the cathode. The expressions for the normal component of velocity at the anode and the cathode respectively are

$$u^A = \frac{f_t^A}{\left[\left(f_x^A\right)^2 + 1\right]^{1/2}} \tag{2.9}$$

and

$$u^C = \frac{-f_t^C}{\left[\left(f_x^C\right)^2 + 1\right]^{1/2}} \tag{2.10}$$

where u^A ought to be positive and u^C ought to be negative.

The mean curvature of the surface is defined so that it is positive at a trough, where the solution protrudes into the electrode, and negative at a crest, where the electrode protrudes in the solution. The mean curvature at the anode is

$$2H^A = \frac{f_{xx}^A}{\left[\left(f_x^A\right)^2 + 1\right]^{3/2}} \tag{2.11}$$

and at the cathode

$$2H^C = \frac{-f_{xx}^C}{\left[\left(f_x^C\right)^2 + 1\right]^{3/2}} \tag{2.12}$$

In equations (2.7)-(2.12), f_x and f_{xx} stand for the first and second derivatives of f with respect to x. And f_t stands for the first derivative of f with respect to time. Figure 2-1 shows by a picture what the surface variables stand for and what some of the equations involving these variables are.

Having defined the important surface variables, we now write the equations that serve as boundary conditions at a surface. The first set of these equations express conservation conditions across a surface and they are

$$\left[\vec{n}\cdot\left[\vec{N}_1 - c_1\vec{u}\right]\right]^{metal} - \left[\vec{n}\cdot\left[\vec{N}_1 - c_1\vec{u}\right]\right]^{solution} = 0 \tag{2.13}$$

and

$$\left[\vec{n}\cdot\left[\vec{N}_2 - c_2\vec{u}\right]\right]^{metal} - \left[\vec{n}\cdot\left[\vec{N}_2 - c_2\vec{u}\right]\right]^{solution} = 0 \tag{2.14}$$

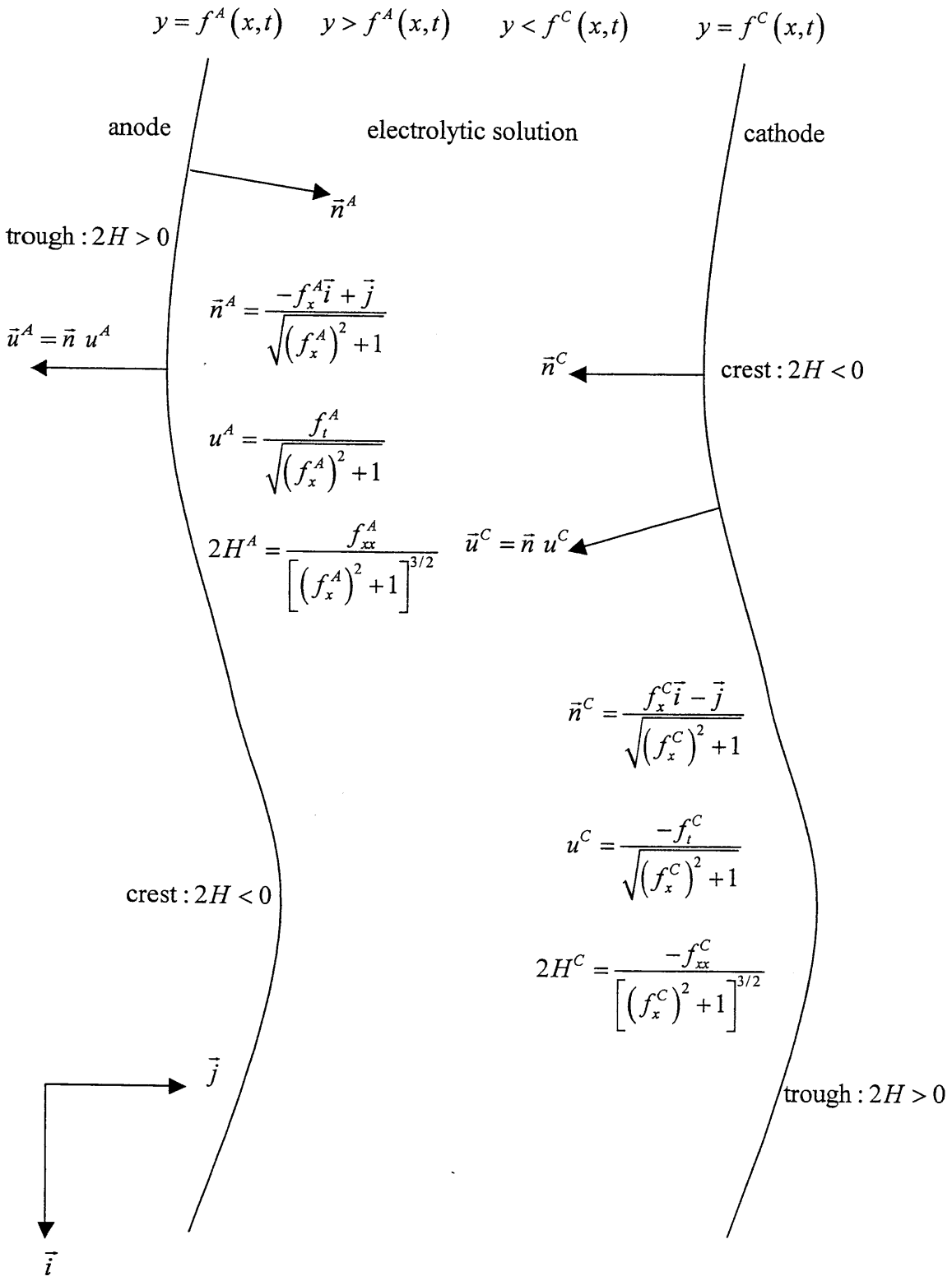


Figure 2-1. Important variables and formulas associated with the surfaces (Krishnan *et al.*, 2002).

for the ionic species, and for the mass as a whole

$$\left[\vec{n}\cdot\rho\left[\vec{v}-\vec{u}\right]\right]^{metal}-\left[\vec{n}\cdot\rho\left[\vec{v}-\vec{u}\right]\right]^{solution}=0 \qquad (2.15)$$

where the superscript denotes the phase and subscript denotes the species and where subscript 1 stands for copper and 2 for sulphate ions respectively. As both the electrodes are assumed to be made entirely of species 1, the density of species 1 in the solid is equal to the density of the electrode ρ_M and the density of species 2 in the solid is zero. So, on the metal side of either surface set

$$\vec{v}=-\vec{U}\ ,\ \vec{N}_1=-c_1\vec{U}\ \text{and}\ N_2=-c_2\vec{U}$$

where $\vec{U}=U\vec{j}$ and also set $c_1=c_M$ and $c_2=0$. Now these equations, which are written for the moving frame, state that the two electrodes, but not their surfaces, remain at rest in the laboratory frame and that each is composed completely of copper, species 1. It is here where the variable $\vec{U}$ appears in the moving frame equations.

Dropping the superscripts denoting the metal and the solution, all variables from now on, except c_M and ρ_M, refer to the solution and the equations, where the electrolytic solution contacts the electrode surfaces, simplify into

$$\vec{n}\cdot\vec{N}_1=\left[c_1-c_M\right]\vec{n}\cdot\vec{u}-c_M\vec{n}\cdot\vec{U} \qquad (2.16)$$

$$\vec{n}\cdot\vec{N}_2=\left[c_2\right]\vec{n}\cdot\vec{u} \qquad (2.17)$$

and

$$\vec{n}\cdot\vec{v}=\left[1-\frac{\rho_M}{\rho}\right]\vec{n}\cdot\vec{u}-\frac{\rho_M}{\rho}\vec{n}\cdot\vec{U} \qquad (2.18)$$

where ρ_M and c_M denote the mass density in kg/m^3 and the molar density in kg-mole/m^3 of the metal respectively.

The normal current density at a surface obtained by substituting equations (2.16) and (2.17) into equation (2.6), is

$$\vec{n}\cdot\vec{i} = \sum Fz_i\vec{n}\cdot\vec{N}_i = \sum Fz_ic_i\vec{n}\cdot\vec{u} - Fz_1c_M\left[\vec{n}\cdot\vec{u}+\vec{n}\cdot\vec{U}\right] \tag{2.19}$$

The total current crossing a surface, which is measured by an ammeter and which is denoted I, is

$$I = \int_S dA\,\vec{n}\cdot\left[\vec{i} - F\sum z_ic_i\vec{u}\right] \tag{2.20}$$

where S denotes the surface dividing an electrode and the solution and the integration on the right hand side is carried out over the solution side of the interface whence $\vec{i}$ and c_i pertain to the ionic solution. Figure 2-2 is drawn to illustrate this formula. In this figure the current flows to the right as copper ions enter the solution, while the surface itself moves to the left as copper metal dissolves. Then $\int_S dA\,\vec{n}\cdot\vec{i}$ is positive and if the charge density in the solution (i.e., $F\left[z_1c_1+z_2c_2\right]$) is positive, I must be greater than $\int_S dA\,\vec{n}\cdot\vec{i}$ to account both for the current flowing in the solution and for the positive charge density being produced in the solution at the interface as the surface moves to the left. The second term accounts for this charge production.

The total current is the sum of the local currents and these are produced by the electron transfer reactions taking place at each point along the surface of an electrode. The net rate of these reactions is what the Butler-Volmer equation predicts. To complete the statement of the surface boundary conditions we turn to the electrode kinetics and discuss the Butler-Volmer equation.

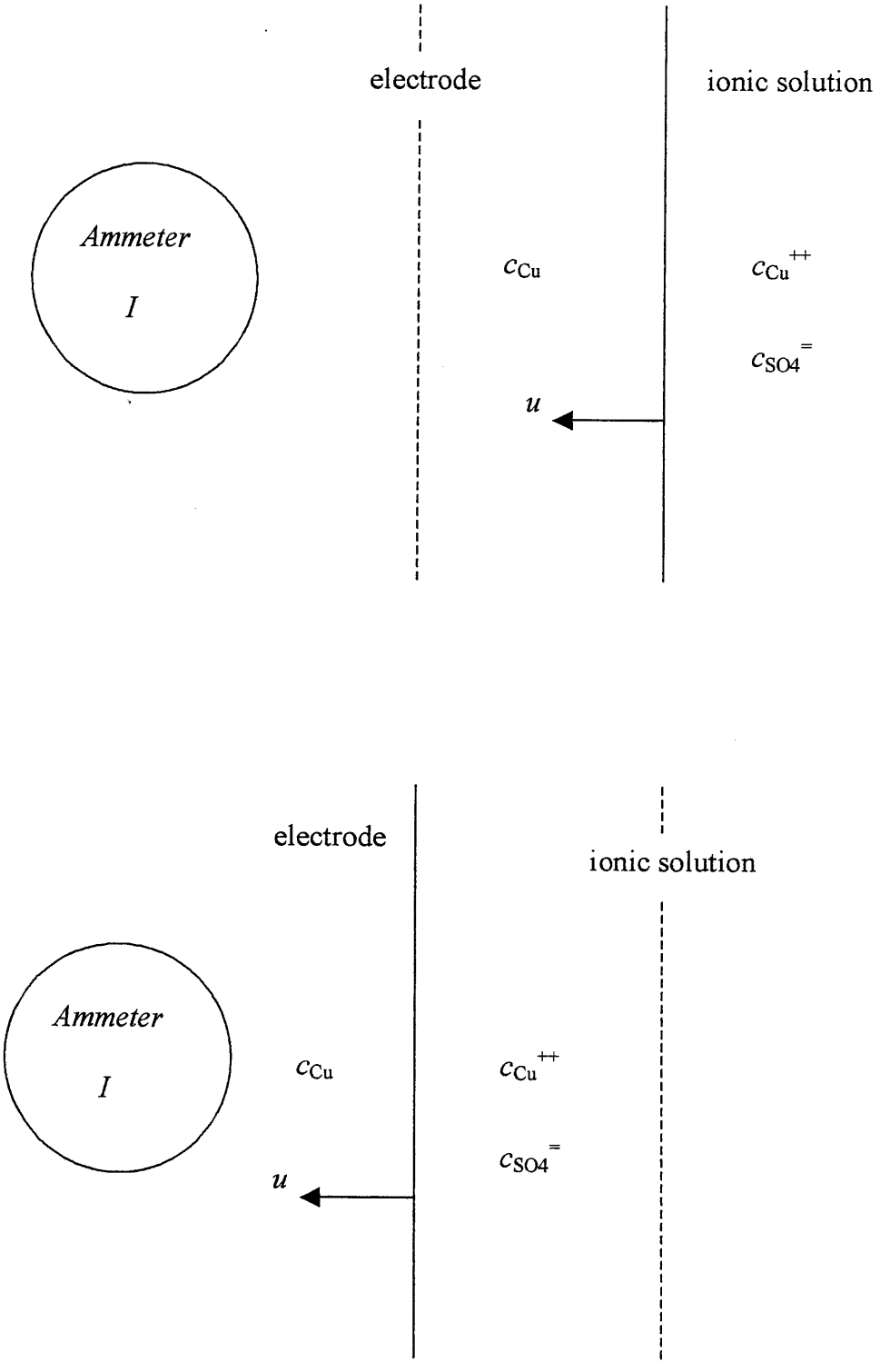


Figure 2-2. Explaining the contribution of different terms in equation (2.20) for the total current.

2.1.3 Electrode Kinetics

This section deals with the reactions that are taking place on the electrode surfaces. When there is a potential difference between the two electrodes, electrons will start to flow in the circuit and there will be a net transfer of electrons across each surface. Both oxidation and reduction are electron transfer reactions. The reduction reaction is taken to be the forward reaction while the oxidation reaction, is the backward reaction. As shown in Figure 2-1 the normal vector points into the solution, the normal current density is positive if $\vec{i}$ is in the direction of $\vec{n}$. Hence, the oxidation reaction produces positive current while the reduction reaction produces negative current.

The Butler-Volmer equation predicts the net rate of the electron transfer reaction as the difference between the oxidation and reduction steps and it can be written as (Bockris et *al.*, 2000)

$$\vec{n}\cdot\frac{\left[\vec{i}-F\sum z_i c_i \vec{u}\right]}{z_1 F} = \vec{k} c_M e^{[1-\beta]\frac{z_1 F}{RT}\left[\Delta\phi - \frac{\gamma}{z_1 F c_M}2H\right]} - \vec{k} c_1 e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi - \frac{\gamma}{z_1 F c_M}2H\right]} \tag{2.21}$$

where γ denotes the surface tension and where β, $0<\beta<1$, denotes a factor having to do with the activation step. The chemical reaction rate constants $\vec{k}$ and $\vec{k}$ depend on the temperature at which the electrodeposition reaction is taking place. It is obvious from equation (2.21) that the current, the left hand side, is a function of three variables that appear on the right hand side. These variables are $\Delta\phi$, the difference in the electrical potential across the surface, the concentration of the metal ions near the surface namely c_1 and the curvature of the surface $2H$. The effect of these variables on the reactions is explained next.

The difference in the electrical potential across the surface is denoted $\Delta\phi$, where it is always taken to be $\phi^{metal} - \phi^{solution}$. It is obvious from the Butler-Volmer equation that a positive $\Delta\phi$ favors the metal dissolving in the solution while a negative $\Delta\phi$ favors the opposite. At the anode, $\Delta\phi$ is always positive. This will encourage oxidation over reduction by increasing the exponential factor in the oxidation term and decreasing it in the reduction term. On the other hand, at the cathode $\Delta\phi$ is always negative; this will discourage oxidation and encourage reduction. Figure 2-3 depicts the effect of the electrical potential on the reactions when copper is selected as an example. In the figure, the voltage is higher at the anode than that at the cathode. This higher voltage at the anode will favor the oxidation reaction (i.e., $Cu \rightarrow Cu^{++} + 2e^{-}$) on the reduction reaction namely $Cu^{++} + 2e^{-} \rightarrow Cu$. The lengths of the arrows in Figure 2-3 represent a measure of how fast each reaction is. At the cathode where the voltage is low, the opposite scenario will take place.

The effect of the metal ion concentration adjacent to the electrode surface is clear since decreasing c_1 will also decrease the reduction rate (i.e., the second term on the right hand side of equation (2.21)). One could also refer to Figure 2-3 and recognize that making the concentration of the copper ions lower near the surface will also lower the rate of reduction reaction given by $Cu^{++} + 2e^{-} \rightarrow Cu$ since less ions will be available to support this reaction.

The effect of the surface curvature can be visualized by studying how a crest or a trough will help or harm either the oxidation or the reduction reaction. At a crest, where the curvature is taken to be negative, the oxidation reaction is favored over the reduction reaction since it will be easier to lose a copper atom from the metal. On the other hand, at

the trough the opposite is true as the metal atom will be closer to its neighbors so it is difficult to detach it from the surface. It is in this curvature effect that surface tension comes into the picture, being a factor that determines the stability of the system as will be shown in the next chapter.

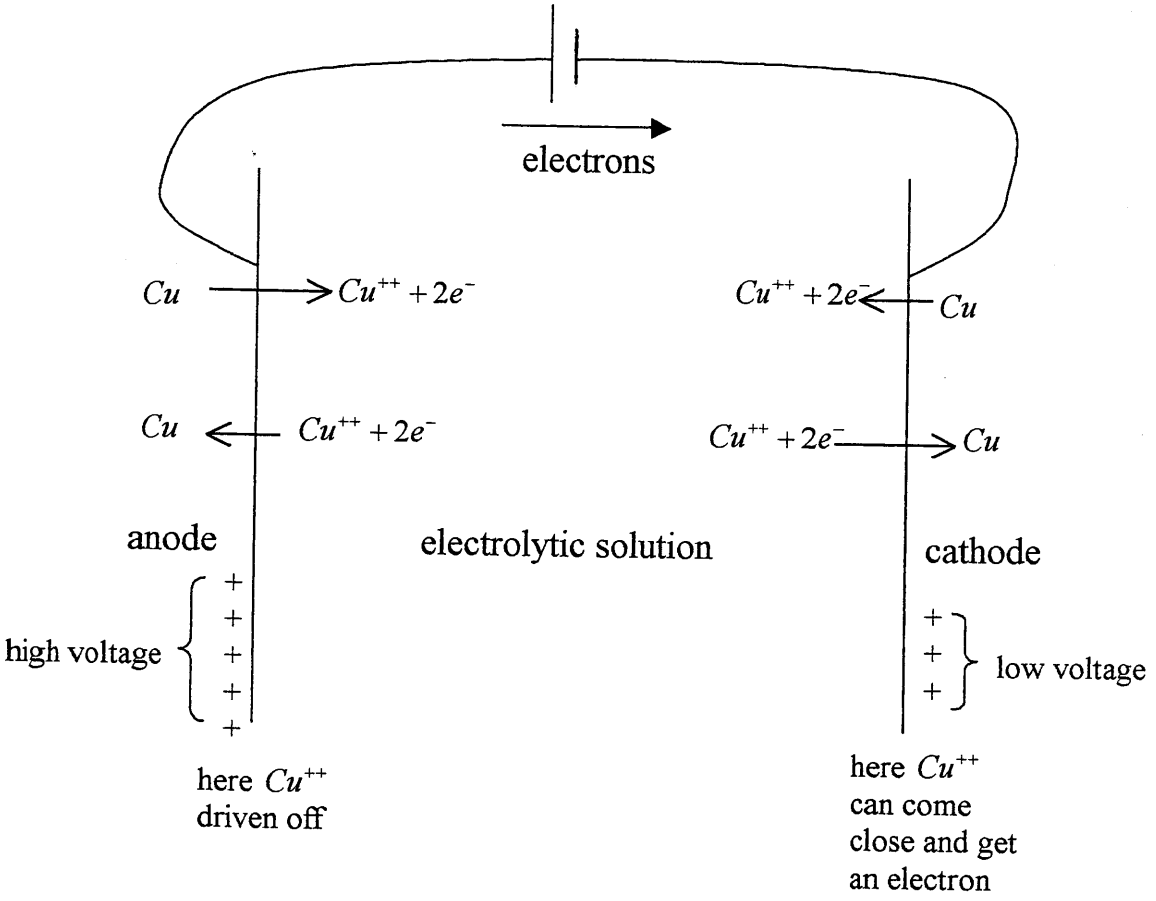


Figure 2-3. The effect of the electrical potential on the extent of the oxidation and reduction reactions.

To summarize the effects of the potential difference and the curvature, refer to the first term on the right hand side of equation (2.21), the oxidation term. Positive values of $\Delta\phi$ and negative values of $2H$ produce higher rates of oxidation than do negative values of $\Delta\phi$ and positive values of $2H$. For the reduction reaction, which is accounted for by the second term in the Butler-Volmer equation, the opposite is the case. Figure 2-4

summarizes the effect of the potential difference and the surface curvature on the reaction rates.

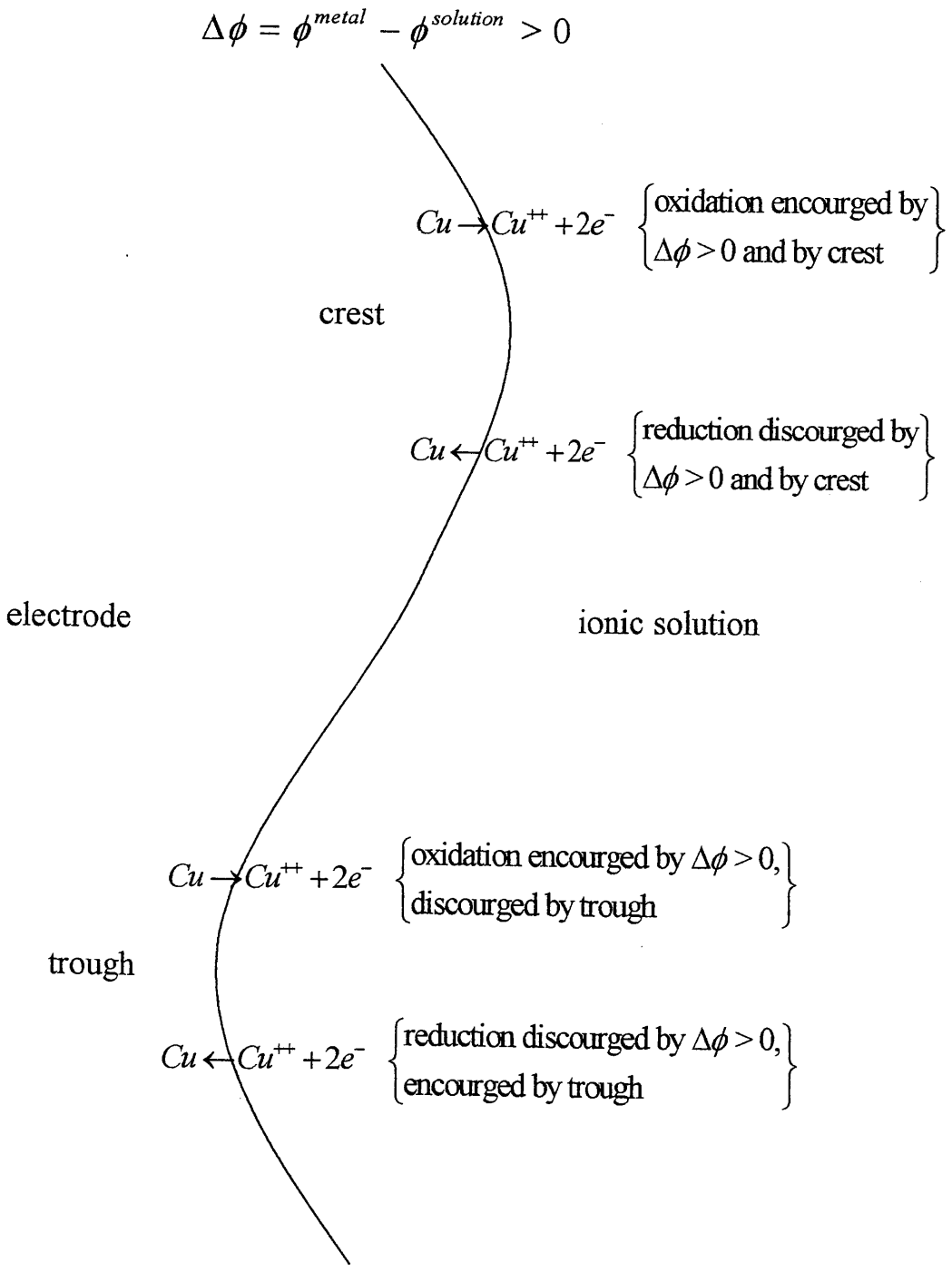
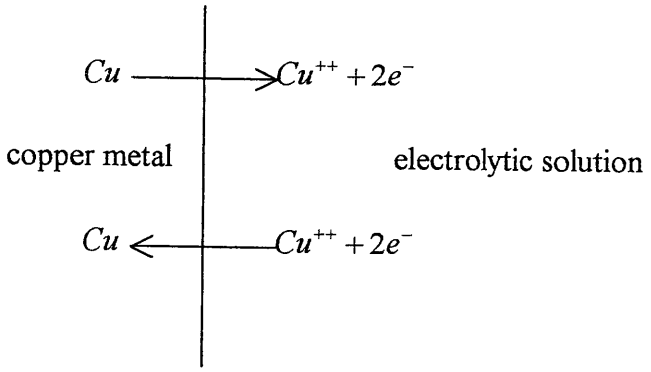
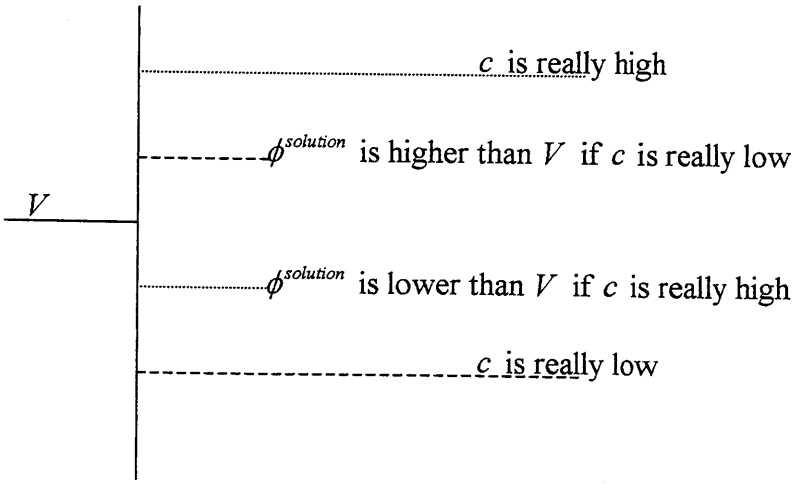


Figure 2-4. The effect of surface curvature on the reaction rates at both electrodes.

Now by introducing a reference metal ion concentration, the constants $\bar{k}c_M$ and $\bar{k}$ can be eliminated from the Butler-Volmer equation in favor of the exchange current density, denoted by i_0, and the equilibrium potential difference, denoted by $\Delta\phi_{EQ}$. The equilibrium condition implies that a constant exchange of charge carriers takes place across the metal-solution interphase. Figure 2-5 (a) depicts the equilibrium situation where both oxidation and reduction reactions run at the same rate.



(a)



(b)

Figure 2-5. Explaining the equilibrium situation (a) At equilibrium, both the oxidation and the reduction reactions run at the same speed. (b) At equilibrium, $\phi^{solution}$ might be higher or lower than V depending on the ionic concentration near the electrode.

At equilibrium, then one might wonder if the potential of the solution (i.e., $\phi^{solution}$) at the surface is higher or lower than the metal potential namely ϕ^{metal} or V. To answer this question let us consider Figure 2-5 (b) where an electrode at a voltage V is taken to be in contact with a solution at uniform concentration c. Now, as the figure shows, if c is low, $\phi^{solution}$ must be higher than V to help the reduction reaction and to bring the situation to equilibrium, however, if c is high, then $\phi^{solution}$ will be lower than V to support the oxidation reaction. This explains the jump required in ϕ. So for every concentration of the electrolytic solution, there is an equilibrium electrical potential and moving the electrical potential away from equilibrium helps one or the other reaction.

Now the exchange current density, i_0, is defined as the current density predicted by the oxidation term when the rates of oxidation and reduction are equal (i.e., at equilibrium). Both i_0 and $\Delta\phi_{EQ}$ refer to a reference surface, a surface which is flat and across which the electrode is in contact with a solution at the reference metal ion concentration, $\overline{c}_1$. During the electrodeposition process, $\overline{c}_1$, i_0 and $\Delta\phi_{EQ}$ remain constant. The resulting modified Butler-Volmer equation, which is going to be used hereafter, is given as (Johns and narayanan, 2002)

$$\vec{n}\cdot\left[\vec{i}-F\sum z_i c_i \vec{u}\right]=i_0\left[e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}-\frac{\gamma}{z_1Fc_M}2H\right]}-\frac{c_1}{\overline{c}_1}e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}-\frac{\gamma}{z_1Fc_M}2H\right]}\right] \qquad (2.22)$$

The values of $\Delta\phi_{EQ}$ and i_0 at a standard concentration must be measured. The value of $\Delta\phi_{EQ}$ at any reference concentration can then be obtained from the Nernst equation via

$$\Delta\phi_{EQ}\left(c_{1\,ref}\right)-\Delta\phi_{EQ}\left(c_{1\,std}\right)=\frac{RT}{z_1F}\ln\frac{c_{1\,ref}}{c_{1\,std}}$$

whence i_0, given in terms of $\Delta\phi_{EQ}$ by

$$i_0=F\bar{k}c_M e^{[1-\beta]\frac{z_1F}{RT}\Delta\phi_{EQ}}$$

is

$$\frac{i_0\left(c_{1\,ref}\right)}{i_0\left(c_{1\,std}\right)}=\left[\frac{c_{1\,ref}}{c_{1\,std}}\right]^{[1-\beta]}$$

The value of $\Delta\phi_{EQ}$ and i_0 at a standard concentration, then, become parameters of the system replacing $\bar{k}c_M$ and $\bar{k}$. The values of $\Delta\phi_{EQ}$ and i_0 at a specified reference concentration are then parameters of a specific experiment.

The nonlinear equations presented in section 2.1 can be simplified by applying an assumption called local electrical neutrality. The meaning of this and the simplified equations obtained after applying this assumption are given next.

2.2 The Nonlinear Equations Simplified by Local Electrical Neutrality

This section will show how the nonlinear equations can be simplified by making an assumption, namely local electrical neutrality. What is assumed is this: if a sample is drawn from any place throughout the solution, it will contain an equal number of positive and negative charges, and therefore the sample has a zero net charge. In other words, local electrical neutrality states that over a given volume element there will be as many positive charges as there are negative charges. This is a valid assumption as long as double layer effects are neglected, where the double layer is the region near an electrode where charges must certainly be separated. This layer is usually very thin (on the order of 10 Å (Prentice, 1991)) compared to the distance between the electrodes and hence double

layer effects are usually negligible. Consequently, local electrical neutrality is an appropriate assumption for a large section of the electrolytic solution. The local electrical neutrality can be stated as

$$\sum z_i c_i = z_1 c_1 + z_2 c_2 = 0 \tag{2.23}$$

It must be emphasized that departures from local electrical neutrality in an ionic solution, where they occur at all, are very small. They are so minuscule that the most sensitive chemical methods cannot detect any disparity between $z_1 c_1$ and $z_2 c_2$ (Oldham and Myland, 1994).

Now let the shapes of the two electrode surfaces be specified, in addition to the function $\vec{v}$ and turn to equation (2.3) on the domain, which can be written for species 1 and 2 as

$$\vec{N}_1 = -D_1 \nabla c_1 - \frac{z_1 F}{RT} D_1 c_1 \nabla \phi + c_1 \vec{v} \tag{2.24}$$

and

$$\vec{N}_2 = -D_2 \nabla c_2 - \frac{z_2 F}{RT} D_2 c_2 \nabla \phi + c_2 \vec{v} \tag{2.25}$$

Now multiply equation (2.24) by z_1 and equation (2.25) by z_2 and add to get

$$\begin{aligned} z_1 \vec{N}_1 + z_2 \vec{N}_2 = & -D_1 \nabla [z_1 c_1] + D_2 \nabla [-z_2 c_2] \\ & + \left[-\frac{F}{RT} [D_1 z_1][z_1 c_1] - \frac{F}{RT} [-D_2 z_2][-z_2 c_2] \right] \nabla \phi + [z_1 c_1 + z_2 c_2] \vec{v} \end{aligned} \tag{2.26}$$

also multiply equation (2.24) by $z_1 z_2 D_2$ and equation (2.25) by $z_1 z_2 D_1$ and add to get

$$\begin{aligned} z_1 z_2 D_2 \vec{N}_1 + z_1 z_2 D_1 \vec{N}_2 = & -z_2 D_1 D_2 \nabla [z_1 c_1] + z_1 D_1 D_2 \nabla [-z_2 c_2] \\ & - \frac{F}{RT} D_1 D_2 z_1 z_2 [z_1 c_1 + z_2 c_2] \nabla \phi + \left[z_2 D_2 [z_1 c_1] - z_1 D_1 [-z_2 c_2] \right] \vec{v} \end{aligned} \tag{2.27}$$

Now using the local electrical neutrality assumption, equation (2.23), define c via $c = z_1 c_1 = -z_2 c_2$. Equations (2.26) and (2.27) then become

$$z_1 \vec{N}_1 + z_2 \vec{N}_2 = -\left[D_1 - D_2\right]\nabla c - \frac{F}{RT}\left[D_1 z_1 - D_2 z_2\right] c \nabla \phi \tag{2.28}$$

and

$$z_1 z_2 D_2 \vec{N}_1 + z_1 z_2 D_1 \vec{N}_2 = D_1 D_2 \left[z_1 - z_2\right]\nabla c - \left[z_1 D_1 - z_2 D_2\right] c \vec{v} \tag{2.29}$$

Equations (2.28) and (2.29) can be used to simplify the domain equations and the boundary conditions. Equation (2.1) on the domain can be written for species 1 and 2 as follows

$$\frac{\partial c_1}{\partial t} + \nabla \cdot \vec{N}_1 = 0 \tag{2.30}$$

and

$$\frac{\partial c_2}{\partial t} + \nabla \cdot \vec{N}_2 = 0 \tag{2.31}$$

Now multiply equation (2.30) by z_1 and equation (2.31) by z_2 and add. Also multiply equation (2.30) by $z_1 z_2 D_2$ and equation (2.31) by $z_1 z_2 D_1$ and add. The result is

$$\frac{\partial c}{\partial t} = D\nabla^2 c - \vec{v} \cdot \nabla c \tag{2.32}$$

and

$$P\nabla^2 c + \frac{z_1 F}{RT}\nabla \cdot \left[c \nabla \phi\right] = 0 \tag{2.33}$$

where D and P in the above equations are defined by $D = \frac{D_1 D_2}{z_1 D_1 - z_2 D_2}\left[z_1 - z_2\right]$ and $P = \frac{z_1\left[D_1 - D_2\right]}{z_1 D_1 - z_2 D_2}$.

Let us turn to the equations at the boundary and multiply equation (2.16) by z_1 and equation (2.17) by z_2 and add. In addition, multiply equation (2.16) by $z_1 z_2 D_2$ and equation (2.17) by $z_1 z_2 D_1$ and add. This gives the following two equations

$$D\vec{n}\cdot\nabla c - c\vec{n}\cdot\left[\vec{v}-\vec{u}\right] = \frac{-z_1 z_2 D_2 c_M}{z_1 D_1 - z_2 D_2}\left[\vec{n}\cdot\vec{u}+\vec{n}\cdot\vec{U}\right] \tag{2.34}$$

and

$$P\vec{n}\cdot\nabla c + \frac{z_1 F}{RT} c\vec{n}\cdot\nabla\phi = \frac{z_1^2 c_M}{z_1 D_1 - z_2 D_2}\left[\vec{n}\cdot\vec{u}+\vec{n}\cdot\vec{U}\right] \tag{2.35}$$

where both apply at each electrode.

At this stage all the equations needed to complete the model have been obtained, the only thing left is to apply the local electrical neutrality assumption to equation (2.19) to get the normal current density at an electrode which is

$$\vec{n}\cdot\vec{i} = -z_1 F c_M\left[\vec{n}\cdot\vec{u}+\vec{n}\cdot\vec{U}\right] \tag{2.36}$$

and applying electrical neutrality again on equation (2.20) the total current is going to be

$$I = \int_S dA\ \vec{n}\cdot\vec{i} \tag{2.37}$$

again these equations apply at both electrodes.

One can easily see that $\left[\vec{n}\cdot\vec{u}+\vec{n}\cdot\vec{U}\right]$ appears on the right hand side of equations (2.34), (2.35) and (2.36) and it is going to be predicted by the Butler-Volmer equation.

Now for a specified geometry, equations (2.32), (2.33), (2.34) and (2.35) would be enough to find both c and ϕ if their initial values were assigned all through the solution and if $\vec{v}$ were to be ignored. However, the shape of the electrodes is unknown and it needs to be determined. But that is the role of the Butler- Volmer equation. Indeed

equations (2.22) and (2.36) can be combined, along with the local electrical neutrality assumption, to get

$$\vec{n}\cdot\vec{i} = -z_1 F c_M \left[\vec{n}\cdot\vec{u} + \vec{n}\cdot\vec{U}\right] = i_0\left[e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}-\frac{\gamma}{z_1Fc_M}2H\right]} - \frac{c}{\bar{c}}e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}-\frac{\gamma}{z_1Fc_M}2H\right]}\right] \tag{2.38}$$

which holds at both the anode and the cathode. At the anode it is

$$\vec{n}^A\cdot\vec{i} = i_y^A = -z_1 F c_M \left[\vec{n}^A\cdot\vec{u}^A + \vec{n}^A\cdot\vec{U}\right] = i_0\left[e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi^A-\Delta\phi_{EQ}-\frac{\gamma}{z_1Fc_M}2H^A\right]} - \frac{c^A}{\bar{c}}e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi^A-\Delta\phi_{EQ}-\frac{\gamma}{z_1Fc_M}2H^A\right]}\right] \tag{2.39}$$

and at the cathode it is

$$\vec{n}^C\cdot\vec{i} = -i_y^C = z_1 F c_M \left[\vec{n}^C\cdot\vec{u}^C + \vec{n}^C\cdot\vec{U}\right] = i_0\left[e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi^C-\Delta\phi_{EQ}-\frac{\gamma}{z_1Fc_M}2H^C\right]} - \frac{c^C}{\bar{c}}e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi^C-\Delta\phi_{EQ}-\frac{\gamma}{z_1Fc_M}2H^C\right]}\right] \tag{2.40}$$

These two equations can be used to advance the shape of the two surfaces by relating the local values of c and ϕ to the local speeds of the surfaces where the local speed of a surface is given by

$$\vec{n}\cdot\vec{u} = u = \frac{\pm\frac{\partial f}{\partial t}}{\sqrt{1+\left[\frac{\partial f}{\partial x}\right]^2}} \tag{2.41}$$

so the problem appears to be closed.

Now local electrical neutrality has some important implications and we present them here. By applying this assumption, the volume of the solution and the average ionic concentration at any instant must be equal to the initial volume of the solution and the

initial average ionic concentration. This is because the amount of the negative charge in the solution cannot change since no negative ions can cross an electrode surface. Hence, at local electrical neutrality, the amount of positive charge in the solution cannot change. Therefore the rate at which the anode dissolves is the rate at which the cathode grows. And as the volume of the solution cannot change neither therefore can the average concentration of positive ions in solution.

In all of the above, $\vec{v}$ was set aside. The reason is that we plan to neglect convection. A discussion of this is presented next.

2.3 The Effect of Convection

It was mentioned earlier that if $\vec{v}$ were to be ignored, the proposed problem could be solved to get both c and ϕ. This turns out to be a reasonable assumption and it avoids the introduction of a lot of complexity for the following reason. Any convection in this model must come from the motion of the surfaces working on the density difference. This motion is very slow. To see how it affects concentration gradients at the surfaces substitute for $\vec{n}\cdot\vec{v}$ from equation (2.18) into equation (2.34) to obtain

$$D\vec{n}\cdot\nabla c = -\frac{\rho_M}{\rho}c\left[\vec{n}\cdot\vec{u}+\vec{n}\cdot\vec{U}\right]-\frac{z_1z_2D_2}{z_1D_1-z_2D_2}c_M\left[\vec{n}\cdot\vec{u}+\vec{n}\cdot\vec{U}\right] \qquad (2.42)$$

In equation (2.42), the first term on the right hand side represents the convection effect. If this term is small compared with the second term on the right hand side, then the effect of convection ought to be negligible. In order to compare these two terms, an order of magnitude analysis could be used. The ratio $\frac{z_1z_2D_2}{z_1D_1-z_2D_2}$ has an order of magnitude of 1, so the only thing to compare is $\frac{\rho_M}{\rho}c$ in the convection term and c_M in the second

term. Now remember that $c = c_1 z_1$ and $c_1 = \frac{\rho_1}{M_1}$ so the term $\frac{\rho_M}{\rho} c$ in the convection term will be $z_1 \frac{\rho_1}{M_1} \frac{\rho_M}{\rho}$. Noticing that $\frac{\rho_M}{M_1}$ is just c_M, it is obvious that the first term is very small compared to the second since $\frac{\rho_1}{\rho} \ll 1$ which is the dilute solution assumption. Consequently we will ignore convection through out this dissertation.

The next section will summarize all the assumptions and hence the limitations of our model.

2.4 Main Assumptions and Limitations

We conclude with a summary of the assumptions and limitations discussed earlier in this chapter and then proceed to the next chapter where a steady one-dimensional solution will be obtained and its stability analysis will be carried out. The main assumptions are:

1. Dilute electrolytic solution- As a result of this assumption, diffusion coefficients are considered to be constants so too ρ.
2. Complete ionization of the electrolytic solution. This means that no reactions will be considered throughout the solution leaving us only with surface reactions that take place on the anode and the cathode.
3. Convection is negligible. As a result, the velocity $\vec{v}$ is neglected.
4. Electrical neutrality throughout the solution is assumed. As a result, the equations are simplified and constant solution volume follows.
5. Only one reaction is assumed to take place. This limits the potential difference that can be applied to ranges where other reactions do not occur.

Now after getting all the equations of the model and knowing the assumptions used to arrive at these equations, we are ready to go on and try to solve these equations. In the next chapter, an approximation that will simplify the Butler-Volmer equation will be

introduced and the nonlinear equations will be solved based on this approximation. The benefit of this approximation will be clear as we are going to compare the results with and without the implementation of such approximation. It is worth mentioning here that the approximation in the next chapter will simplify the kinetics while another approximation will be presented later in chapter 4 that will simplify the transport processes. All of these approximations serve one purpose of simplifying the nonlinear equations of the model for further complicated calculation that are going to be presented later in chapter 6.

CHAPTER 3
LINEAR STABILITY ANALYSIS OF THE CHEMICAL REACTION EQUILIBRIUM (CRE) MODEL

The aim of this chapter is to find a base solution for the problem explained previously and investigate under what conditions this solution ought to be unstable. An approximation involving chemical reaction equilibrium (CRE) will be used to simplify the Butler-Volmer equation (B-V) and this approximation will benefit us mainly in obtaining a simpler relation between the voltage drop and the velocity of the surface in the base case. The CRE approximation will be seen to be good under certain conditions namely, low values of surface velocity, low average electrolytic concentration and large values of electrode spacing.

The term "chemical reaction equilibrium" refers to the assumption that the rates of reactions at the surfaces are very fast compared to the rates of diffusion and migration throughout the electrolytic solution. If this is true, the reaction ought to look like it is at equilibrium.

A system is considered to be stable with respect to a particular small disturbance if the disturbance dies with time, if it is unstable to at least one disturbance the system is considered to be unstable. If a system is unstable to disturbances of infinitesimal amplitude, it is unstable to larger disturbances and is called unconditionally unstable. If it is unstable to large amplitude disturbances, it is conditionally unstable for it could remain stable to small amplitude perturbations. We proceed to consider instability to infinitesimal disturbances. As the disturbances given are assumed to be very small, their

products and powers, higher than the first, can be ignored. Consequently, the stability analysis, a linear problem, is just concerned with the first power of the disturbances and will determine when the steady state under investigation becomes unstable. The point at which the disturbances neither grow nor die is called the neutral or critical point and it sets a boundary between the stable and unstable regions. It is expected that this critical point will depend on the values of the input variables and it is our first objective to discover this dependence.

We begin by finding a steady one-dimensional base solution for the model proposed in chapter 2. The stability of this base solution is then studied using a perturbation method with the aim of getting the critical wavelength dividing the ranges of stable and unstable displacements. Next, results obtained by applying the CRE assumption are compared with previous work by Sundström and Bark (S&B) and Johns and Narayanan (J&N). These people took into account the full B-V equation to describe the kinetics part of the electrodeposition problem. We will investigate how close the results we are getting compared to their results. Finally we will show the reader why the CRE approximation turned to be good when compared with the full B-V model.

Now to show how the CRE approximation will help in simplifying the relation between the voltage drop and the velocity of the surface, we present the base solution for both cases (i.e., with and without applying the CRE).

3.1 The Base Solution

3.1.1 Getting the Base Solution Using the B-V Equation

The base solution is a steady, one-dimensional solution with the electrodes taking the shapes of parallel planes laying at rest in the moving frame where the distance between them is denoted L_0 where L_0 is taken to be an input variable.

The anode-solution interface is chosen as the origin. The superscripts A and C refer to the anode-solution interface, $y = 0$, and the cathode-solution interface, $y = L_0$, respectively. As only the one-dimensional planar-surface problem is considered, one can write

$$f^A = 0, \quad \vec{n}^A = \vec{j}, \quad u^A = 0, \quad 2H^A = 0$$

at the anode, and

$$f^C = 0, \quad \vec{n}^C = -\vec{j}, \quad u^C = 0, \quad 2H^C = 0$$

at the cathode.

Then using equation (2.6) in the bulk, i_y must satisfy

$$0 = \nabla \cdot \left[z_1 N_1 + z_2 N_2 \right] = \nabla \cdot \vec{i} = \frac{di_y}{dy} \tag{3.1}$$

From the above equation, i_y remains constant across the solution, and its value can be determined via equation (2.19), which is valid at the electrode- solution interfaces. Hence the expressions for i_y is

$$i_y = -z_1 F c_M U \tag{3.2}$$

where $|U|$ is the speed at which a laboratory observer sees the two interfaces moving to the left. The variable U, then is just a different way of talking about the electrical current density, i_y, in the cell under steady, one-dimensional conditions.

To determine the base solution we have to find the ionic concentration, c, and the electrical potential, ϕ, throughout the solution. Now consider the equations in the domain i.e., equations (2.32) and (2.33) viz.,

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

and

$$P\nabla^2 c + \frac{z_1 F}{RT}\nabla\cdot\left[c\nabla\phi\right] = 0$$

At steady state, equation (2.32) will become

$$D\frac{d^2c}{dy^2} = 0 \tag{3.3}$$

and equation (2.33) will become

$$P\frac{d^2c}{dy^2} + \frac{d}{dy}\left[c\frac{d}{dy}\left[\frac{z_1F}{RT}\phi\right]\right] = \frac{d}{dy}\left[P\frac{dc}{dy} + c\frac{d}{dy}\left[\frac{z_1F}{RT}\phi\right]\right] = 0 \tag{3.4}$$

These must be solved subject to equations (2.34) and (2.35). The reader is reminded that equation (2.34) is

$$D\frac{dc}{dy} = \frac{-z_1z_2D_2}{z_1D_1 - z_2D_2}c_M U \tag{3.5}$$

while equation (2.35) is

$$P\frac{dc}{dy} + c\frac{d}{dy}\left[\frac{z_1F}{RT}\phi\right] = \frac{z_1^2}{z_1D_1 - z_2D_2}c_M U \tag{3.6}$$

both of which hold at both anode and cathode. Integrating equations (3.3) and (3.4), and making use of equations (3.5) and (3.6), we get

$$D\frac{dc}{dy} = \text{constant} = \frac{-z_1z_2D_2}{z_1D_1 - z_2D_2}c_M U \tag{3.7}$$

and

$$P\frac{dc}{dy}+c\frac{d}{dy}\left[\frac{z_1F}{RT}\phi\right]=\text{constant}=\frac{z_1^2}{z_1D_1-z_2D_2}c_MU \tag{3.8}$$

which can be written as

$$\frac{dc}{dy}=-\frac{z_1z_2D_2}{z_1D_1-z_2D_2}\frac{c_MU}{D}=-\frac{z_1z_2D_2}{z_1D_1-z_2D_2}\frac{c_MU}{D} \tag{3.9}$$

and

$$\frac{d}{dy}\left[\frac{z_1F}{RT}\phi\right]=\frac{1}{c}\left[\frac{z_1^2}{z_1D_1-z_2D_2}c_MU-P\frac{dc}{dy}\right]=\frac{z_1^2U}{cD_1\left[z_1-z_2\right]}\left[c_M+\frac{D_1-D_2}{z_1D_2}\frac{\rho_M}{\rho}c\right] \tag{3.10}$$

As explained in section 2.3, where the effect of convection was shown to be negligible, omit the second term in the right hand side of equation (3.10) because $\frac{\rho_M}{\rho}c \ll c_M$, As a result, equations (3.9) and (3.10) can be written as

$$-\frac{1}{\overline{c}}\frac{dc}{dy}=\frac{z_1z_2D_2}{z_1D_1-z_2D_2}\frac{c_M}{\overline{c}}\frac{U}{D} \tag{3.11}$$

and

$$-\frac{d}{dy}\left[\frac{z_1F}{RT}\phi\right]=\frac{-z_1^2c_MU}{D_1\left[z_1-z_2\right]c}\frac{1}{} \tag{3.12}$$

Now these equations determine c and ϕ up to constants of integration and each requires the specification of one more condition in order to determine these constants. In the case of c we note that

$$\overline{c}=\frac{1}{L_0}\int_0^{L_0}c\,dy \tag{3.13}$$

where $\overline{c}$ is an input variable. Hence by using equations (3.11) and (3.13), the concentration profile can be found to be

$$c = \bar{c} + \frac{-z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} c_M \frac{U}{D}\left[y - \frac{1}{2} L_0 \right] \tag{3.14}$$

which gives c as a function of y and it shows how c is affected by the values of $\bar{c}$, L_0 and U.

The above equation for c can be used to determine the concentration at the anode and at the cathode (i.e., c^A and c^C respectively) in terms of U. By setting y to zero in equation (3.14) the expression for c^A is

$$c^A = \bar{c} - \frac{-z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} c_M \frac{U}{D} \frac{1}{2} L_0 \tag{3.15}$$

and at the cathode, where $y = L_0$, using equation (3.14) once again, the expression for c^C is

$$c^C = \bar{c} + \frac{-z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} c_M \frac{U}{D} \frac{1}{2} L_0 \tag{3.16}$$

Let us now turn our attention to finding the potential profile across the cell. First, by differentiating equation (3.14) with respect to y one gets

$$dc = \frac{-z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} c_M \frac{U}{D} dy \tag{3.17}$$

and by substituting for dy in equation (3.12) we find

$$d\left[\frac{z_1 F}{RT} \phi \right] = -\frac{z_1}{z_2} \frac{dc}{c} \tag{3.18}$$

then solving this equation will lead us to the electrical potential equation viz.,

$$\frac{z_1 F}{RT} \phi = \frac{z_1 F}{RT} \phi^A + \frac{z_1}{-z_2} \ln \frac{c}{c^A} \tag{3.19}$$

where ϕ^A is not yet known, being a constant of integration at this point. So the difference $\phi^C - \phi^A$ can be written as

$$\frac{z_1 F}{RT}\left(\phi^C - \phi^A\right) = \frac{z_1}{-z_2}\ln\frac{c^C}{c^A} \tag{3.20}$$

Now to complete the base solution we need to connect the voltage drop, which is an input variable, to the velocity of the surfaces. This can be achieved using the B-V equation at the anode and at the cathode. At the anode, the B-V equation for a flat surface is

$$-\frac{z_1 F c_M U}{i_0} = e^{[1-\beta]\frac{z_1 F}{RT}\left[\Delta\phi^A - \Delta\phi_{EQ}\right]} - \frac{c^A}{\overline{c}} e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi^A - \Delta\phi_{EQ}\right]} \tag{3.21}$$

Here we will assign a value for β to be one half, which is usually the value used for this parameter in the literature and which we will utilize throughout our calculations. So putting $\beta = \frac{1}{2}$ and calling $e^{\frac{1}{2}\frac{z_1 F}{RT}\left[\Delta\phi^A - \Delta\phi_{EQ}\right]} = Q$, equation (3.21) can be written as

$$Q^2 + \frac{z_1 F c_M U}{i_0} Q - \frac{c^A}{\overline{c}} = 0 \tag{3.22}$$

where this is a quadratic equation in Q whose solution

$$Q = e^{\frac{1}{2}\frac{z_1 F}{RT}\left[\Delta\phi^A - \Delta\phi_{EQ}\right]} = -\frac{1}{2}\frac{z_1 F c_M U}{i_0} \pm \frac{1}{2}\sqrt{\left(\frac{z_1 F c_M U}{i_0}\right)^2 + 4\frac{c^A}{\overline{c}}} \tag{3.23}$$

and since the left hand side cannot be anything except a positive number, we will reject the root corresponding to the negative sign of the second term on the right-hand side and take the natural logarithm of both sides of the equation to get

$$\frac{z_1 F}{RT}\left[\Delta\phi^A - \Delta\phi_{EQ}\right] = 2\ln\left(-\frac{1}{2}\frac{z_1 F c_M U}{i_0} + \frac{1}{2}\sqrt{\left(\frac{z_1 F c_M U}{i_0}\right)^2 + 4\frac{c^A}{\overline{c}}}\right) \tag{3.24}$$

Now turning to the B-V equation at the cathode, namely,

$$\frac{z_1 F c_M U}{i_0} = e^{[1-\beta]\frac{z_1 F}{RT}\left[\Delta\phi^C - \Delta\phi_{EQ}\right]} - \frac{c^C}{\overline{c}} e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi^C - \Delta\phi_{EQ}\right]} \tag{3.25}$$

and following the same procedure that helped us to get equation (3.24) from equation (3.21), we arrive at

$$\frac{z_1 F}{RT}\left[\Delta\phi^C - \Delta\phi_{EQ}\right] = 2\ln\left(\frac{1}{2}\frac{z_1 F c_M U}{i_0} + \frac{1}{2}\sqrt{\left(\frac{z_1 F c_M U}{i_0}\right)^2 + 4\frac{c^C}{\overline{c}}}\right) \tag{3.26}$$

then subtracting equation (3.26) from equation (3.24) and realizing that $\Delta\phi^A = V^A - \phi^A$ and $\Delta\phi^C = V^C - \phi^C$ along with the application of equation (3.20) we finally get

$$\begin{aligned}\frac{z_1 F}{RT}\left[V^A - V^C\right] = {} & 2\ln\left(-\frac{1}{2}\frac{z_1 F c_M U}{i_0} + \frac{1}{2}\sqrt{\left(\frac{z_1 F c_M U}{i_0}\right)^2 + 4\frac{c^A}{\overline{c}}}\right) + \frac{z_1}{z_2}\ln\frac{c^C}{c^A} \\ & -2\ln\left(\frac{1}{2}\frac{z_1 F c_M U}{i_0} + \frac{1}{2}\sqrt{\left(\frac{z_1 F c_M U}{i_0}\right)^2 + 4\frac{c^C}{\overline{c}}}\right)\end{aligned} \tag{3.27}$$

By obtaining this relation, we can now predict the velocity of the surface, U when the other input parameters, mainly $V^A - V^C$, are assigned. This completes the base solution. The next step will be to introduce the CRE approximation and see how it will simplify the base solution particularly equation (3.27).

3.1.2 Getting the Base Solution Using the CRE Approximation

The only place in the base solution where the effect of the CRE approximation will be apparent is in the relation between the voltage drop and the velocity of the surface. So all the equations obtained in the previous case will be valid here except equation (3.27).

Consider the B-V equation i.e., equation (2.38)

$$\vec{n}\cdot\vec{i} = i_0\left[e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}-\frac{\gamma}{z_1Fc_M}2H\right]} - \frac{c}{\bar{c}}e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}-\frac{\gamma}{z_1Fc_M}2H\right]}\right]$$

and as part of the chemical reaction equilibrium, use the equality of the two terms on the right-hand side to establish a relation between c and ϕ at each electrode surface. At CRE, the reaction will be so fast that i_0, the exchange current density which represents the speed of the reaction, will be much larger than $\vec{n}\cdot\vec{i}$ due to the difference between $e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}-\frac{\gamma}{z_1Fc_M}2H\right]}$ and $\frac{c}{\bar{c}}e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}-\frac{\gamma}{z_1Fc_M}2H\right]}$ being near zero. Moreover, for a flat surface where $2H = 0$ (since a plane surface has no curvature), the B-V equation at equilibrium can be simplified to

$$e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}\right]} - \frac{c}{\bar{c}}e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}\right]} = 0 \tag{3.28}$$

so the ratio $\frac{c}{\bar{c}}$ is

$$\frac{c}{\bar{c}} = e^{\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}\right]} \tag{3.29}$$

which with a little algebra becomes

$$\Delta\phi = \Delta\phi_{EQ} + \frac{RT}{z_1F}\ln\frac{c}{\bar{c}} \tag{3.30}$$

This equation can be written at the anode in the following form

$$\Delta\phi^A = \Delta\phi_{EQ} + \frac{RT}{z_1F}\ln\frac{c^A}{\bar{c}} \tag{3.31}$$

while at the cathode it is

$$\Delta\phi^C = \Delta\phi_{EQ} + \frac{RT}{z_1 F}\ln\frac{c^C}{\overline{c}} \tag{3.32}$$

then subtracting equation (3.32) from equation (3.31) and realizing that $\Delta\phi^A = V^A - \phi^A$ and $\Delta\phi^C = V^C - \phi^C$ along with the application of equation (3.20) one will arrive at

$$\frac{z_1 F}{RT}\left[V^A - V^C\right] = \left[1 - \frac{z_1}{z_2}\right]\ln\frac{c^A}{c^C} \tag{3.33}$$

where c^A and c^C are functions of U and are given by equations (3.15) and (3.16).

It is evident how the CRE lead us to a simpler relation between the voltage drop and the velocity of the surface, a simplification that will be crucial for further calculations as those that will be done in chapter 6. In addition to this major simplification, one can also realize that when the CRE is applied, the B-V equation will be replaced by the following equation

$$\frac{c}{\overline{c}} = e^{\frac{z_1 F}{RT}\left[\Delta\phi - \Delta\phi_{EQ} - \frac{\gamma}{z_1 F c_M}2H\right]} \tag{3.34}$$

Working with this equation will simplify the algebra when we decide to study the perturbation calculations or when we decide later to go study the nonlinear regime. One of the additional advantages of the CRE approximation is that we did not need to specify a value for β.

So after getting the base solution of the model and showing why the CRE approximation is useful, we are ready to continue our work and study the stability of the base solution. But before that, the signs of $\frac{dc}{dy}$ and $\frac{d\phi}{dy}$ will turn out to be important in the stability calculations. The next section will discuss what signs $\frac{dc}{dy}$ and $\frac{d\phi}{dy}$ possess.

3.1.3 The Signs of $\frac{dc}{dy}$ and $\frac{d\phi}{dy}$

The signs of $\frac{dc}{dy}$ and $\frac{d\phi}{dy}$ will be important when we study the stability of the base solution. To determine these signs, recall equation (3.11) viz.,

$$\frac{1}{\bar{c}}\frac{dc}{dy} = -\frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\frac{c_M}{\bar{c}}\frac{U}{D}$$

In this equation, we know the signs of all of the terms on the right hand side and see that as U is negative, z_1 is positive and z_2 is negative, as a result, $\frac{dc}{dy}$ is always negative.

Turning to $\frac{d\phi}{dy}$, consider equation (3.12) viz.,

$$\frac{d}{dy}\left[\frac{z_1 F}{RT}\phi\right] = \frac{z_1^2 c_M U}{D_1\left[z_1 - z_2\right]}\frac{1}{c}$$

It is obvious that the right hand side is always going to be negative since U is always negative. So finally we conclude that both $\frac{dc}{dy}$ and $\frac{d\phi}{dy}$ are always negative.

3.2 The Perturbation Problem

In this and in the following section, a perturbation method will be used to investigate the stability of the base solution when current is drawn and a small disturbance is introduced to the surface. The growing interface is considered to be morphologically stable when any infinitesimal perturbation introduced to the electrode surface decays with time. On the other hand, when the perturbation grows with time, the interface is regarded as morphologically unstable.

The perturbations that we carry out here namely, domain perturbations, are different from the regular type of perturbations. The domain perturbations shall be carried out in a region where its shape is not known and needs to be found as the movement of the boundary will change the boundary conditions that one is familiar with. The problem will not be solved on the unknown domain (i.e., the present domain) but it will be solved on the original domain namely, the reference domain. For more information on how to perform domain perturbations, the reader can refer to Appendix B where the method is explained in detail.

Now the base solution will be denoted by affixing the subscript zero to the base variables. It is defined on the reference domain i.e.,

$$0 < y_0 < L_0, \quad -\infty < x_0 < \infty$$

where x_0 represent the transverse direction and by requiring this direction to extend from $-\infty$ to ∞, it is obvious that we are performing our calculations with a cell of infinite width (i.e., no boundaries in the transverse direction).

In order to investigate the stability of the base solution, a small displacement is imposed on the shape of the electrode surfaces. Taking ε to denote the amplitude of this displacement, the new displaced domain which now lies between the surfaces viz.,

$$y = Y^A(x,t,\varepsilon) \tag{3.35}$$

and

$$y = Y^C(x,t,\varepsilon) \tag{3.36}$$

will be the current domain. Figure 3-1 depicts both the reference surface and the current surface.

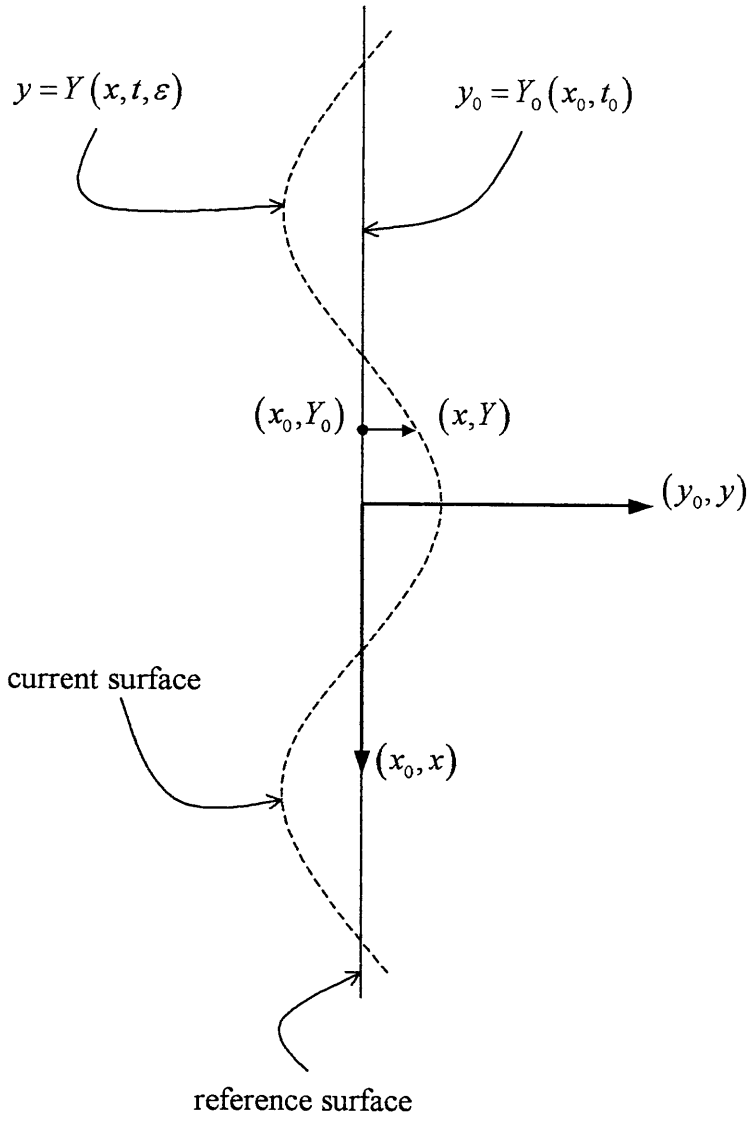


Figure 3-1. The Perturbed Surface.

These perturbed surfaces are taken to be near the planar surfaces in the base solution (i.e., $y = Y_0^A$ and $y = Y_0^C$) and can be expressed as

$$Y^A = Y_0^A + \varepsilon Y_1^A(x_0,t_0) + \ldots \tag{3.37}$$

and

$$Y^C = Y_0^C + \varepsilon\, Y_1^C(x_0,t_0) + \ldots \tag{3.38}$$

to account for a small disturbance at the reference or the base surface, where $Y_0^A = 0$ and $Y_0^C = L_0$ while Y_1^A and Y_1^C determine the displacement of the surfaces to order ε. It is important to note that the shape of the surface is specified at only one instant of time, after that, it is part of the solution to the problem and it must be found.

The plan is to turn the nonlinear problem on the current domain into a sequence of problems on the reference domain. This sequence corresponds to an expansion in powers of ε and it starts out with the base problem at zeroth order, being succeeded in turn by the perturbation problem at first order. Our interest here is in the first order problem.

The surface variables (i.e., the surface normal, the surface local velocity and the surface curvature) acquire their expansions via the expansion of Y, however, domain variables evaluated at the surface are expanded in the form

$$c = c_0 + \varepsilon\left[c_1 + Y_1 \frac{dc_0}{dy_0}\right] + \ldots \tag{3.39}$$

and

$$\phi = \phi_0 + \varepsilon\left[\phi_1 + Y_1 \frac{d\phi_0}{dy_0}\right] + \ldots \tag{3.40}$$

Here c_1 and ϕ_1 are functions of x_0, y_0 and t_0 and the subscript 1 no longer stands for species 1 but stands for the term arising in the expansion of a variable in powers of ε, except in the case of z_1.

Before going on to the stability criteria, it is essential to draw the reader's attention to the input variables that are going to be set when running an experiment. The next section will explain what the control variables are.

3.2.1 The Input Variables to the Electrodeposition Problem

Every experiment has three types of variables: input or control variables, process variables and output variables. The stability analysis is intended to predict whether the system is stable or unstable for certain input variables. The input variables to the electrodeposition problem are

1. The distance between the two electrodes, L_0.
2. The average molar concentration of the electrolytic solution, $\bar{c}$.
3. The electrical potential drop, $V^A - V^C$.

The total current drawn by the cell is an output variable. Now let us proceed to find the perturbation equations once L_0, $\bar{c}$ and $V^A - V^C$ are set.

3.2.2 The Perturbation Equations at Fixed Values of L_0, $\bar{c}$ and $V^A - V^C$

The perturbation equations can be obtained by substituting the expansions for c, ϕ, Y^A and Y^C into the nonlinear equations. Collecting the terms to first order in ε will produce the perturbation equations. To solve these equations, we will turn our problem into an eigenvalue problem by taking the time dependence to be of the form $e^{\sigma t_0}$. The variable σ is the growth constant or the eigenvalue by which one can decide whether a perturbation will grow or die. If the real part of σ is greater than zero, the process is unstable, and the perturbations that are in the form of the eigenfunctions for a positive σ will grow and for an initial condition that does not have that component the perturbations will not grow. If the real part of σ is smaller than zero for all perturbations, the system is stable, and the electrode surface will always return to its flat state.

Now when we put in the substitutions for Y^A, Y^C, c and ϕ given by equations (3.37)-(3.40), we get equations which at first order need to be solved for the variables c_1,

ϕ_1, Y_1^A and Y_1^C. These equations will be homogeneous and we have solutions for certain $\sigma's$. The solutions are of the form

$$c_1 = \hat{c}_1(y_0)e^{\sigma t_0}e^{ikx_0} \tag{3.41}$$

$$\phi_1 = \hat{\phi}_1(y_0)e^{\sigma t_0}e^{ikx_0} \tag{3.42}$$

$$Y_1^A = \hat{Y}_1^A(y_0)e^{\sigma t_0}e^{ikx_0} \tag{3.43}$$

and

$$Y_1^C = \hat{Y}_1^C(y_0)e^{\sigma t_0}e^{ikx_0} \tag{3.44}$$

where k is the wave number which is inversely proportional to the wavelength.

Substituting the expansions given by equations (3.39) and (3.40) for c and ϕ into equations (2.32) and (2.33) and using the separation of variables i.e., equations (3.41) and (3.42) will lead to the equations for $\hat{c}_1$ and $\hat{\phi}_1$ on the reference domain, $0 < y_0 < L_0$. These equations are

$$D\left[\frac{d^2}{dy_0^2} - k^2\right]\hat{c}_1 = \sigma\hat{c}_1 \tag{3.45}$$

and

$$\begin{aligned} P\left[\frac{d^2}{dy_0^2} - k^2\right]\hat{c}_1 + \frac{dc_0}{dy_0}\left[\frac{z_1F}{RT}\right]\frac{d\hat{\phi}_1}{dy_0} + c_0\left[\frac{z_1F}{RT}\right]\left[\frac{d^2}{dy_0^2} - k^2\right]\hat{\phi}_1 \\ + \left[\frac{z_1F}{RT}\right]\frac{d\phi_0}{dy_0}\frac{d\hat{c}_1}{dy_0} + \left[\frac{z_1F}{RT}\right]\frac{d^2\phi_0}{dy_0^2}\hat{c}_1 = 0 \end{aligned} \tag{3.46}$$

Turning to the boundary equations, the equations at the anode-solution interface are obtained and the same procedure is used to find the equations at the cathode-solution interface. First, remember that

$$Y = Y_0 + \varepsilon Y_1 + \ldots$$

and consider the expansion of the boundary variables (i.e., $\vec{n}$, $u = \vec{n} \cdot \vec{u}$ and $2H$) to the first order. At the anode we have

$$\vec{n}^A = \vec{j} - \varepsilon \frac{\partial Y_1^A}{\partial x_0} \vec{i} \tag{3.47}$$

$$u^A = \varepsilon \frac{\partial Y_1^A}{\partial t_0} \tag{3.48}$$

and

$$2H^A = \varepsilon \frac{\partial^2 Y_1^A}{\partial x_0^2} \tag{3.49}$$

then turn to equation (2.35) viz.,

$$P\vec{n} \cdot \nabla c + c\left[\frac{z_1 F}{RT}\right] \vec{n} \cdot \nabla \phi = \frac{z_1^2}{z_1 D_1 - z_2 D_2} c_M \left[\vec{n} \cdot \vec{u} + \vec{n} \cdot \vec{U}\right]$$

To get the perturbed equation at the anode, write

$$\nabla c = \nabla_0 c_0 + \varepsilon \left[\nabla_0 c_1 + Y_1 \frac{d}{dy_0} \nabla_0 c_0 \right] \tag{3.50}$$

and

$$\nabla \phi = \nabla_0 \phi_0 + \varepsilon \left[\nabla_0 \phi_1 + Y_1 \frac{d}{dy_0} \nabla_0 \phi_0 \right] \tag{3.51}$$

and notice that $\vec{U}$, $\nabla_0 c_0$ and $\nabla_0 \phi_0$ all lie in the $\vec{j}$ direction. Using the expansions of $\vec{n}$ and ∇c, $\vec{n} \cdot \nabla c$ can be found to be

$$\vec{n} \cdot \nabla c = \frac{dc_0}{dy_0} + \varepsilon \left[\frac{\partial c_1}{\partial y_0} + Y_1 \frac{d^2 c_0}{dy_0^2} \right] \tag{3.52}$$

Likewise, the expansions of c, $\vec{n}$ and $\nabla \phi$ lead to

$$c\vec{n}\cdot\nabla\phi = c_0\frac{d\phi_0}{dy_0} + \varepsilon\left[\left[c_1 + Y_1\frac{dc_0}{dy_0}\right]\frac{d\phi_0}{dy_0} + c_0\left[\frac{\partial\phi_1}{\partial y_0} + Y_1\frac{d^2\phi_0}{dy_0^2}\right]\right] \tag{3.53}$$

The first order equations appear when these are substituted into equation (2.35), the nonlinear equation, and equation (3.4) is used to eliminate the term

$$Y_1\left[P\frac{d^2c_0}{dy_0^2} + \frac{dc_0}{dy_0}\left[\frac{z_1F}{RT}\right]\frac{d\phi_0}{dy_0} + c_0\left[\frac{z_1F}{RT}\right]\frac{d^2\phi_0}{dy_0^2}\right] \tag{3.54}$$

which would otherwise appear on the left hand side. The perturbed version of equation (2.35) is then

$$P\frac{d\hat{c}_1}{dy_0} + c_0\left[\frac{z_1F}{RT}\right]\frac{d\hat{\phi}_1}{dy_0} + \left[\frac{z_1F}{RT}\right]\frac{d\phi_0}{dy_0}\hat{c}_1 = \frac{z_1^2}{z_1D_1 - z_2D_2}c_M\sigma\hat{Y}_1^A \tag{3.55}$$

By following the same steps, the perturbed version of equation (2.34) at the anode when convection is neglected is

$$D\frac{d\hat{c}_1}{dy_0} = -\frac{z_1z_2D_2}{z_1D_1 - z_2D_2}c_M\sigma\hat{Y}_1^A \tag{3.56}$$

The last equation at the anode comes from the B-V equation. Starting with the B-V equation at the anode viz.,

$$i_y^A = -z_1Fc_MU = i_0\left[e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi^A - \Delta\phi_{EQ} - \frac{\gamma}{z_1Fc_M}2H\right]} - \frac{c^A}{\overline{c}}e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi^A - \Delta\phi_{EQ} - \frac{\gamma}{z_1Fc_M}2H\right]}\right] \tag{3.57}$$

and assuming chemical reaction equilibrium, we get as explained earlier

$$e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi^A - \Delta\phi_{EQ} - \frac{\gamma}{z_1Fc_M}2H\right]} - \frac{c^A}{\overline{c}}e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi^A - \Delta\phi_{EQ} - \frac{\gamma}{z_1Fc_M}2H\right]} = 0 \tag{3.58}$$

which will reduce to

$$\frac{c^A}{\overline{c}} = e^{\frac{z_1F}{RT}\left[V^A - \phi^A - \Delta\phi_{EQ} - \frac{\gamma}{z_1Fc_M}2H\right]} \tag{3.59}$$

Substituting the perturbed forms for c^A, ϕ^A and $2H$ and using the Taylor series expansion: $e^{-x} = 1 - x$ where $x = \varepsilon \frac{z_1 F}{RT}\left[\phi_1 + \frac{d\phi_0}{dy_0} Y_1^A + \frac{\gamma}{z_1 F c_M}\frac{\partial^2 Y_1^A}{\partial x_0^2}\right]$ in the resulting equation then applying the separation of variables given by equations (3.41)-(3.43) we get

$$\frac{z_1 F}{RT}\left[-\hat{\phi}_1^A - \hat{Y}_1^A \frac{d\phi_0^A}{dy_0} + \frac{\gamma}{z_1 F c_M} k^2 \hat{Y}_1^A\right] = e^{-\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{RQ}\right]}\left[\frac{\hat{c}_1^A}{\overline{c}} + \hat{Y}_1^A \frac{dc_0^A/dy_0}{\overline{c}}\right] \tag{3.60}$$

where $\Delta\hat{\phi}_1^A = -\hat{\phi}_1^A$ as V^A is fixed.

Likewise, by following the same procedure at the cathode, the corresponding equations can be written

$$D\frac{d\hat{c}_1}{dy_0} = -\frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} c_M \sigma \hat{Y}_1^C \tag{3.61}$$

$$P\frac{d\hat{c}_1}{dy_0} + c_0\left[\frac{z_1 F}{RT}\right]\frac{d\hat{\phi}_1}{dy_0} + \left[\frac{z_1 F}{RT}\right]\frac{d\phi_0}{dy_0}\hat{c}_1 = \frac{z_1^2}{z_1 D_1 - z_2 D_2} c_M \sigma \hat{Y}_1^C \tag{3.62}$$

and

$$\frac{z_1 F}{RT}\left[-\hat{\phi}_1^C - \hat{Y}_1^C \frac{d\phi_0^C}{dy_0} - \frac{\gamma}{z_1 F c_M} k^2 \hat{Y}_1^C\right] = e^{-\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{RQ}\right]}\left[\frac{\hat{c}_1^C}{\overline{c}} + \hat{Y}_1^C \frac{dc_0^C/dy_0}{\overline{c}}\right] \tag{3.63}$$

where $\Delta\hat{\phi}_1^C = -\hat{\phi}_1^C$ as V^C is a constant.

In summary, what we have done in this section is to find the perturbation equations on the domain and at both electrodes. Equations (3.45) and (3.46) are the perturbed equations on the domain. At the anode three perturbed equations were obtained namely (3.55), (3.56) and (3.60) while at the cathode the three equations were (3.61), (3.62) and (3.63).

Having these equations, we solve for $\hat{c}_1$, $\hat{\phi}_1$, $\hat{Y}_1^A$ and $\hat{Y}_1^C$. There will be certain $\sigma's$ for which these are not all zero. But k^2 is now an input and our target is to find $\hat{c}_1$, $\hat{\phi}_1$, $\hat{Y}_1^A$ and $\hat{Y}_1^C$ given both k^2 and σ. We ask under what conditions $\sigma = 0$ is possible.

3.3 The Stability of the Base Solution when Current Passes Through the Cell

Once we put $\sigma = 0$ in the perturbation eigenvalue problem, it will be turned into an eigenvalue problem in k^2 which becomes the output to the problem and the values of k^2 at which this problem has a solution other than $\hat{c}_1$, $\hat{\phi}_1$, $\hat{Y}_1^A$ and $\hat{Y}_1^C$ all zero are then the critical values of k^2 (i.e., $k^2_{critical}$).

On the domain (i.e., $0 < y_0 < L_0$) by setting $\sigma = 0$ equations (3.45) and (3.46) become

$$D\left[\frac{d^2}{dy_0^2} - k^2\right]\hat{c}_1 = 0 \tag{3.64}$$

and

$$\begin{aligned} P\left[\frac{d^2}{dy_0^2} - k^2\right]\hat{c}_1 + \frac{dc_0}{dy_0}\left[\frac{z_1F}{RT}\right]\frac{d\hat{\phi}_1}{dy_0} + c_0\left[\frac{z_1F}{RT}\right]\left[\frac{d^2}{dy_0^2} - k^2\right]\hat{\phi}_1 \\ + \left[\frac{z_1F}{RT}\right]\frac{d\phi_0}{dy_0}\frac{d\hat{c}_1}{dy_0} + \left[\frac{z_1F}{RT}\right]\frac{d^2\phi_0}{dy_0^2}\hat{c}_1 = 0 \end{aligned} \tag{3.65}$$

and at the boundaries (i.e., at $y_0 = 0$ and $y_0 = L_0$) equations (3.55) and (3.62) will take the form

$$P\frac{d\hat{c}_1}{dy_0} + c_0\left[\frac{z_1F}{RT}\right]\frac{d\hat{\phi}_1}{dy_0} + \left[\frac{z_1F}{RT}\right]\frac{d\phi_0}{dy_0}\hat{c}_1 = 0 \tag{3.66}$$

while equations (3.56) and (3.61) become

$$D\frac{d\hat{c}_1}{dy_0} = 0 \tag{3.67}$$

In these equations, we notice that $\hat{c}_1$ and $\hat{\phi}_1$ appear, but Y_1^A and Y_1^C do not, coming in only the perturbed CRE equations at $y_0 = 0$ and at $y_0 = L_0$.

Now equation (3.64) can be satisfied by writing

$$\hat{c}_1 = Ae^{ky_0} + Be^{-ky_0} \tag{3.68}$$

where A and B must be set in order to satisfy equation (3.67) at both $y_0 = 0$ and $y_0 = L_0$. This requires

$$k\,A - k\,B = 0 \tag{3.69}$$

and

$$e^{kL_0}k\,A - e^{-kL_0}k\,B = 0 \tag{3.70}$$

whereupon $A = 0 = B$ due to the fact that

$$\det\begin{pmatrix} k & -k \\ e^{kL_0}k & -e^{-kL_0}k \end{pmatrix} = -k^2\left[e^{-kL_0} - e^{kL_0}\right] \tag{3.71}$$

and this is not zero so long as k^2 is not zero. By this $\hat{c}_1$ must be zero and substituting $\hat{c}_1 = 0$ into equation (3.65), $\hat{\phi}_1$ must satisfy

$$\frac{d}{dy_0}\left[c_0\frac{d\hat{\phi}_1}{dy_0}\right] - k^2c_0\hat{\phi}_1 = 0 \tag{3.72}$$

on $0 < y_0 < L_0$ and

$$c_0\frac{d\hat{\phi}_1}{dy_0} = 0 \tag{3.73}$$

at $y_0 = 0$ and $y_0 = L_0$. Now as c_0 is positive for all values of y_0, equation (3.73) has only the solution $\hat{\phi}_1 = 0$.

Our first conclusion then is that at neutral conditions $\hat{c}_1$ and $\hat{\phi}_1$ must both vanish and by this the critical value of k^2 must come out of the perturbed CRE equations. Now in order to get $\hat{Y}_1^A$, and after setting $\hat{c}_1$ and $\hat{\phi}_1$ equal to zero, the CRE equation at the anode is

$$\left[-\frac{z_1 F}{RT}\frac{d\phi_0^A}{dy_0}+\frac{\gamma}{c_M RT}k^2\right]\hat{Y}_1^A - e^{-\frac{z_1 F}{RT}\left[-\phi_0^A-\Delta\phi_{EQ}\right]}\left[\frac{1}{\bar{c}}\frac{dc_0^A}{dy_0}\right]\hat{Y}_1^A = 0 \qquad (3.74)$$

and when $\hat{Y}_1^A$ is taken as a common factor, we arrive at

$$\left[-\frac{z_1 F}{RT}\frac{d\phi_0^A}{dy_0}+\frac{\gamma}{c_M RT}k^2 - e^{-\frac{z_1 F}{RT}\left[-\phi_0^A-\Delta\phi_{EQ}\right]}\left(\frac{1}{\bar{c}}\frac{dc_0^A}{dy_0}\right)\right]\hat{Y}_1^A = 0 \qquad (3.75)$$

This equation is a linear, homogeneous equation in $\hat{Y}_1^A$ and as $\frac{d\phi_0^A}{dy_0}$ and $\frac{dc_0^A}{dy_0}$ must both be negative, the factor multiplying $\hat{Y}_1^A$ cannot vanish. So the only solution is $\hat{Y}_1^A = 0$. This tells us that the eigenfunctions at $\sigma = 0$ is now known to be $\hat{c}_1 = 0$, $\hat{\phi}_1 = 0$ and $\hat{Y}_1^A = 0$ with $\hat{Y}_1^C$ yet to be found.

At the cathode after setting σ, $\hat{c}_1^C$ and $\hat{\phi}_1^C$ to zero, the perturbed CRE equation after taking $\hat{Y}_1^C$ as a common factor becomes

$$\left[-\frac{\gamma}{c_M RT}k^2 - \frac{z_1 F}{RT}\frac{d\phi_0^C}{dy_0} - e^{-\frac{z_1 F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{EQ}\right]}\left(\frac{1}{\bar{c}}\frac{dc_0^C}{dy_0}\right)\right]\hat{Y}_1^C = 0 \qquad (3.76)$$

This is a linear, homogeneous equation in $\hat{Y}_1^C$ and it has a solution other than $\hat{Y}_1^C = 0$ if k^2 can be chosen so that the factor multiplying $\hat{Y}_1^C$ can be made to vanish. In this equation, we have three terms multiplying $\hat{Y}_1^C$. Two of these terms have the same sign, namely, the second and the third, while the first, which stands for the surface tension, has a different sign and it must be the stabilizing term.

As a result, the cathode alone, not the anode, determines the critical value of k^2 given L_0, $\bar{c}$ and $V^A - V^C$. The only difference between equations (3.74) and (3.76) is the sign of the term $\frac{\gamma}{c_M RT}k^2$. Setting the factor multiplying $\hat{Y}_1^C$ to zero leads to the critical wave number

$$\frac{\gamma}{c_M RT}k^2_{critical} = -\frac{z_1 F}{RT}\frac{d\phi_0^C}{dy_0} - \frac{1}{e^{\frac{z_1 F}{RT}\left[V^C - \phi_0^C - \Delta\phi_{EQ}\right]}}\frac{1}{\bar{c}}\frac{dc_0^C}{dy_0} \tag{3.77}$$

This equation is explicit in $k^2_{critical}$ and one can see that all the input variables appear on the right-hand side and the way they will affect $k^2_{critical}$ is known since we have formulas for every term in equation (3.77). It is obvious that increasing the electrical potential and the concentration gradients will increase $k^2_{critical}$ while increasing the surface tension will decrease it.

The above equation is the heart of this chapter. It gives the boundary between the stable and unstable regions and it also shows that every problem is unstable if all k^2 are allowed. So, given the input variables, one can then decide the critical wave number below which the cell will become unstable.

If the B-V equation was used instead of the CRE in sections 3.4 and 3.5, then one will reach the same conclusions regarding $\hat{c}_1$, $\hat{\phi}_1$ and $\hat{Y}_1^A$. When solving for $\hat{Y}_1^C$, the cathode will still determine the critical values of k^2 by the following equation

$$\frac{\gamma}{c_M RT} k_{critical}^2 = -\frac{z_1 F}{RT}\frac{d\phi_0^C}{dy_0} - \frac{1}{[1-\beta]e^{\frac{z_1 F}{RT}\left[V^C - \phi_0^C - \Delta\phi_{EQ}\right]} + \beta\frac{c_0^C}{\overline{c}}}\frac{1}{\overline{c}}\frac{dc_0^C}{dy_0} \qquad (3.78)$$

It is obvious that this equation is very close to equation (3.77) with only two little differences. The first is that $e^{\frac{z_1 F}{RT}\left[V^C - \phi_0^C - \Delta\phi_{EQ}\right]}$ is multiplied by a constant (i.e., $1-\beta$). The second is the appearance of the term $\beta\frac{c_0^C}{\overline{c}}$ added to $[1-\beta]e^{\frac{z_1 F}{RT}\left[V^C - \phi_0^C - \Delta\phi_{EQ}\right]}$. These are not huge differences and one can comment then that the real benefit of using the CRE approximation is to simplify the base solution.

So what is left now is to compare the results that are obtained upon using equations (3.77) and (3.78) to evaluate our approximation. In order to do this we will draw graphs using these two equations for the copper/copper sulphate system. But before that, let us introduce the concept of the limiting current, $U_{\lim}$, and write equation (3.77) as a function of $U_{\lim}$ so the comparison can be made.

3.4 Putting the Solution in Terms of the Limiting Current $U_{\lim}$

In order to compare the results obtained from this study with previous work by Sundström and Bark (1995) and Johns and Narayanan (2002), we define $U_{\lim}$ which is the limiting speed corresponding to the limiting current $I_{\lim}$. When values for $\overline{c}$ and L_0 are assigned, there is a limiting current that corresponds to c^C; the ion concentration at

the cathode, falling to zero as $V^A - V^C$ increases to infinity. To get the expression for $U_{\lim}$, refer to equation (3.16) and set c^C to zero to obtain

$$U_{\lim} = \frac{2}{L_0}\frac{z_1 D_1 - z_2 D_2}{z_1 z_2 D_2} D \frac{\overline{c}}{c_M} \tag{3.79}$$

Now $\frac{dc_0^C}{dy_0}$, $\frac{d\phi_0^C}{dy_0}$, c_0^A and c_0^C can be evaluated directly in terms of $U_{\lim}$. We see that

$$-\frac{1}{\overline{c}}\frac{dc_0^C}{dy_0} = \frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\frac{c_M}{\overline{c}}\frac{U}{D} = \frac{2}{L_0}\frac{U}{U_{\lim}} \tag{3.80}$$

$$-\frac{d}{dy_0}\left[\frac{z_1 F}{RT}\phi_0\right]^C = -\frac{z_1^2 c_M U}{D_1[z_1 - z_2]}\frac{1}{c_0^C} = \frac{z_1}{-z_2}\frac{2}{L_0}\frac{U/U_{\lim}}{1 - U/U_{\lim}} \tag{3.81}$$

$$\frac{c_o^A}{\overline{c}} = 1 + \frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\frac{c_M}{\overline{c}}\frac{U}{D}\frac{1}{2}L_0 = 1 + \frac{U}{U_{\lim}} \tag{3.82}$$

and

$$\frac{c_o^C}{\overline{c}} = 1 - \frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\frac{c_M}{\overline{c}}\frac{U}{D}\frac{1}{2}L_0 = 1 - \frac{U}{U_{\lim}} \tag{3.83}$$

In addition, the term $e^{\frac{z_1 F}{RT}\left[V^C - \phi_0^C - \Delta\phi_{EQ}\right]}$, which appears in equation (3.77), can be written in terms of $U/U_{\lim}$ using equations (3.29) and (3.83) to get

$$e^{\frac{z_1 F}{RT}\left[V^C - \phi_0^C - \Delta\phi_{EQ}\right]} = 1 - \frac{U}{U_{\lim}} \tag{3.84}$$

This relation is needed in order to be able to draw the figures for the critical wave number using equation (3.77).

Finally, the voltage drop and the velocity of the surfaces can be related simply by the use of $U_{\lim}$, namely,

$$\frac{z_1 F}{RT}\left[V^A - V^C\right] = \left[1 - \frac{z_1}{z_2}\right] \ln\left[\frac{1 + \dfrac{U}{U_{\lim}}}{1 - \dfrac{U}{U_{\lim}}}\right] \tag{3.85}$$

It is obvious in this equation how $\left[V^A - V^C\right]$ and $\dfrac{U}{U_{\lim}}$ are related. Increasing $\left[V^A - V^C\right]$ will increase $U/U_{\lim}$ and vise versa.

Now if we look at equations (3.80)-(3.84), it is clear that U or $U/U_{\lim}$ appears in all of these equations not $\left[V^A - V^C\right]$, except equation (3.85) which originates from the B-V equation. Consequently, it is extremely convenient to regard $U/U_{\lim}$ as the control variable even if it is really not. We shall refer to $U/U_{\lim}$ as the current because it is proportional to the current. Moreover, it is determined by the voltage drop which is our true input variable. So from here on, we are going to draw our graphs as though $U/U_{\lim}$ is the control variable and we shall use $U/U_{\lim}$ interchangeably with $I/I_{\lim}$.

3.5 Results, Discussion and Comparison with Previous Work

In this section, the results obtained from the stability analysis of the CRE model will be applied to the copper/copper sulphate system. Graphs of the critical wave number, $k^2_{critical}$, as a function of the control parameters will be drawn using data given in Table 3-1 for the copper/copper sulphate system. It will be shown that the CRE model is very successful in matching the results obtained using the full B-V equation. The last part of this section, will explain the reason behind this agreement.

Before giving any graphs, an important point must be raised here. Based on equation (3.77) for the critical wave number, we learned that the system is always unstable if all k^2 are allowed except at equilibrium where $\left[V^A - V^C\right] = 0$ and $k^2_{critical} = 0$.

Table 3-1. Data for the copper/copper sulphate system.

Parameters, Input, Output, Constants	Symbol	Value
Density of copper deposited (kg/m^3)	ρ_M	8920
Density of electrolyte (kg/m^3)	ρ	1015
Charge number of cupric ions	z_1	+2
Charge number of sulphate ions	z_2	-2
Molar mass of cupric ion (kg/kg-mole)	M_1	63.54
Isotropic surface energy/surface tension of electrode-electrolyte interface (J/m^2)	γ	1.5
Temperature of electrolyte (K)	T	298
Diffusion coefficient of cupric ions (m^2/sec)	D_1	$7.2\text{x}10^{-10}$
Diffusion coefficient of sulphate ions (m^2/sec)	D_2	$1.07\text{x}10^{-9}$
Equilibrium exchange current density for flat electrode at the average concentration and temperature (A/m^2)	i_0	10 for $\bar{c}$ = 0.1 kg-mole/m^3 3.16 for $\bar{c}$ = 0.01 kg-mole/m^3
Distance between electrodes (m)	L_0	Varied
Current density (A/m^2)	i	Varied
Current passed (A)	I	Varied
Gas constant (J/kg-mole.K)	R	8314
Faraday's constant (A.sec/kg-mole)	F	$9.65\text{x}10^{7}$
A factor describing the activation step	β	0.5

This is because we have assumed in our calculations infinitely wide electrodes so that all wave numbers are possible. But then one might wonder about the meaning of $k^2_{critical}$ that separates the stable from the unstable regions.

The only way then to have a stable system while having a potential drop across the cell is to run a finite width cell so long wave lengths (i.e., small wave numbers) will be cut off. If we were successful in eliminating the unstable disturbances then we will have stable wave numbers that we can look at and the system might be called stable.

To clarify what is meant by the above discussion and to help the reader understand the figures to come, Figure 3-2 is given. Figure 3-2 shows that there is a value of the critical wave number that separates the stable from the unstable region. As the critical wave number increases, the stable region decreases. So disturbances with wave numbers greater than the critical will render the cell stable, otherwise, it will be unstable. It is clear from Figure 3-2 that increasing the potential difference or $U/U_{\lim}$ will make the cell more unstable by decreasing the stable region and increasing the unstable region.

3.5.1 Main Results and Discussion

Figure 3-3 is drawn using equation (3.77) with equations (3.79)-(3.85) and the data in Table 3-1. Figure 3-3 shows the effect of the current in the cell, $U/U_{\lim}$ on the critical wave number, $k^2_{critical}$. As seen in the figure, as $U/U_{\lim}$ increases at a fixed L_0 and $\bar{c}$, the critical wave number also increases, hence $U/U_{\lim}$ can be thought as a driving force for instability. This can be explained by looking at equation (3.85) and referring to Figure1-5. It is known from the base solution that increasing $U/U_{\lim}$, which is similar to increasing $V^A - V^C$, will increase the gradients of both the concentration and the

electrical potential according to equations (3.80) and (3.81) making the cell more unstable.

Another thing that we can learn from Figure 3-3 is that any increase in the electrode spacing, L_0, at a constant U/U_{lim} moves the curve to the more stable side. This is because increasing the distance between the electrodes at a constant U/U_{lim} will decrease the concentration and the electrical potential gradients leading to the opposite effect to what is explained above.

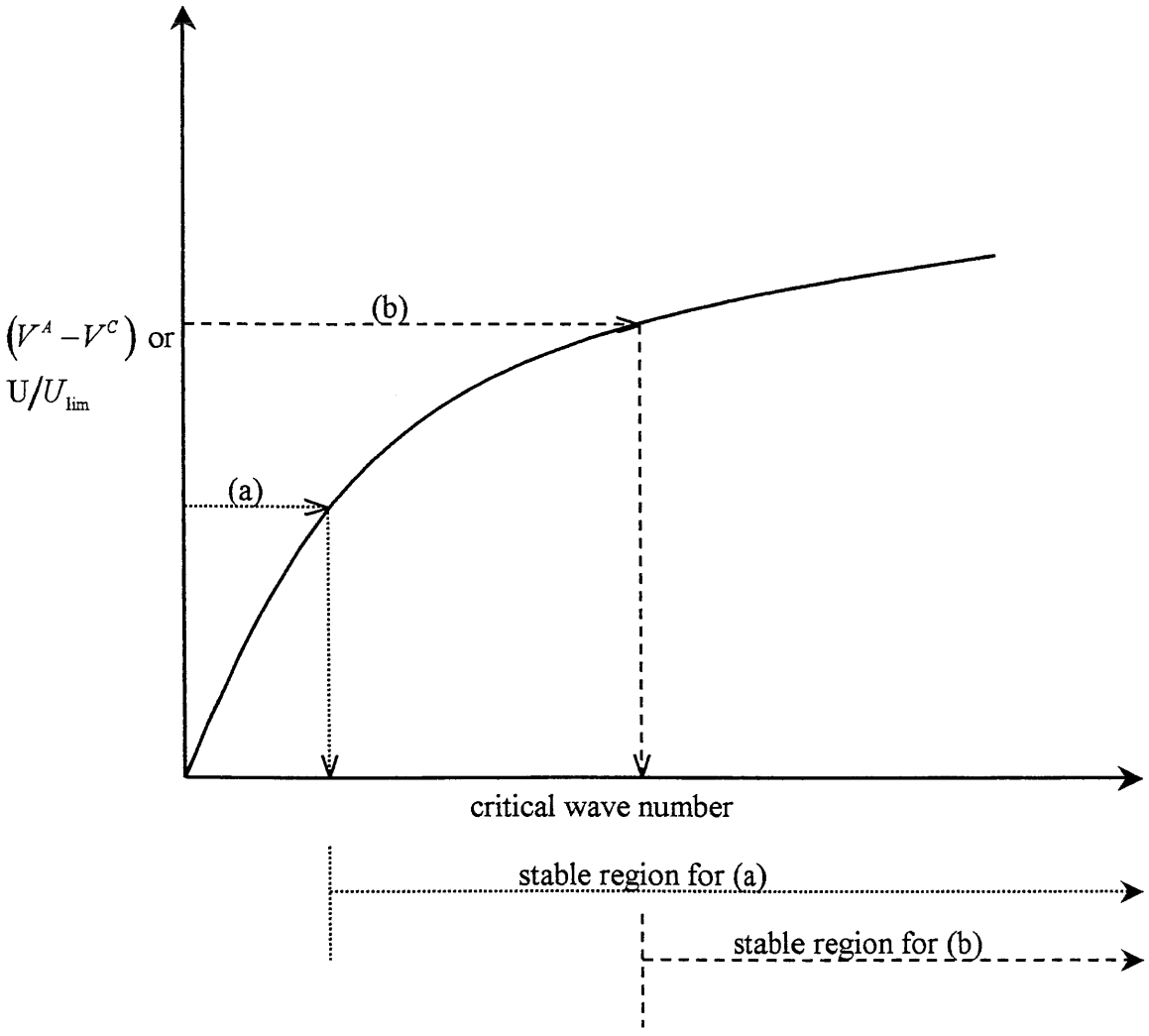


Figure 3-2. As $V^A - V^C$ or U/U_{lim} increases, the critical wave number increases and the stable region is reduced.

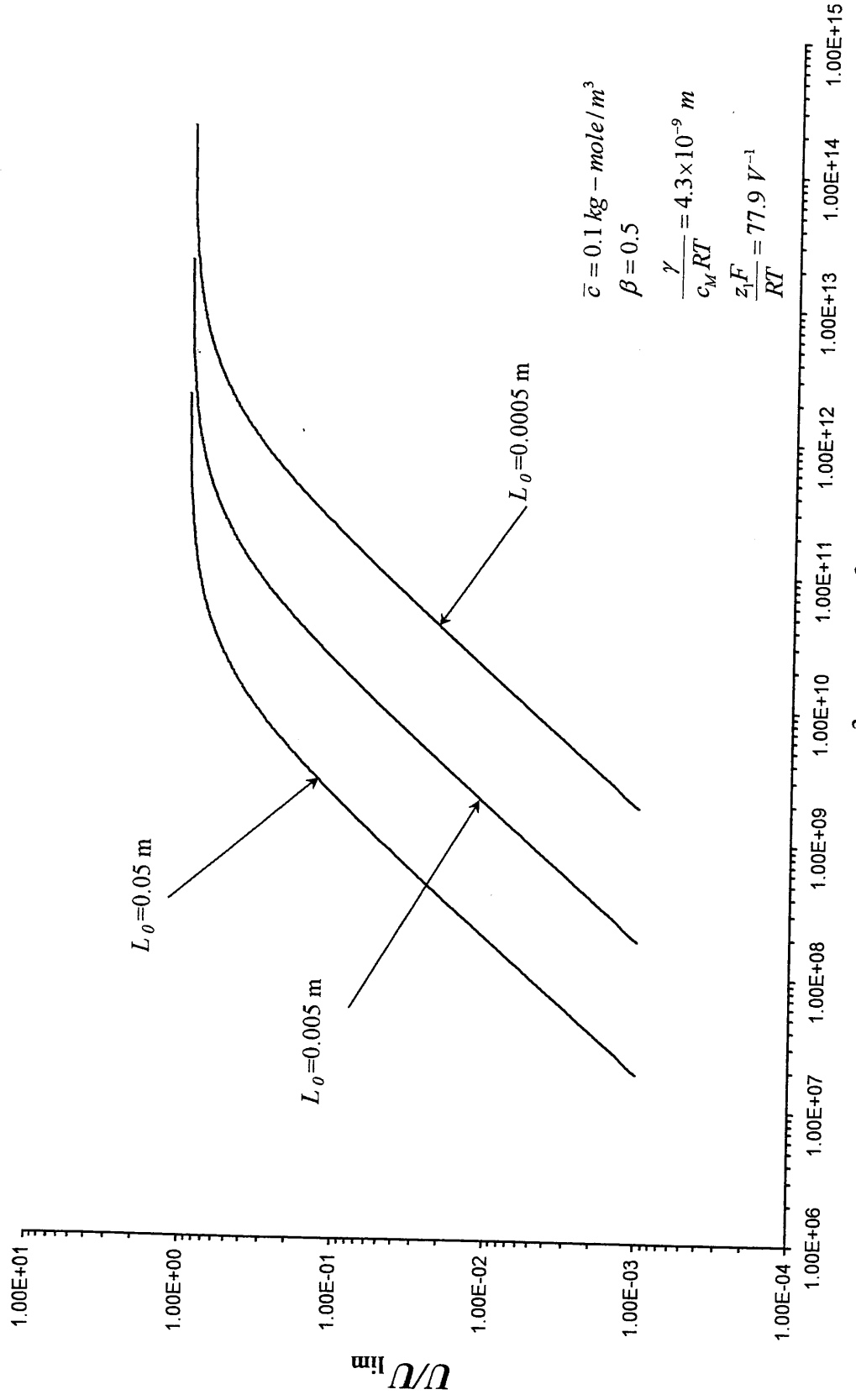


Figure 3-3. The effect of U/U_{lim} on the critical wave number for different electrode spacing.

Now to explain why the curves behave differently at lower values of $U/U_{\lim}$ than at higher ones in Figure 3-3, we need to focus on equation (3.77). When we write the right hand side of equation (3.77) in terms of $U/U_{\lim}$ and set $z_1 = 2$ and $z_2 = -2$ we get the following relation between $k^2_{critical}$ and $U/U_{\lim}$

$$\frac{\gamma}{c_M RT} k^2_{critical} = \frac{4}{L_0} \frac{U/U_{\lim}}{1 - U/U_{\lim}} \tag{3.86}$$

So at low values of $U/U_{\lim}$ the right hand side of equation (3.86) can be approximated by $\frac{4}{L_0}\frac{U}{U_{\lim}}$ since the denominator will be close to unity due to the small values of $U/U_{\lim}$. This explains the linear portion of the curves and then the effect of increasing L_0 will just be in shifting the lines to the left giving smaller $k^2_{critical}$ without affecting the slope of the lines. On the other hand, when $U/U_{\lim}$ is close to unity, then the denominator of the right hand side of equation (3.86) will be very small leading to the sharp increase in $k^2_{critical}$ and the leveling off of the curves.

We can think of Figure 3-3 as having two parts. One part-the linear portion- is due to diffusion and migration, which is the low $U/U_{\lim}$ part. And the second part at large values $U/U_{\lim}$ is mainly due to migration. So at very large values of $U/U_{\lim}$, the electrical potential gradient will become very large so $k^2_{critical}$ will grow exponentially and the cathode will become more unstable.

After studying the effect of changing $U/U_{\lim}$ and L_0 on the stability of the system, we now turn to study the effect of our last input variable namely the average ionic concentration, $\bar{c}$. In Figure 3-4, $U/U_{\lim}$ is drawn for three different values of $\bar{c}$ namely

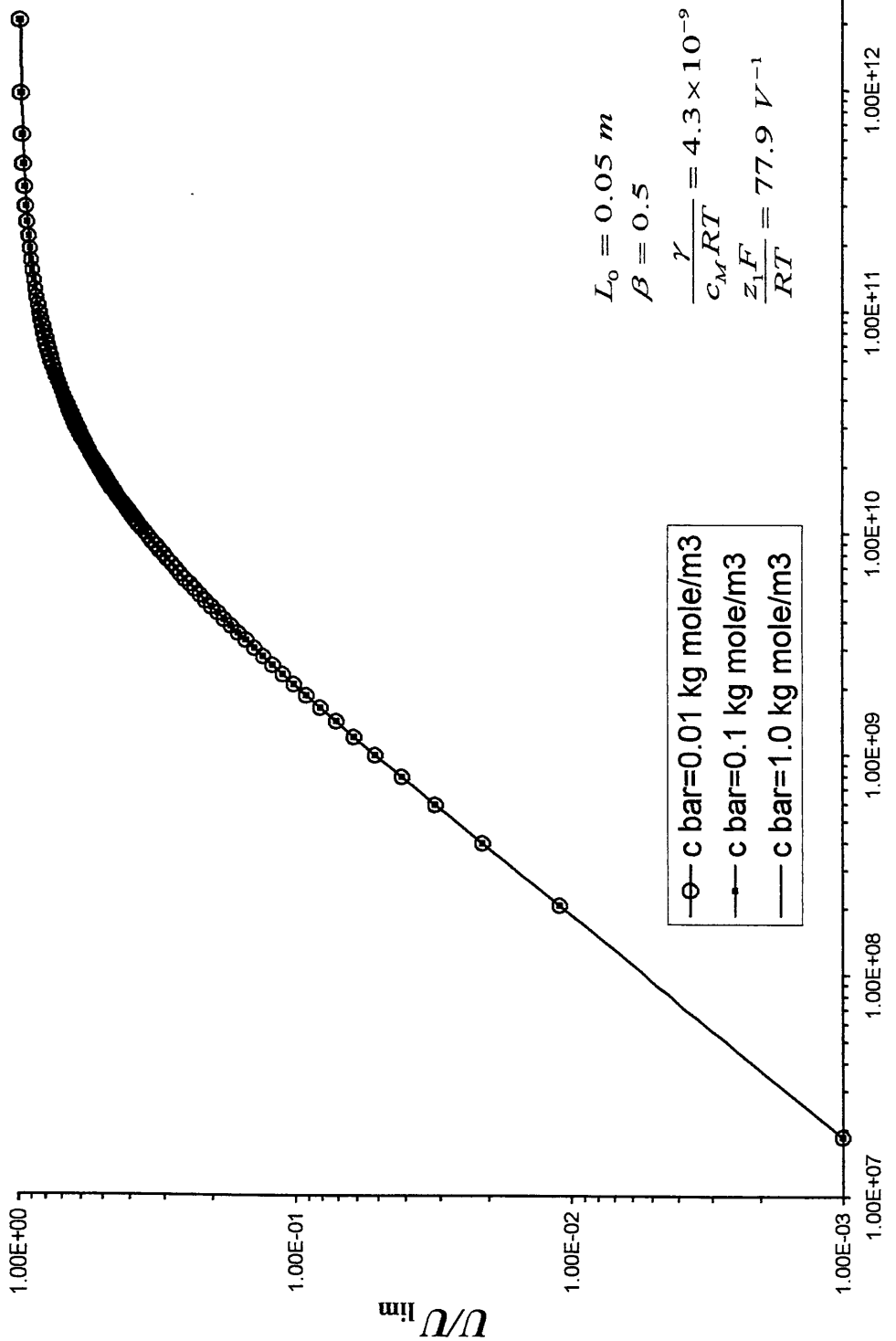


Figure 3-4. The effect of U/U_{lim} on the critical wave number for different average ionic concentrations.

0.01, 0.1 and 1.0 kg-mole/m^3. It is obvious from Figure 3-4 that changing $\overline{c}$ has no effect on the critical wave number. This is not surprising because by looking at equation (3.86) one can realize that $\overline{c}$ is hidden inside $U/U_{\lim}$ and by setting a value for $U/U_{\lim}$ the value of $\overline{c}$ will be already set hence no effect of changing $\overline{c}$ can be seen from Figure 3-4.

At this stage, we have completed studying the effect of changing the input variables namely $U/U_{\lim}$, L_0 and $\overline{c}$ on $k^2_{critical}$. In the next section we will evaluate the CRE approximation by comparing its results with previous work.

3.5.2 Comparison with Previous Work

Turn to the results obtained by the (CRE) model and compare them with the results of S&B who used the full B-V equation. Figure 3-5 shows $\log \dfrac{U/U_{\lim}}{1-U/U_{\lim}}$ vs. $\log\left(k_{critical}L_0\right)$. Note again that $U_{\lim}$ is the maximum velocity of the surface corresponding to the limiting current in the cell and this depends on L_0 and $\overline{c}$. To obtain Figure 3-5, the (CRE) model was used with the data provided by S&B. The conditions under which this figure is drawn are shown on the figure. The result obtained from the (CRE) model shows excellent agreement with S&B over the whole range of values they used. A small deviation was noticed for higher values of $U/U_{\lim}$. This may be due to a slight error in reading the S&B curves, or it maybe that the model fits lower values of $U/U_{\lim}$ better than higher values, which is true for the reasons that will be explained later.

It is important to note here that S&B obtained their results based on numerical calculations and we do not know if their numerical calculations are right or wrong. But

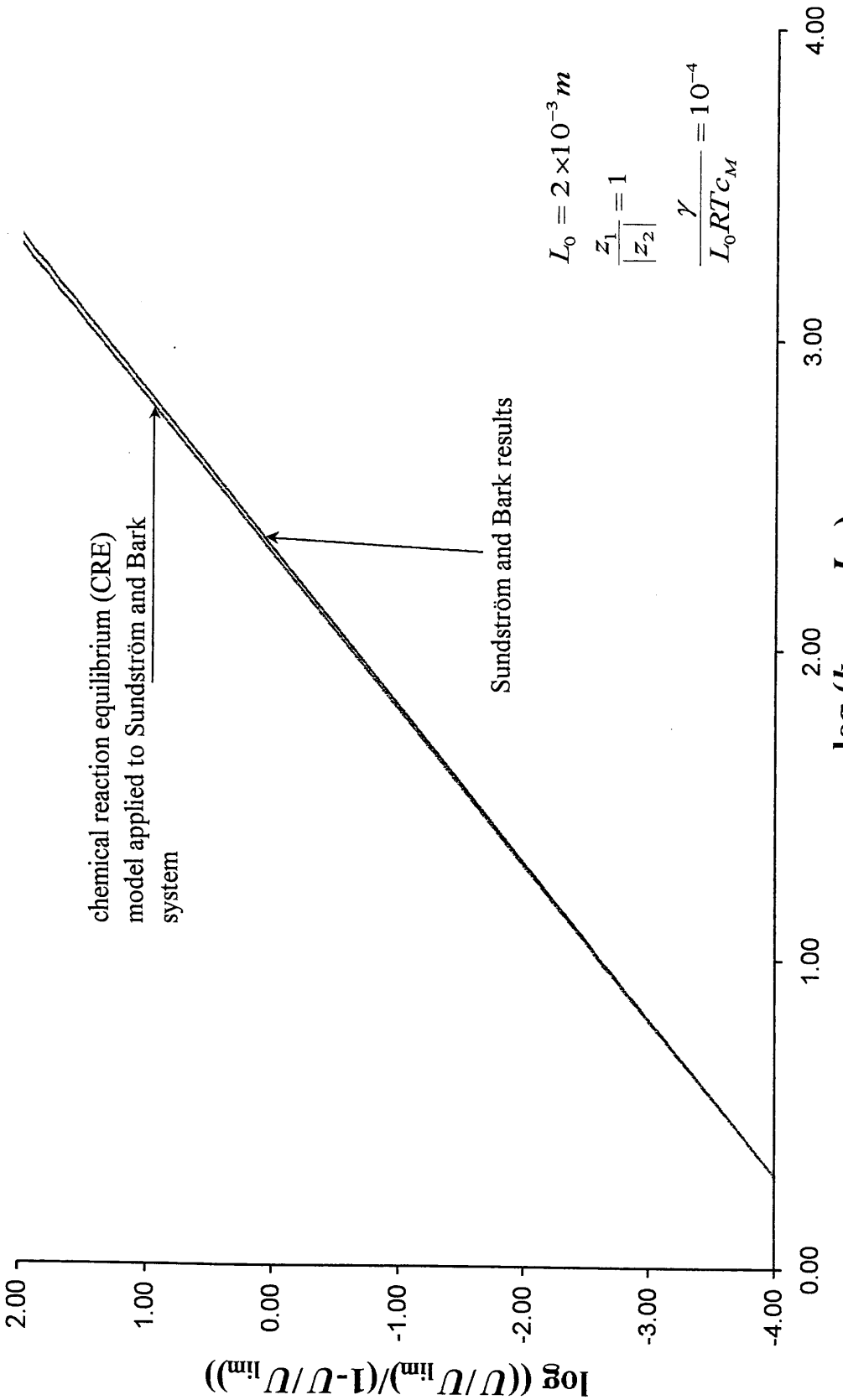


Figure 3-5. Comparison of the (CRE) model with the model by Sundström and Bark.

we do know that when numerical calculations are used, a person cannot really sample a lot of conditions because the work is too time consuming and S&B mentioned that it took them 10 CPU hours to solve the full problem. Consequently, when we replace a numerical work with simpler calculations, then we can do a lot of more cases. So one of the main reasons of doing this calculation is that S&B calculations are of limited help since they just showed that they can calculate something from their model for few cases and their calculations were lengthy and expensive.

Now let us compare the CRE model with the calculations of J&N. In the figures to come, it will be very hard to differentiate between the curve corresponding to the CRE model and the one that is close to it. This shows that under certain conditions the CRE model will be successful in matching the full B-V model to a great accuracy. The equations that J&N used to draw their curves are (3.27) to relate $V^A - V^C$ to U/U_{lim} in addition to equation (3.78) for the critical wave number since they did not assume chemical reaction equilibrium and they used the full B-V equation

Figure 3-6 shows U/U_{lim} vs. $k^2_{critical}$ for different values of L_0 when $\overline{c} = 0.1$ kg-mole/m^3. The CRE model agrees best with the full model for J&N for higher values of electrode spacing. This is expected as increasing the distance between the surfaces will shift the system more towards equilibrium as will be shown later.

Figure 3-7 shows U/U_{lim} vs. $k^2_{critical}$ for different values of L_0 when $\overline{c} = 0.01$ kg-mole/m^3. It is obvious that the equilibrium model is close to the results obtained by J&N for $L_0 = 0.05$ m and $L_0 = 0.005$ m. And it continues to remain very

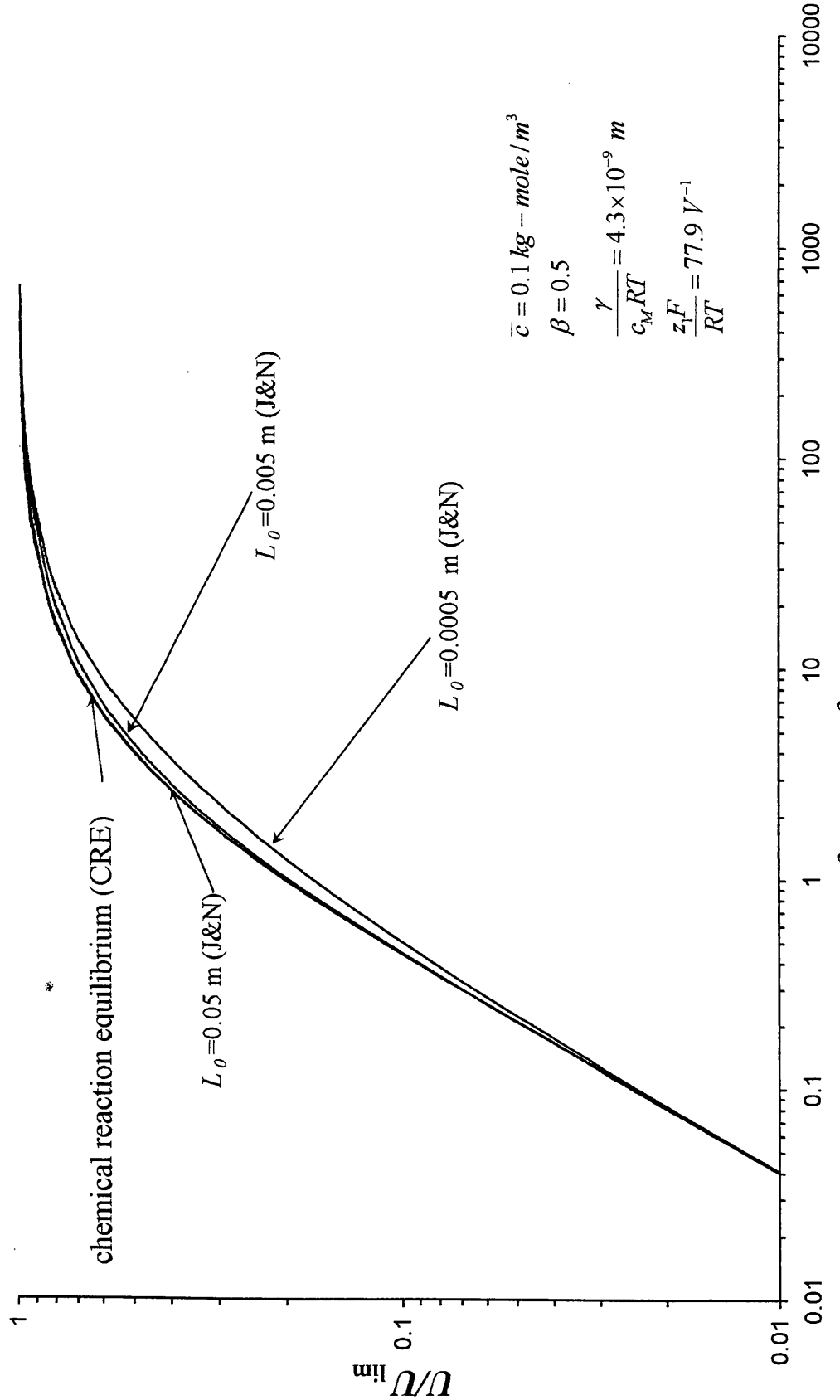


Figure 3-6. The agreement of the (CRE) model with the results by Johns and Narayanan for large electrode spacing, L_0.

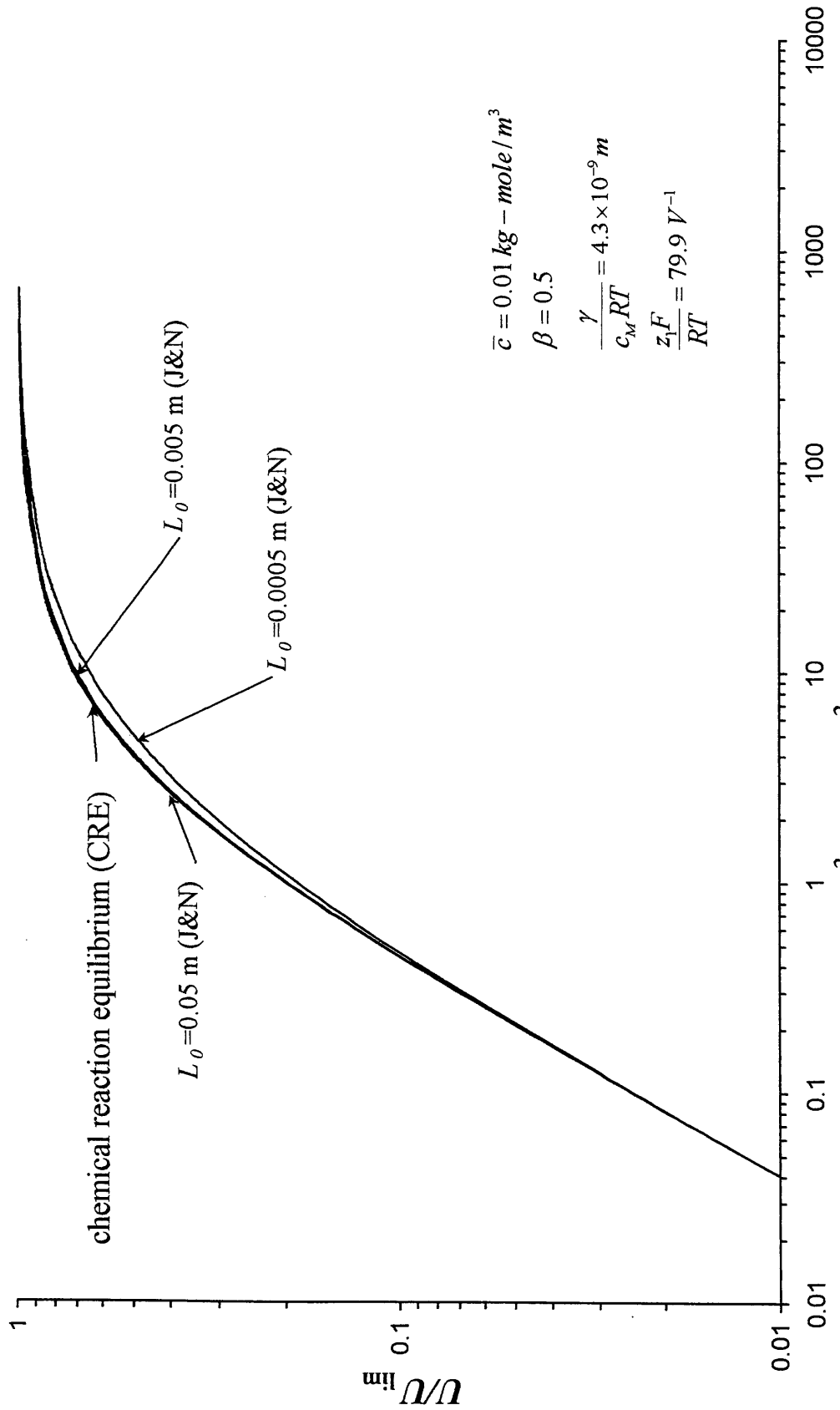


Figure 3-7. Excellent agreement with Johns and Narayanan for higher L_0 and lower average electrolytic concentration.

close to the case of $L_0 = 0.0005$ m which makes this model excellent even for very small distances for low concentrations of the electrolytic solution.

It is obvious from the previous discussion that better results are achieved for the CRE model as L_0 gets larger or $\overline{c}$ gets smaller. To understand why this makes sense, a simpler problem which shows that systems are expected to shift more towards equilibrium as the distance between the surfaces increases or the concentration decreases is given in Appendix C.

Now a person might wonder why the chemical reaction equilibrium turned to be such a good approximation? The answer to this question will be presented next.

3.5.3 The Reason Why the CRE Turns to be a Good Approximation

To check why the CRE turns out to be an excellent approximation, the criteria upon which it is based is examined. The argument given here will be based on the base case (i.e., before performing the perturbations). But this does not mean that we cannot use it to support our results from the first order calculations since the approximation proved its validity when the graphs of the perturbed case were drawn.

First, let us have a look at the Butler-Volmer equation i.e., equation (2.36) viz.,

$$\vec{n}\cdot\vec{i} = -z_1 F c_M \left[\vec{n}\cdot\vec{u} + \vec{n}\cdot\vec{U}\right] = i_0\left[e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}-\frac{\gamma}{z_1Fc_M}2H\right]} - \frac{c}{\overline{c}}e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}-\frac{\gamma}{z_1Fc_M}2H\right]}\right]$$

For a steady one-dimensional base solution with flat parallel electrodes, the Butler-Volmer equation can be written at the anode as

$$i_y^A = -z_1 F c_M U = i_0\left[e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}\right]} - \frac{c^A}{\overline{c}}e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}\right]}\right] \qquad (3.87)$$

In the above equation, the anode was picked just for the purpose of illustration since a similar equation can be written at the cathode. In order to check why the results from the CRE approximation matched the Butler-Volmer equation, we should look to equation (3.87) and see how i_0, which represents the rate of the reaction, compares with the left hand side (i.e., $z_1 F c_M U$) which reflects the speed of the transport processes.

The CRE model is based on the assumption that the reaction rate is very fast compared to diffusion and migration. In other words, i_0 is very large compared to $z_1 F c_M U$. If we can prove that this is really the case in the Butler-Volmer equation, then this will answer the question on why the CRE model matches the results of the B-V model as well.

In order to compare i_0 to $z_1 F c_M U$, let us pick some values for our input variables (i.e., $\bar{c}$ and L_0). If $\bar{c}$ and L_0 were chosen to be 0.1 kg-mole/m^3 and 0.05 m respectively, then U_{lim} can be calculated using equation (3.79) and the data given in Table 3-1. The value of U_{lim}, which turns out to be $-2.05\text{x}10^{-11}$ m/s, represents the upper limit of U. So an average value for U such as $-1\text{x}10^{-11}$ m/s is a reasonable value that can be used to calculate the left hand side of equation (3.87). By multiplying z_1, F and c_M, which are given in Table 3-1, with U the term $z_1 F c_M U$ can be calculated to be 0.27 A/m^2.

On the other hand, at the chosen $\bar{c}$, the value of i_0, as given in Table 3-1, is 10 A/m^2. In this case, i_0 is almost 40 times $z_1 F c_M U$ and the ratio $\frac{z_1 F c_M U}{i_0}$ is really very small. Based on this observation, the exponential term in equation (3.87) i.e.,

$\left[e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}\right]} - \frac{c^A}{\overline{c}} e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}\right]} \right]$ must be very small, almost equal to zero, and this is exactly what we assumed when we applied the CRE assumption. So it turns out that this assumption is valid because $i_0 >> z_1 F c_M U$ in the real situation when the whole Butler-Volmer equation is used. And this explains why the two models deviate for larger values of $U/U_{\lim}$ or $\left[V^A - V^C\right]$, since the ratio $\frac{z_1 F c_M U}{i_0}$ will become larger and the CRE assumption will become weaker in representing the real situation.

Then to study the effect of changing the electrode spacing we have to look to its effect on the ratio $\frac{z_1 F c_M U}{i_0}$. As we know from our discussion of Figure 3-3 that increasing L_0 at a constant $U/U_{\lim}$ will decrease both the concentration and the electrical potential gradients which in turn reduce the velocity of the surface. So if L_0 becomes larger then U becomes smaller and this will make the CRE approximation better.

Understanding the effect of $\overline{c}$ is not as straight forward as understanding the effect of L_0. We know that i_0 depends on $\overline{c}$ and it decreases as $\overline{c}$ becomes smaller, yet the approximation gets better as $\overline{c}$ goes down. To resolve this inconsistency one has to look not only at the effect of $\overline{c}$ on i_0 but also at the effect of $\overline{c}$ on U. As given in chapter 2, the exchange current density, i_0 and $\overline{c}$ are related by

$$\frac{i_0\left(\overline{c}_{ref}\right)}{i_0\left(\overline{c}_{std}\right)} = \left[\frac{\overline{c}_{ref}}{\overline{c}_{std}}\right]^{1-\beta}$$

In our calculations we set β to one half and we know that $i_0\left(\overline{c}_{std}\right) = 10$ A/m^2 for $\overline{c}_{std} = 0.1$ kg-mole/m^3. So for any $\overline{c}$, i_0 can be calculated by

$$i_0 = 10\sqrt{10\,\bar{c}} \tag{3.88}$$

Then according to this equation, decreasing $\bar{c}$ by ten times (i.e., $\bar{c} = 0.01$ kg-mole/m^3) will decrease i_0 from 10 A/m^2 to 3.16 A/m^2 which is almost 3 times. On the other hand, by looking at the definition of $U_{\lim}$ viz.,

$$U_{\lim} = \frac{2}{L_0}\frac{z_1 D_1 - z_2 D_2}{z_1 z_2 D_2} D \frac{\bar{c}}{c_M}$$

decreasing $\bar{c}$ by ten times will decrease $U_{\lim}$ by ten times. Remember the base relation between $\left[V^A - V^C\right]$ and $U/U_{\lim}$ viz.,

$$\frac{z_1 F}{RT}\left[V^A - V^C\right] = 2\ln\left(\frac{1+U/U_{\lim}}{1-U/U_{\lim}}\right)$$

since we are looking at the case where $\left[V^A - V^C\right]$ and L_0 are held fixed, then the decrease in $U_{\lim}$ by ten times must be accompanied by a decrease of U by ten times so the equation above is satisfied. Consequently, even though decreasing $\bar{c}$ will decrease i_0, it will decrease U even more, so $\frac{z_1 F c_M U}{i_0}$ will be smaller for smaller $\bar{c}'s$ making the CRE approximation better.

The approximation in this chapter simplifies the reaction part of the model. In the next chapter we will introduce another approximation that will simplify the transport part of the model getting rid of the nonlinearity from the migration term.

What we have done in this chapter was to introduce an approximation that assumes the rate of the reactions to be very fast compared to the rate of the transport processes. This approximation turned to be a fair one and it even gets better under certain

conditions. Even though the CRE approximation simplifies the B-V equation slightly for performing the perturbation calculations, its main advantage was evident in simplifying the base relation between the voltage drop and the velocity of the surface. The benefit of this will appear in chapter 6 where we perform the weak nonlinear calculations.

CHAPTER 4
CALCULATION OF THE GROWTH CONSTANT AND ITS APPROXIMATIONS

In the previous chapter, the CRE approximation was used to simplify the problem and it was shown how effective it was in getting results close to the full B-V model when neutral stability (i.e., $\sigma = 0$) is considered. Here in the interest of going one more step and estimating the growth constants, we make one more approximation. In this approximation, we get rid of the non-linearity in the migration term by exchanging c with $\overline{c}$; this will make the problem much easier to solve analytically.

This approximation will simplify the model by the following way. When c is replaced by $\overline{c}$ in the migration term then the perturbation equations, which are linear, will be constant coefficients equations. On the other hand, if this approximation was not used, then the perturbation equations, which continue to be linear, will be equations with variable coefficients because c is a function of y. So the reason behind using this approximation is to get constant coefficient differential equations instead of variable coefficient differential equations, which are harder to solve.

A question that can be raised here is then: Why did not the variable coefficient equations bother us in the previous chapter when we dealt with the case $\sigma = 0$? The answer to this question is that it did not matter if we use the $c = \overline{c}$ approximation because the solution to the problem turned out to be $c_1 = 0$, $\phi_1 = 0$ and $Y_1^A = 0$ which is the case whether or not we have constant or variable coefficient equations. This is not the case

when $\sigma = 0$ is not assumed since c_1, ϕ_1 and Y_1^A will not be zero and we have to solve the differential equations with the variable coefficients, which is not easy.

So our target in this chapter is to calculate the growth constants, $\sigma's$, as a function of the wave number, k^2, analytically and then extend our calculations to the nonlinear region, which will be done in chapter 6, to see what happens beyond critical. Calculating the growth constants, $\sigma's$, is important since their values will show how fast a perturbation will grow or die with time.

It is important to notice here that, although this approximation will give us linear equations, the non-linearity will still be present in the problem due to the B-V equation and more importantly, due to the fact that the shape of the domain is unknown and as before must be calculated. So the same procedure that was used in chapter 3 will be followed here. First the model equations will be written after assigning c to be $\overline{c}$ in the migration term. Then, a steady base solution will be obtained. Finally, the instability calculation is used to get a set of linear equations from which a relation between the wave number and the growth constant will be found.

Later on in this chapter, another approximation will be introduced. It will be noticed that while the unknown σ appears in several places in our equations and everywhere it appears it represents the resulting growth or decline of the perturbation, it is thought that the motion of the displaced surface might be the rate-controlling step and that the domain equations could adjust to this motion rapidly. Hence an approximation to simplify algebra by dropping σ from the domain will be entertained and shown to be fair.

This chapter will be concluded by trying to understand the behavior of the σ vs. k^2 curves. In order to achieve this goal, the approximations introduced in this chapter along with the CRE will be combined to get the simplest model from which the effect of the different parameters on the relation between σ and k^2 will be visualized.

4.1 The Nonlinear Equations Obtained by Setting $c = \bar{c}$ in the Migration Term

In this section we will show how setting $c = \bar{c}$ in the migration term will simplify the equations of the model presented previously in chapter 2. The CRE model discussed in chapter 3 was shown to be an excellent approximation if one is interested in finding the critical wave number corresponding to the case $\sigma = 0$. Here, we shall go beyond getting the neutral stability points. Setting $c = \bar{c}$ in the migration term will enable us to calculate the wave number for any given growth constant σ, or visa versa, without limiting our selves to the case $\sigma = 0$. In the previous chapter, when σ was set to zero, the wave number, k^2 was treated as the unknown, however, in this chapter, since we are looking for σ, k^2 will be treated as an input variable in addition to the usual input variables (i.e., the distance between the electrodes, the average ionic concentration and the voltage drop across the cell).

One of the grounds for making the $c = \bar{c}$ in the migration term approximation would be that migration is not nearly as important as diffusion. And this will be true at low voltage drops and low current densities across the cell where the effect of migration will be small. Based on that, this approximation will not be good near the limiting current (i.e., when the concentration at the cathode will drop to nearly zero) conversely, it will be better the more slight the concentration variation is. Actually, in the next chapter we are going to see where this approximation will make sense and where it does not when we

solve the model without any approximations. So we introduce this approximation for the algebraic simplicity it offers for our later work if we are working in ranges where it is applicable.

Now once convection is ignored and c is replaced with $\bar{c}$ in the migration term we get the following equations instead of equations (2.32) and (2.33) viz.,

$$\frac{\partial c}{\partial t} = D\,\nabla^2 c \tag{4.1}$$

and

$$P\,\nabla^2 c + \frac{z_1 F}{RT}\bar{c}\,\nabla^2 \phi = 0 \tag{4.2}$$

These are two second-order, linear, partial differential equations in c and ϕ where boundary conditions are required in order to solve them. Let us now write the equations at the boundary i.e., equations (2.34) and (2.35) after applying the migration term approximation and neglecting convection that is

$$D\,\vec{n}\cdot\nabla c = \frac{-z_1 z_2 D_2 c_M}{z_1 D_1 - z_2 D_2}\left[\vec{n}\cdot\vec{u} + \vec{n}\cdot\vec{U}\right] \tag{4.3}$$

and

$$P\,\vec{n}\cdot\nabla c + \frac{z_1 F}{RT}\bar{c}\,\vec{n}\cdot\nabla\phi = \frac{c_M z_1^2}{z_1 D_1 - z_2 D_2}\left[\vec{n}\cdot\vec{u} + \vec{n}\cdot\vec{U}\right] \tag{4.4}$$

In addition, the full B-V equation is going to be used here, not the CRE approximation. Even though, the CRE is an excellent approximation, we are not going to use it here because we want to study the effect of putting $c = \bar{c}$ without encountering this with another approximation. As noted, the main advantage of the CRE is for the simplification it offers to the base solution, not so much in the first order calculations. The advantage will reappear when dealing with the nonlinear calculations.

We know that the B-V equation that is going to be used here in its full form is

$$\vec{n}\cdot\vec{i} = -z_1 F c_M\left[\vec{n}\cdot\vec{u} + \vec{n}\cdot\vec{U}\right] = i_0\left[e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}-\frac{\gamma}{z_1Fc_M}2H\right]} - \frac{c}{\overline{c}}e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}-\frac{\gamma}{z_1Fc_M}2H\right]}\right] \tag{4.5}$$

It is worth mentioning here that we do not put $c=\overline{c}$ in the B-V equation because c is going to vary from c^A to c^C. So the fact that we are putting $c=\overline{c}$, is not an approximation to the c part of the problem or even to the B-V equation. The B-V equation will remain a nonlinear equation even if we put $c=\overline{c}$ in it and we are able to deal with the problem even if the non-linearity persists in the B-V equation.

Equations (4.3), (4.4) and (4.5) then are the boundary conditions that are valid at both the anode and the cathode. Having the domain equations and the boundary conditions written, we are ready to find a steady base solution for the problem.

4.2 The Base Solution

Since equation (4.1) with its boundary conditions are similar to what we had in the previous chapter, there is no need to repeat the solution procedure in getting the concentration profile and it will be enough to rewrite the main results for c as a function of y as follows

$$c = \overline{c} + \frac{-z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} c_M \frac{U}{D}\left[y - \frac{1}{2}L_0\right] \tag{4.6}$$

then the concentration at the anode c^A and the concentration at the cathode c^C are simply

$$c^A = \overline{c} - \frac{-z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} c_M \frac{U}{D}\frac{1}{2}L_0 \tag{4.7}$$

and

$$c^C = \overline{c} + \frac{-z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} c_M \frac{U}{D} \frac{1}{2} L_0 \tag{4.8}$$

Let us now turn our attention to getting the solution for the electrical potential equation i.e., equation (4.2), and by observing that $\nabla^2 c = 0$ at steady state, this equation will reduce to

$$\frac{z_1 F}{RT} \overline{c}\ \nabla^2 \phi = 0 \tag{4.9}$$

Noticing that $\frac{z_1 F}{RT} \overline{c}$ is not zero; we conclude that $\nabla^2 \phi$ must be zero. Consequently, $\frac{d\phi}{dy}$ is a constant that can be determined from equation (4.3) to be

$$\frac{d\phi}{dy} = \frac{c_M}{\overline{c}} \frac{RT}{z_1 F} \frac{z_1^2}{D_1 (z_1 - z_2)} U \tag{4.10}$$

Equation (4.10) shows that the electrical potential gradient is equal to a constant (i.e., a graph of ϕ vs. y is a straight line with a negative slope). This is where the first simplification appears since $\frac{d\phi}{dy}$ from chapter 3 given by equation (3.12) was found to be a nonlinear function of y. So one can easily find ϕ by integrating equation (4.10) to get

$$\phi = \frac{c_M}{\overline{c}} \frac{RT}{z_1 F} \frac{z_1^2\ U}{D_1 (z_1 - z_2)} y + \text{constant} \tag{4.11}$$

The constant in the equation above can be found by applying the boundary conditions $\phi = \phi^A$ at $y = 0$ and $\phi = \phi^C$ at $y = L_0$. Now ϕ^A and ϕ^C are not known but the relation between them can be found by using these boundary conditions to get

$$\frac{z_1 F}{RT} \left[\phi^C - \phi^A \right] = \frac{c_M}{\overline{c}} \frac{z_1^2\ U}{D_1 (z_1 - z_2)} L_0 \tag{4.12}$$

Finally when the relation between the voltage drop and the velocity of the surfaces is sought, the B-V equation is the source for such a relation. By going back to chapter 3 and following the same procedure to get such a relation and using equation (4.12) instead of equation (3.12), since $\phi^C - \phi^A$ now is different due to the approximation, one will find

$$\frac{z_1 F}{RT}\left[V^A - V^C\right] = 2\ln\left(-\frac{1}{2}\frac{z_1 F c_M U}{i_0} + \frac{1}{2}\sqrt{\left(\frac{z_1 F c_M U}{i_0}\right)^2 + 4\frac{c^A}{\bar{c}}}\right) - \frac{c_M}{\bar{c}}\frac{z_1^2 U}{D_1\left(z_1 - z_2\right)}L_0$$
$$-2\ln\left(\frac{1}{2}\frac{z_1 F c_M U}{i_0} + \frac{1}{2}\sqrt{\left(\frac{z_1 F c_M U}{i_0}\right)^2 + 4\frac{c^C}{\bar{c}}}\right) \tag{4.13}$$

with the only difference between this equation and equation (3.27) coming from the different value of $\phi^C - \phi^A$. The reader is reminded that β was set to one half when we obtained both equations (3.27) and (4.13).

This is all what we need from the base solution in order to be able to go on and study the stability of the problem. The next step will be to use the linearized stability method to find the perturbed linear equations, which is the business of the next section.

4.3 The Perturbation Problem

Our objective here is to linearize the equations presented in section 4.1 using the perturbation method. In order to get the perturbed equations, we will use equations (3.35)-(3.44) which serve the purposes of linearizing the equations and separating the variables.

Starting with the domain equations (i.e., the equations for c and ϕ valid on $0 < y_0 < L_0$) and substituting the expansion for c given by equation (3.39) along with using separation of variables will turn equation (4.1) into an equation for $\hat{c}_1$ viz.,

$$D\left[\frac{d^2}{dy_0^2}-k^2\right]\hat{c}_1=\sigma\hat{c}_1 \tag{4.14}$$

which is the same as equation (3.45) since the new approximation will not affect the concentration equation. After using equation (3.40) to substitute for the expansion for ϕ and using separation of variables, equation (4.2) will become

$$P\left[\frac{d^2}{dy_0^2}-k^2\right]\hat{c}_1+\frac{z_1F}{RT}\bar{c}\left[\frac{d^2}{dy_0^2}-k^2\right]\hat{\phi}_1=0 \tag{4.15}$$

This is the domain equation for $\hat{\phi}_1$. It is a linear, second-order ordinary differential equation with constant coefficient that replaces equation (3.46) viz.,

$$P\left[\frac{d^2}{dy_0^2}-k^2\right]\hat{c}_1+\frac{dc_0}{dy_0}\left[\frac{z_1F}{RT}\right]\frac{d\hat{\phi}_1}{dy_0}+c_0\left[\frac{z_1F}{RT}\right]\left[\frac{d^2}{dy_0^2}-k^2\right]\hat{\phi}_1$$
$$+\left[\frac{z_1F}{RT}\right]\frac{d\phi_0}{dy_0}\frac{d\hat{c}_1}{dy_0}+\left[\frac{z_1F}{RT}\right]\frac{d^2\phi_0}{dy_0^2}\hat{c}_1=0$$

which is more complicated due to the fact that it is a variable coefficient linear differential equation as c_0, which is a function of y_0, multiplies $\hat{\phi}_1$.

Let us now turn our attention to equations (4.3) and (4.4) which hold at both the anode $y=0$ and the cathode $y=L_0$. By starting with the anode, the perturbed equation corresponding to the concentration profile, equation (4.3), will be no different than the one in the previous chapter i.e., equation (3.56) and can be written as

$$D\frac{d\hat{c}_1}{dy_0}=-\frac{z_1z_2D_2}{z_1D_1-z_2D_2}c_M\sigma\hat{Y}_1^A \tag{4.16}$$

But when the perturbation method is applied to equation (4.4) the following equation is found

$$P\frac{d\hat{c}_1}{dy_0}+\frac{z_1F}{RT}\bar{c}\frac{d\hat{\phi}_1}{dy_0}=\frac{c_M z_1^2}{z_1D_1-z_2D_2}\sigma\hat{Y}_1^A \tag{4.17}$$

The only remaining boundary condition is the B-V equation i.e., equation (4.5). Remember that the CRE approximation will not be used here, so we have to work with the full B-V equation. While this will not be an obstacle in solving the problem, it will make the algebra more tedious. Now, following the perturbation procedure used to handle the CRE equation previously, one can get the following perturbed B-V equation at the anode

$$\begin{aligned}-\frac{z_1Fc_M}{i_0}\sigma\hat{Y}_1^A=&\left[\left[1-\beta\right]e^{\left[1-\beta\right]\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}+\frac{c_0^A}{\bar{c}}\beta e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}\right]\\&\times\left[\frac{z_1F}{RT}\right]\left[\Delta\hat{\phi}_1^A+\hat{Y}_1^A\frac{d}{dy_0}\Delta\phi_0^A+\frac{\gamma}{z_1Fc_M}k^2\hat{Y}_1^A\right]\\&-e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}\frac{\left[\hat{c}_1^A+\hat{Y}_1^A\frac{dc_0^A}{dy_0}\right]}{\bar{c}}\end{aligned} \tag{4.18}$$

where $\Delta\hat{\phi}_1^A=-\hat{\phi}_1^A$ as V^A is fixed.

Turning to the cathode, a similar set of equations can be obtained. The corresponding equations holding at $y=L_0$ are

$$D\frac{d\hat{c}_1}{dy_0}=-\frac{z_1z_2D_2}{z_1D_1-z_2D_2}c_M\sigma\hat{Y}_1^C \tag{4.19}$$

$$P\frac{d\hat{c}_1}{dy_0}+\frac{z_1F}{RT}\bar{c}\frac{d\hat{\phi}_1}{dy_0}=\frac{c_M z_1^2}{z_1D_1-z_2D_2}\sigma\hat{Y}_1^C \tag{4.20}$$

and

$$+\frac{z_1 F c_M}{i_0}\sigma\hat{Y}_1^C = \left[[1-\beta]e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{EQ}\right]} + \frac{c_0^C}{\overline{c}}\beta e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{EQ}\right]}\right]$$
$$\times\left[\frac{z_1F}{RT}\right]\left[\Delta\hat{\phi}_1^C + \hat{Y}_1^C\frac{d}{dy_0}\Delta\phi_0^C - \frac{\gamma}{z_1Fc_M}k^2\hat{Y}_1^C\right] \qquad (4.21)$$
$$-e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{EQ}\right]}\frac{\left[\hat{c}_1^C + \hat{Y}_1^C\frac{dc_0^C}{dy_0}\right]}{\overline{c}}$$

where $\Delta\hat{\phi}_1^C = -\hat{\phi}_1^C$ as V^C is fixed.

Equations (4.14)-(4.21) are the complete set of the perturbed equations at the domain and at the two boundaries that defines the eigenvalue problem. The next section will discuss the solving of the eigenvalue problem to achieve our goal of finding σ vs. k^2.

4.4 Solving the Eigenvalue Problem

To solve the eigenvalue problem we find $\hat{c}_1$ and $\hat{\phi}_1$ in terms of $\hat{Y}_1^A$ and $\hat{Y}_1^C$. The $\hat{c}_1$ problem can be solved using equations (4.14), (4.16) and (4.19) while $\hat{\phi}_1$ can be obtained as a function of $\hat{Y}_1^A$ and $\hat{Y}_1^C$ by the use of equations (4.15), (4.17) and (4.20). Then we can turn to the perturbed B-V equations namely, equations (4.18) and (4.21) to find $\hat{Y}_1^A$, $\hat{Y}_1^C$ and σ. Remember that in addition to our traditional input variables (i.e., the voltage drop, the spacing between the electrodes and the average ionic concentration) the wave number is also considered as an input variable when solving for the growth constant.

To begin solving the eigenvalue problem, go back to equation (4.14) and observe that the solution to this equation is

$$\hat{c}_1 = A_1 e^{my} + B_1 e^{-my} \qquad (4.22)$$

where A_1 and B_1 are constants and m denotes $\sqrt{k^2+\frac{\sigma}{D}}$. Using the boundary conditions i.e., equations (4.16) and (4.19) the constants A_1 and B_1 turned out to be

$$A_1 = \frac{-\frac{z_1 z_2 c_M}{mD_1(z_1-z_2)}\sigma\left[\hat{Y}_1^C - e^{mL_0}\hat{Y}_1^A\right]}{e^{mL_0}-e^{-mL_0}} - \frac{z_1 z_2 c_M}{mD_1(z_1-z_2)}\sigma\hat{Y}_1^A \tag{4.23}$$

and

$$B_1 = \frac{-\frac{z_1 z_2 c_M}{mD_1(z_1-z_2)}\sigma\left[\hat{Y}_1^C - e^{mL_0}\hat{Y}_1^A\right]}{e^{mL_0}-e^{-mL_0}} \tag{4.24}$$

Then $\hat{c}_1$ is found by substituting these constants into equation (4.22) and evaluating this equation at the anode where $y_0 = 0$. The result is

$$\hat{c}_1^A = -\frac{\sigma}{m}\frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\frac{c_M}{D}\left[\hat{Y}_1^C \operatorname{csch}(mL_0) - \hat{Y}_1^A \coth(mL_0)\right] \tag{4.25}$$

Similarly, at the cathode, where $y_0 = L_0$, we find for $\hat{c}_1^C$

$$\hat{c}_1^C = -\frac{\sigma}{m}\frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\frac{c_M}{D}\left[\hat{Y}_1^C \coth(mL_0) - \hat{Y}_1^A \operatorname{csch}(mL_0)\right] \tag{4.26}$$

Now, the solution to equation (4.15) can be written as

$$\hat{\phi}_1 = A_2 e^{k y_0} + B_2 e^{-k y_0} - \frac{P}{\bar{c}}\frac{RT}{z_1 F}A_1 e^{m y_0} - \frac{P}{\bar{c}}\frac{RT}{z_1 F}B_1 e^{-m y_0} \tag{4.27}$$

where A_1 and B_1 are the same constants that are given above, where k is the positive root, $\sqrt{k^2}$, and where A_2 and B_2 are two new constants that can be found using equations (4.17) and (4.20). Doing this and evaluating equation (4.27) at $y_0 = 0$ and $y_0 = L_0$, $\hat{\phi}_1^A$ and $\hat{\phi}_1^C$ can be obtained as

$$\hat{\phi}_1^A = \frac{P}{D}\frac{\sigma}{m}\frac{RT}{z_1F}\frac{c_M}{\bar{c}}\frac{z_1z_2D_2}{z_1D_1 - z_2D_2}\left[\hat{Y}_1^C \operatorname{csch}(mL_0) - \hat{Y}_1^A \coth(mL_0)\right] + \frac{\sigma}{k}\frac{RT}{z_1F}\frac{c_M}{\bar{c}}\frac{z_1^2}{z_1D_1 - z_2D_2}\left[\hat{Y}_1^C \operatorname{csch}(kL_0) - \hat{Y}_1^A \coth(kL_0)\right] \tag{4.28}$$

and

$$\hat{\phi}_1^C = \frac{P}{D}\frac{\sigma}{m}\frac{RT}{z_1F}\frac{c_M}{\bar{c}}\frac{z_1z_2D_2}{z_1D_1 - z_2D_2}\left[\hat{Y}_1^C \coth(mL_0) - \hat{Y}_1^A \operatorname{csch}(mL_0)\right] + \frac{\sigma}{k}\frac{RT}{z_1F}\frac{c_M}{\bar{c}}\frac{z_1^2}{z_1D_1 - z_2D_2}\left[\hat{Y}_1^C \coth(kL_0) - \hat{Y}_1^A \operatorname{csch}(kL_0)\right] \tag{4.29}$$

What we have done so far was to eliminate the variables $\hat{c}_1$ and $\hat{\phi}_1$ from the problem leaving only $\hat{Y}_1^A$ and $\hat{Y}_1^C$ to be determined. Note that $\hat{c}_1^A$, $\hat{c}_1^C$, $\hat{\phi}_1^A$ and $\hat{\phi}_1^C$ are linear functions of $\hat{Y}_1^A$ and $\hat{Y}_1^C$ and σ is spread out in these expressions and hidden in a complicated way in m. So this problem turns out to be linear algebraic equations in $\hat{Y}_1^A$ and $\hat{Y}_1^C$.

Before proceeding with our solution to the problem, let us remind ourselves that when neutral stability was studied, $\hat{c}_1^A$, $\hat{\phi}_1^A$, $\hat{c}_1^C$ and $\hat{\phi}_1^C$ were all found to be zero whether or not the CRE is used. The same result would be obtained if σ was set to zero in the above four equations. Hence our approximation preserves a main property of the problem. When σ is not zero, these equations show that its determination is not going to be easy. But it will be shown later that if we set the σ appearing in the domain equation to zero a great simplification will occur that will lead to an explicit relation between the growth constant and the wave number.

Now, having found $\hat{c}_1^A$, $\hat{\phi}_1^A$, $\hat{c}_1^C$ and $\hat{\phi}_1^C$ one can go back and substitute equations (4.25) and (4.28) in (4.18) to get

$$-\frac{z_1Fc_M}{i_0}\sigma\hat{Y}_1^A=\left[[1-\beta]e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}+\frac{c_0^A}{\bar{c}}\beta e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}\right]\left[\frac{z_1F}{RT}\right]$$
$$\times\left[\begin{array}{l}-\frac{P}{D}\frac{\sigma}{m}\frac{RT}{z_1F}\frac{c_M}{\bar{c}}\frac{z_1z_2D_2}{z_1D_1-z_2D_2}\left[\hat{Y}_1^C\mathrm{csch}\left(mL_0\right)-\hat{Y}_1^A\coth\left(mL_0\right)\right]-\\ \frac{\sigma}{k}\frac{RT}{z_1F}\frac{c_M}{\bar{c}}\frac{z_1^2}{z_1D_1-z_2D_2}\left[\hat{Y}_1^C\mathrm{csch}\left(kL_0\right)-\hat{Y}_1^A\coth\left(kL_0\right)\right]+\hat{Y}_1^A\frac{d}{dy_0}\Delta\phi_0^A+\frac{\gamma}{z_1Fc_M}k^2\hat{Y}_1^A\end{array}\right]$$
$$-\frac{e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}}{\bar{c}}\left[-\frac{\sigma}{m}\frac{z_1z_2D_2}{z_1D_1-z_2D_2}\frac{c_M}{D}\left[\hat{Y}_1^C\mathrm{csch}\left(mL_0\right)-\hat{Y}_1^A\coth\left(mL_0\right)\right]+\hat{Y}_1^A\frac{dc_0^A}{dy_0}\right]$$

and substitute equations (4.26) and (4.29) in (4.21) to get

$$+\frac{z_1Fc_M}{i_0}\sigma\hat{Y}_1^C=\left[[1-\beta]e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{EQ}\right]}+\frac{c_0^C}{\bar{c}}\beta e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{EQ}\right]}\right]\left[\frac{z_1F}{RT}\right]$$
$$\times\left[\begin{array}{l}-\frac{P}{D}\frac{\sigma}{m}\frac{RT}{z_1F}\frac{c_M}{\bar{c}}\frac{z_1z_2D_2}{z_1D_1-z_2D_2}\left[\hat{Y}_1^C\coth\left(mL_0\right)-\hat{Y}_1^A\mathrm{csch}\left(mL_0\right)\right]-\\ \frac{\sigma}{k}\frac{RT}{z_1F}\frac{c_M}{\bar{c}}\frac{z_1^2}{z_1D_1-z_2D_2}\left[\hat{Y}_1^C\coth\left(kL_0\right)-\hat{Y}_1^A\mathrm{csch}\left(kL_0\right)\right]+\hat{Y}_1^C\frac{d}{dy_0}\Delta\phi_0^C-\frac{\gamma}{z_1Fc_M}k^2\hat{Y}_1^C\end{array}\right]$$
$$-\frac{e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{EQ}\right]}}{\bar{c}}\left[-\frac{\sigma}{m}\frac{z_1z_2D_2}{z_1D_1-z_2D_2}\frac{c_M}{D}\left[\hat{Y}_1^C\coth\left(mL_0\right)-\hat{Y}_1^A\mathrm{csch}\left(mL_0\right)\right]+\hat{Y}_1^C\frac{dc_0^C}{dy_0}\right]$$

These two equations, the perturbed B-V equations, are linear, homogenous, algebraic equations in $\hat{Y}_1^A$ and $\hat{Y}_1^C$. They can be written as

$$\begin{pmatrix}A_{11} & A_{12}\\ A_{21} & A_{22}\end{pmatrix}\begin{pmatrix}\hat{Y}_1^A\\ \hat{Y}_1^C\end{pmatrix}=\begin{pmatrix}0\\ 0\end{pmatrix}\qquad(4.30)$$

where

$$A_{11}=\left\{\begin{array}{l}\frac{c_M}{\bar{c}}\sigma\left[\frac{P}{D}\frac{1}{m}\frac{z_1z_2D_2}{z_1D_1-z_2D_2}\coth\left(mL_0\right)+\frac{1}{k}\frac{z_1^2}{z_1D_1-z_2D_2}\coth\left(kL_0\right)\right]\\ +\frac{\gamma}{c_MRT}k^2-\frac{z_1F}{RT}\frac{d\phi_0^A}{dy_0}\end{array}\right\}$$
$$\times\left[[1-\beta]e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}+\frac{c_0^A}{\bar{c}}\beta e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}\right]+\frac{z_1Fc_M}{i_0}\sigma$$
$$-\frac{e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}}{\bar{c}}\left[\frac{dc_0^A}{dy_0}+\frac{\sigma}{m}\frac{z_1z_2D_2}{z_1D_1-z_2D_2}\frac{c_M}{D}\coth\left(mL_0\right)\right]$$

$$A_{12} = -\frac{c_M}{\bar{c}}\sigma\left[\frac{P}{D}\frac{1}{m}\frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\operatorname{csch}(mL_0) + \frac{1}{k}\frac{z_1^2}{z_1 D_1 - z_2 D_2}\operatorname{csch}(kL_0)\right]$$
$$\times\left[[1-\beta]e^{[1-\beta]\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]} + \frac{c_0^A}{\bar{c}}\beta e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]}\right]$$
$$+\frac{e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]}}{\bar{c}}\frac{\sigma}{m}\frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\frac{c_M}{D}\operatorname{csch}(mL_0)$$

$$A_{21} = \frac{c_M}{\bar{c}}\sigma\left[\frac{P}{D}\frac{1}{m}\frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\operatorname{csch}(mL_0) + \frac{1}{k}\frac{z_1^2}{z_1 D_1 - z_2 D_2}\operatorname{csch}(kL_0)\right]$$
$$\times\left[[1-\beta]e^{[1-\beta]\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]} + \frac{c_0^C}{\bar{c}}\beta e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]}\right]$$
$$-\frac{e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]}}{\bar{c}}\frac{\sigma}{m}\frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\frac{c_M}{D}\operatorname{csch}(mL_0)$$

and

$$A_{22} = \left\{\begin{array}{l} -\frac{c_M}{\bar{c}}\sigma\left[\frac{P}{D}\frac{1}{m}\frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\coth(mL_0) + \frac{1}{k}\frac{z_1^2}{z_1 D_1 - z_2 D_2}\coth(kL_0)\right] \\ -\frac{\gamma}{c_M RT}k^2 - \frac{z_1 F}{RT}\frac{d\phi_0^C}{dy_0} \end{array}\right\}$$
$$\times\left[[1-\beta]e^{[1-\beta]\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]} + \frac{c_0^C}{\bar{c}}\beta e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]}\right] - \frac{z_1 F c_M}{i_0}\sigma$$
$$-\frac{e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]}}{\bar{c}}\left[\frac{dc_0^C}{dy_0} - \frac{\sigma}{m}\frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\frac{c_M}{D}\coth(mL_0)\right]$$

Now a solution other than $\hat{Y}_1^A = 0 = \hat{Y}_1^C$ can be found if and only if

$$\det\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} = A_{11}A_{22} - A_{12}A_{21} = 0$$

By setting $A_{11}A_{22} - A_{12}A_{21}$ to zero, the relation between σ and k^2 can be found. However, there is no obvious way we can write this equation explicitly for σ as a function of k^2. Again, this is because σ is present inside m (i.e., inside $\sqrt{k^2 + \frac{\sigma}{D}}$) and

m appears in the arguments of the hyperbolic functions. All these complications imply that to get the relation between σ and k^2 one must draw a graph of σ vs. k^2 (i.e., to input the value for k^2 and seek the value of σ that will make the determinant equal to zero). This was done using Maple® VIII and is presented in the next section where the results are given and discussed.

4.5 Results and Discussion

Our goal of this chapter, as stated earlier, is to solve the eigenvalue problem in order to find σ when we input k^2. It might be expected to determine many $\sigma's$ for each k^2 when the eigenvalue problem is solved. We will be interested only in finding the two largest $\sigma's$ which are the leading and most dangerous ones. One of these two will go through $\sigma = 0$ and we call it the first σ, the second σ will be always less than zero and it will be the closest to the first one obtained from the calculations. We concentrate on these two since it is more convenient to focus on the two most dangerous ones, all the others being more negative (i.e., more stable than the second σ).

Now the relation between σ and k^2 will be obtained by setting $A_{11}A_{22} - A_{12}A_{21}$ to zero so let us see what comprising A_{11}, A_{12}, A_{21} and A_{22}. It is clear that two of our input variables namely $\bar{c}$ and L_0 in addition to the physical parameters of the problem given in Table 3-1 such as γ, c_M, D_1, D_2 etc. are all present. Also expressions from the base solution appear in the $A's$ which can be calculated for any $\bar{c}$, L_0 and $V^A - V^C$. Finally, as k^2 is also treated as an input variable, σ is the only unknown to be determined.

In the coming graphs, the effect of the velocity of the electrodes or the current, the distance between the two electrodes and the average ionic concentration on the relation

between σ and k^2 will be studied. As discussed previously in chapter 3, U/U_{lim} will represent the effect of changing the current since $V^A - V^C$ and U/U_{lim} are tied together and changing one of them will change the other.

Now the relations obtained from the base solution can be written in terms of U/U_{lim} as

$$-\frac{1}{\overline{c}}\frac{dc_0^C}{dy_0} = -\frac{1}{\overline{c}}\frac{dc_0^A}{dy_0} = \frac{2}{L_0}\frac{U}{U_{\text{lim}}} \tag{4.31}$$

$$\frac{d}{dy_0}\left[\frac{z_1 F}{RT}\phi_0\right]^C = \frac{d}{dy_0}\left[\frac{z_1 F}{RT}\phi_0\right]^A = \frac{2}{L_0}\frac{z_1}{z_2}\frac{U}{U_{\text{lim}}} \tag{4.32}$$

$$\frac{c_0^A}{\overline{c}} = 1 + \frac{U}{U_{\text{lim}}} \tag{4.33}$$

and

$$\frac{c_0^C}{\overline{c}} = 1 - \frac{U}{U_{\text{lim}}} \tag{4.34}$$

Then from the B-V equation, at both the anode and the cathode, as it appears in the base solution viz.,

$$-z_1 F c_M U = i_0\left[e^{[1-\beta]\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]} - \frac{c_0^A}{\overline{c}}e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]}\right] \tag{4.35}$$

and

$$z_1 F c_M U = i_0\left[e^{[1-\beta]\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]} - \frac{c_0^C}{\overline{c}}e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]}\right] \tag{4.36}$$

we can get the exponential terms e.g., $e^{[1-\beta]\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]}$ as a function of U when β is set to one half as

$$e^{\frac{1}{2}\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{RQ}\right]}=-\frac{1}{2}\frac{z_1Fc_MU}{i_0}+\frac{1}{2}\sqrt{\left(\frac{z_1Fc_MU}{i_0}\right)^2+4\frac{c_0^A}{\bar{c}}} \tag{4.37}$$

and

$$e^{\frac{1}{2}\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{RQ}\right]}=\frac{1}{2}\frac{z_1Fc_MU}{i_0}+\frac{1}{2}\sqrt{\left(\frac{z_1Fc_MU}{i_0}\right)^2+4\frac{c_0^C}{\bar{c}}} \tag{4.38}$$

Though in equations (4.37) and (4.38) it is clear that U not U/U_{lim} appears on the right hand side, we can introduce U/U_{lim} to these equations by multiplying and dividing each term by U_{lim} which is a constant. Now one is ready to treat U/U_{lim} as the input variable and study how it will affect the dependence of σ on k^2.

4.5.1 The Effect of the Current on the σ vs. k^2 Relation

The results that are going to be given in this and the following two sections will be presented without explaining their behavior at this stage. This is because the relation between σ and k^2 is so complicated that it is impossible to trace how each variable will affect this relation. The explanation on the effect of the input variables on the behavior of the curves will be discussed later at the end of this chapter when more approximations will be introduced to simplify the σ vs. k^2 relation.

Figure 4-1 shows the effect of changing the current, which is represented by U/U_{lim} on the relation between σ and k^2. For each input value of U/U_{lim}, two curves are drawn. The first curve corresponds to the most dangerous σ that starts from a small positive value then increasing for small values of k^2 reaching a maximum followed by a monotonic decreasing trend. This curve passes through the neutral stability point where σ changes sign's from positive to negative. So it seems that increasing the wave number

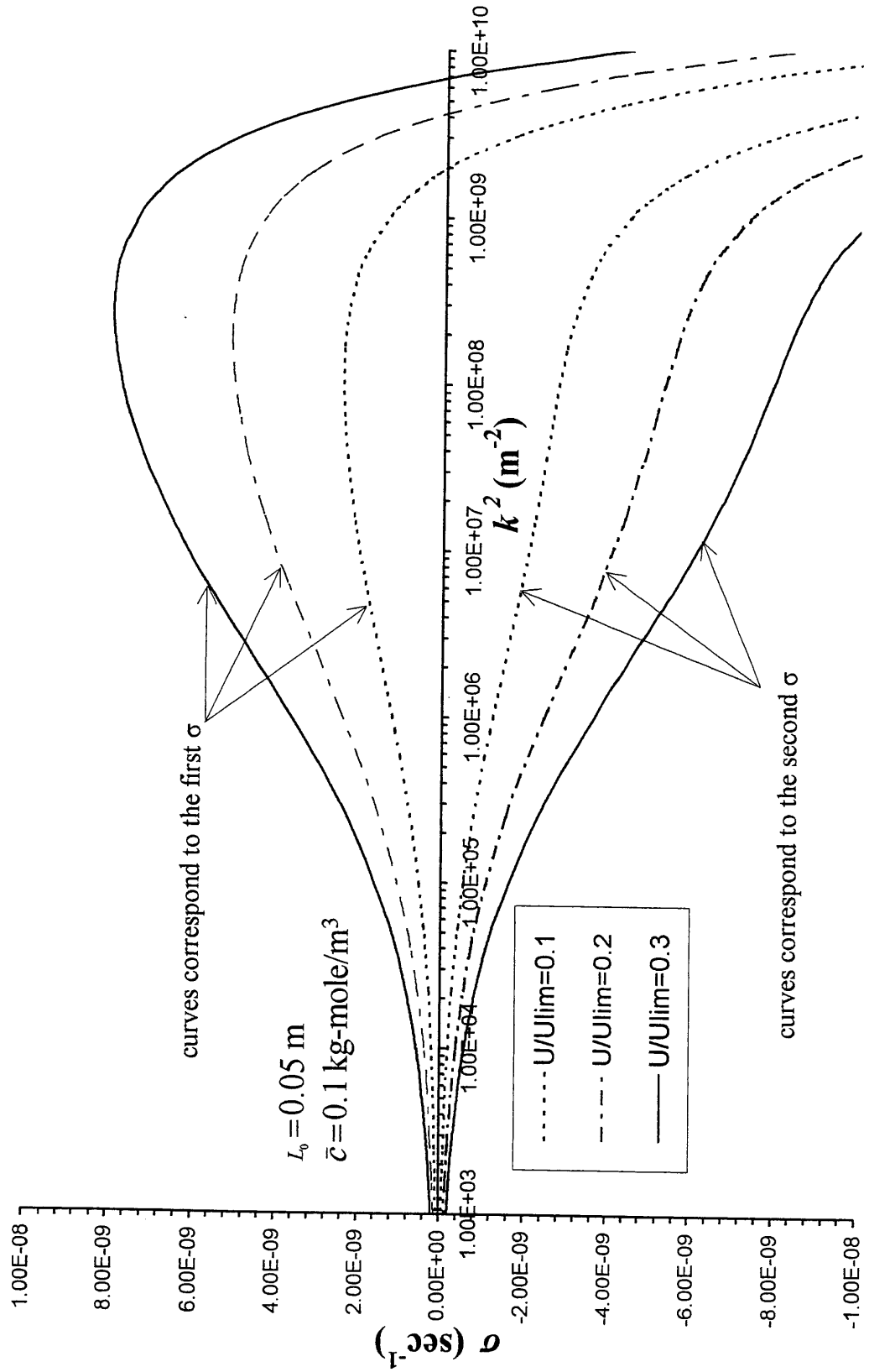


Figure 4-1. σ vs. k^2 relation for small values of U/U_{lim}.

will have a destabilizing effect at the beginning which will turn to a stabilizing effect later for very large values of k^2. The second curve represents the second σ which is shown to start from a negative value and decreasing continuously as k^2 gets larger so k^2 is always stabilizing here.

Now positive $\sigma's$ correspond to growing modes that will result in unstable displacements while negative $\sigma's$ represent decaying modes corresponding to stable displacements. Figure 4-1 was drawn for $\overline{c} = 0.1$ kg-mole/m^3, $L_0 = 0.05$ m and U/U_{lim} equal to 0.1, 0.2 and 0.3. Considering the positive $\sigma's$, it is clear that the system is more stable for lower values of U/U_{lim} than for higher values. Conversely, negative $\sigma's$ become more stable for larger values of U/U_{lim}.

Figure 4-2 is drawn to check if the same behavior is seen for larger currents for the same input concentration and spacing of the electrodes. The values of U/U_{lim} are now 0.4, 0.5 and 0.6 and the pattern inferred from Figure 4-1 is realized.

What we have learned here is that increasing the current will increase the instability, namely, more unstable wave numbers and faster growth at each unstable wave number. It is interesting that the second eigenvalue behaves oppositely, while always negative, it becomes more negative as the current increases.

We now turn to the effect of another input variable, namely, the electrode spacing.

4.5.2 The Effect of the Distance Between the Electrodes on the σ vs. k^2 Relation

Figure 4-3 presents σ vs. k^2 for three electrode spacings namely 0.005 m, 0.0075 m and 0.01 m at $U/U_{\text{lim}} = 0.3$ and $\overline{c} = 0.1$ kg-mole/m^3. The figure shows that the largest distance gives the most stable situation, as it gives the lowest values of

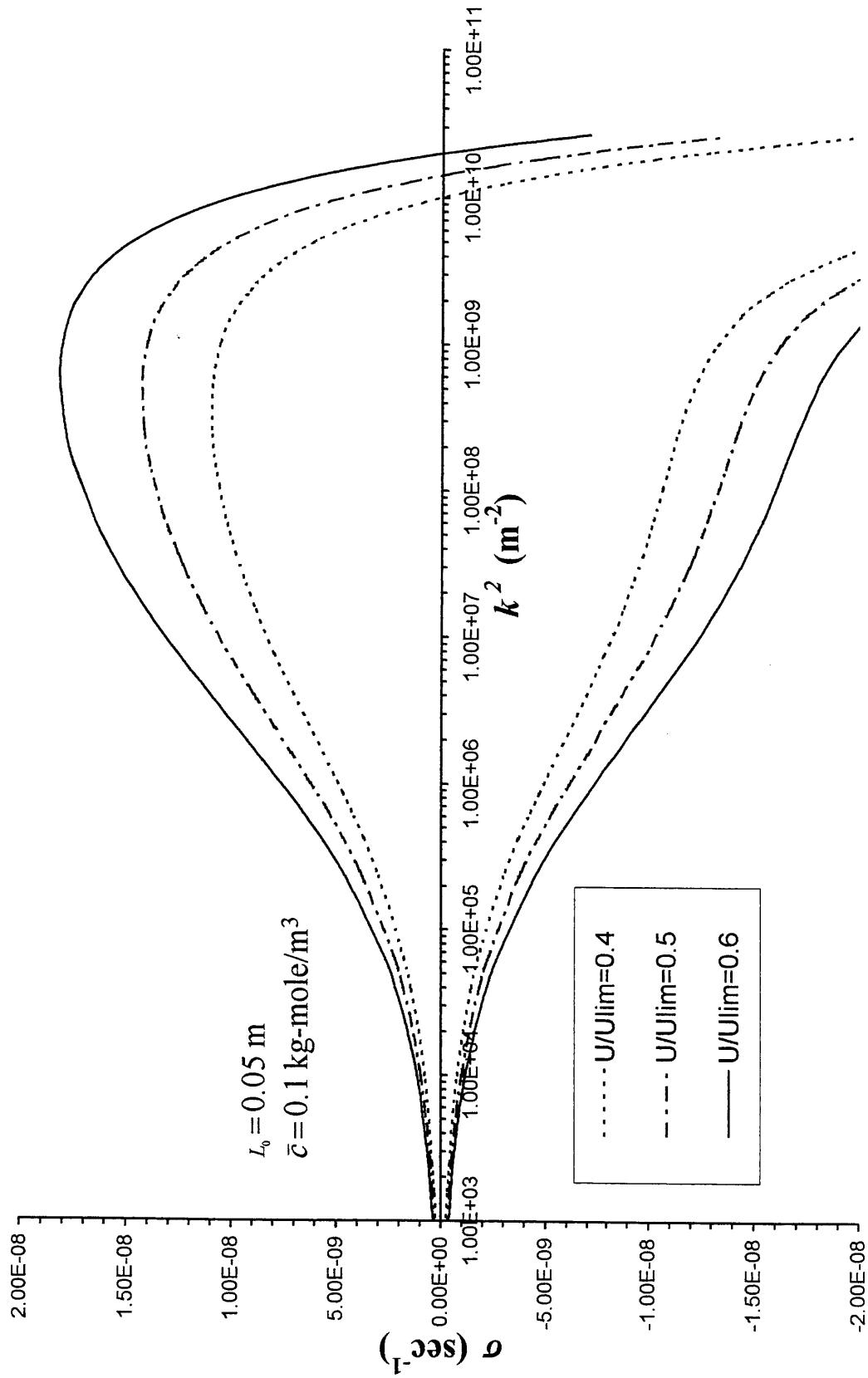


Figure 4-2. σ vs. k^2 relation for large values of U/U_{lim} .

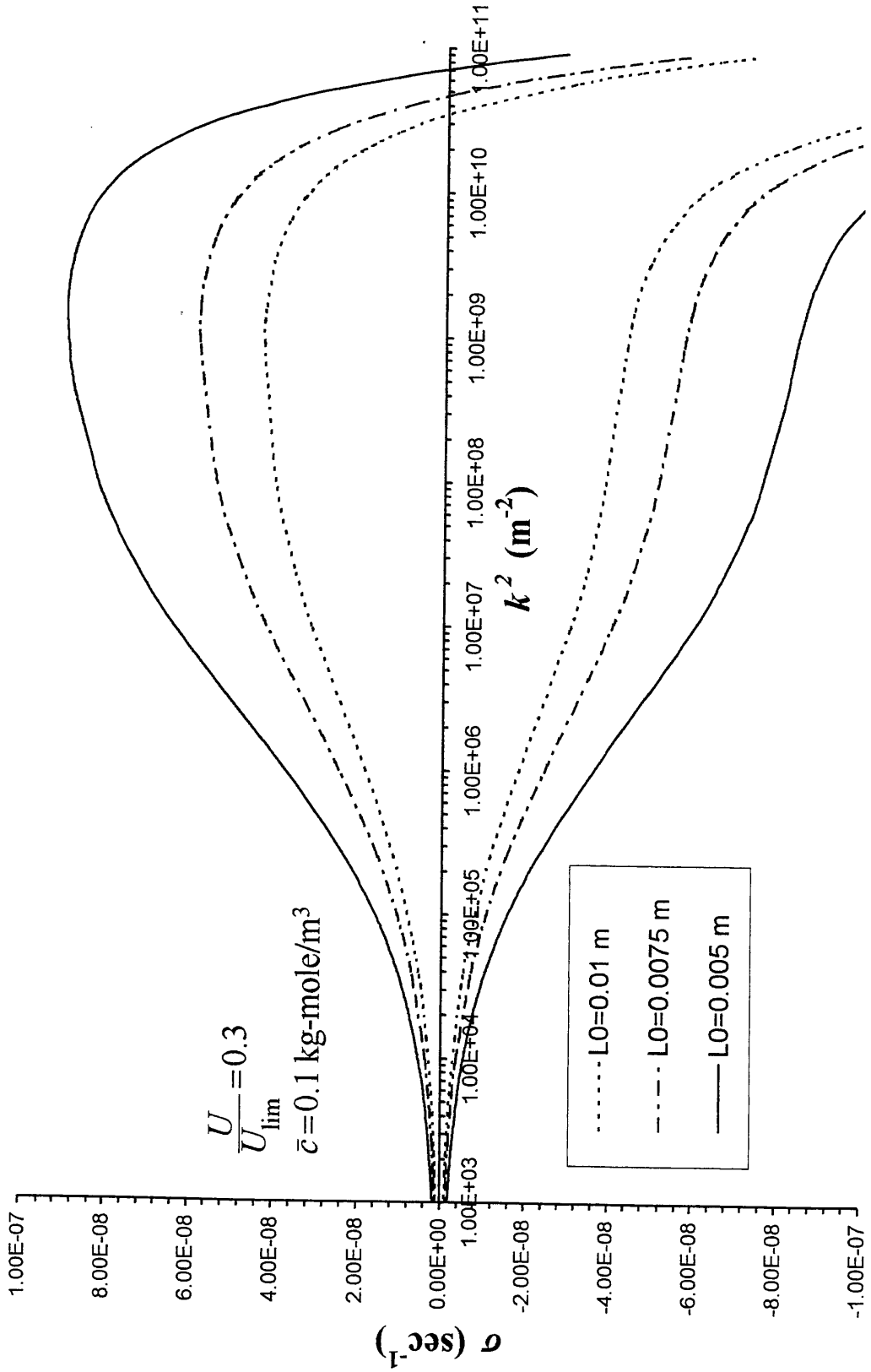


Figure 4-3. σ vs. k^2 relation for different values of electrode spacing.

positive $\sigma's$ and the smallest region of instability. This result agrees qualitatively with what we found previously from the neutral stability analysis. Again, as in the previous section, the wider the range of unstable wave numbers, the larger the σ at the unstable $k^2's$. On the other hand, negative $\sigma's$ become more stable for smaller electrode spacing.

Figure 4-4 is Figure 4-3 drawn for even smaller spacings. The pattern of Figure 4-3 is seen to persist just as Figure 4-2 continues Figure 4-1.

We go on to see the effect of changing the average ion concentration on the graph of σ vs. k^2.

4.5.3 The Effect of the Average Ionic Concentration on the σ vs. k^2 Relation

Figure 4-5 shows σ vs. k^2 curves for average ionic concentrations of 0.005 kg-mole/m^3, 0.0075 kg-mole/m^3 and 0.01 kg-mole/m^3 where $L_0 = 0.05$ m and $U/U_{\text{lim}} = 0.01$. The curve with the highest average ionic concentration (i.e., 0.01 kg-mole/m^3) gives the highest positive $\sigma's$ which means that increasing the average ionic concentration will make the system more unstable. But all the curves share the same $\sigma = 0$ point unlike what we found when we studied the effect of changing U/U_{lim} or L_0. The result that the neutral stability point is independent of the average ionic concentration is not a new result since it was discovered in the previous chapter. Hence while changing the average ionic concentration does not affect the neutral point it does affect the size of the growth constants (i.e., larger $\bar{c}'s$ will lead to larger $\sigma's$). As a corollary, the ordering of the $\sigma's$ now reverses as k^2 increases through the critical point.

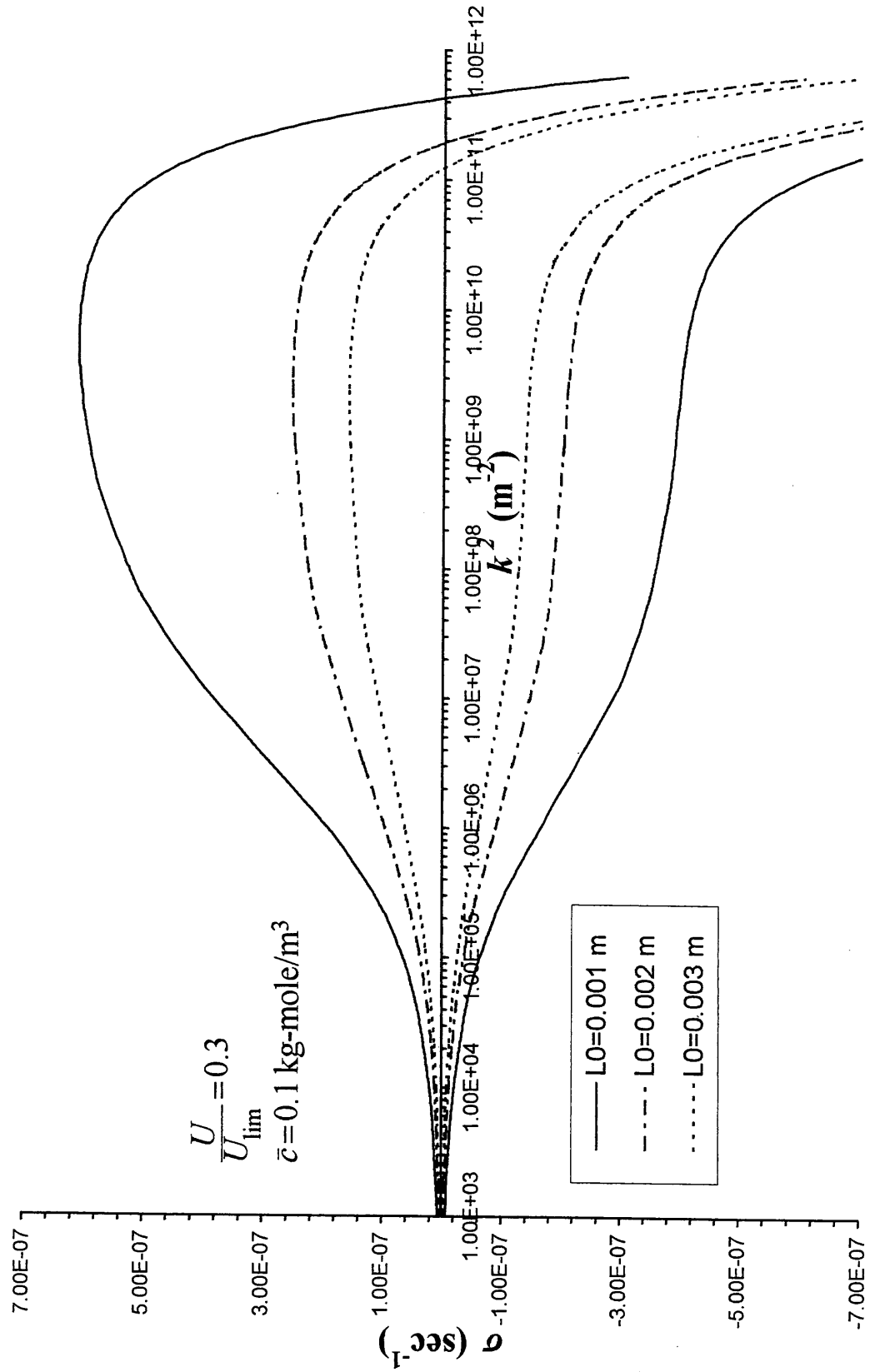


Figure 4-4. σ vs. k^2 relation for smaller values of electrode spacing.

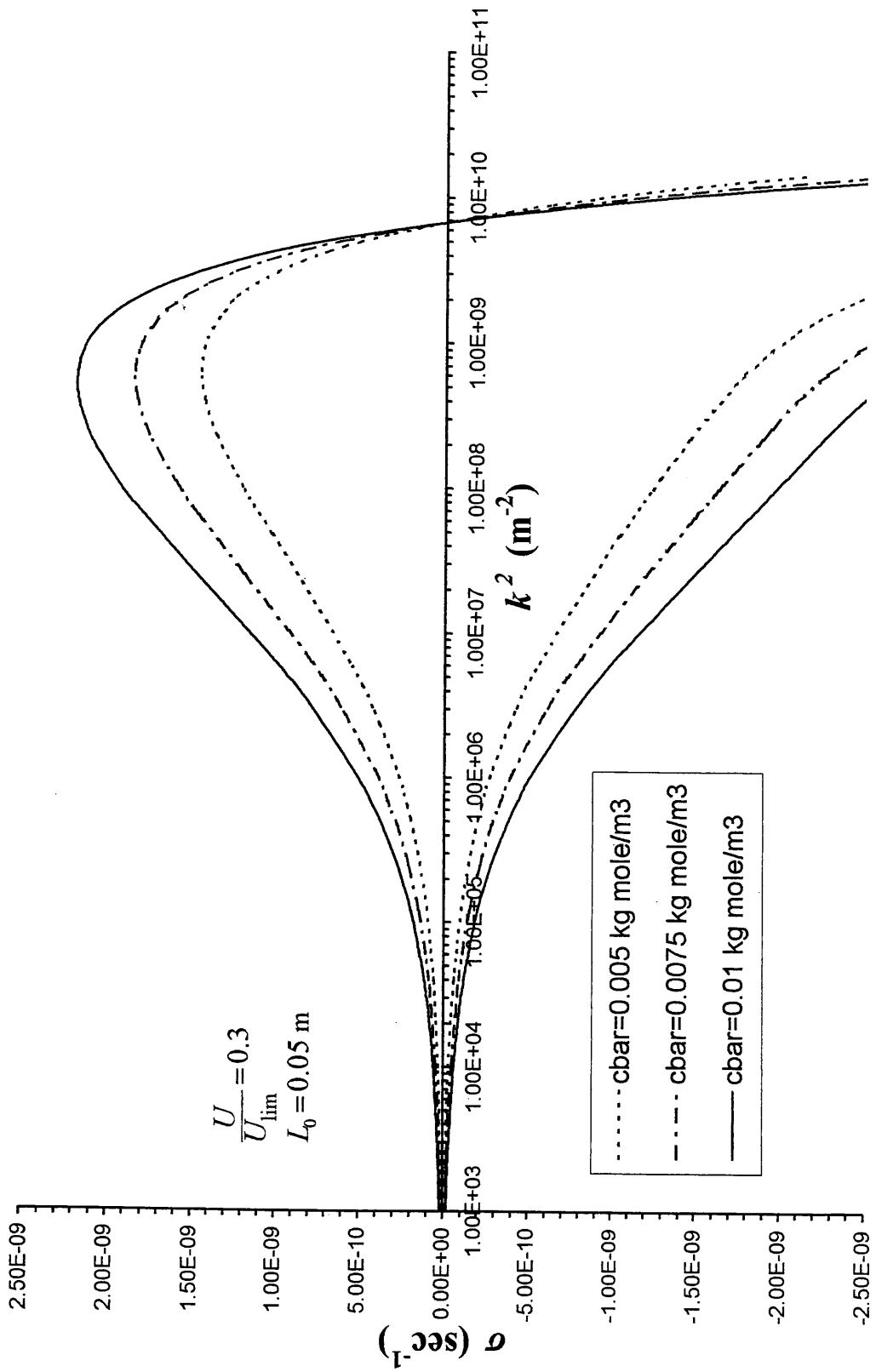


Figure 4-5. σ vs. k^2 relation for different values of average ionic concentration.

Figure 4-6 shows the relation between σ vs. k^2 for higher concentrations (i.e., $\bar{c}$ = 0.05 kg-mole/m^3, 0.075 kg-mole/m^3 and 0.1 kg-mole/m^3) at the same L_0 and U/U_{lim} used before. This figure continues what was seen in the expected direction.

The validation of the results obtained using the $c = \bar{c}$ approximation in the migration term of the domain will be handled in the next chapter when comparing with S&B results and when we solve the problem correctly with no approximation.

Now let us return to one of our objectives which is to get the relation between σ and k^2 explicitly and present one further approximation that will simplify our job greatly. This assumption will be presented next and it will enable us to get an explicit relation between σ and k^2.

4.6 The Effect of Dropping σ from the Domain Equation

The first approximation made in this chapter is to set c equal to $\bar{c}$ in the migration term of the domain equation to get rid of the non-linearity in the domain. Even though this approximation enabled us to simplify the problem and get a relation between σ and k^2, this relation was implicit and had to be graphed to be understood. The algebraic complication seems to be due to σ and k^2 both appearing in m (i.e., it is due to the σ appearing in the domain equation). If we can drop this σ on some grounds, we may be successful in obtaining an explicit relation for σ as a function of k^2. So the purpose of this section is to set σ in equation (4.14) to zero and rework the problem to see how the equations will be simplified, then to compare the results obtained here with the previous results. A simpler problem that inspired us to use this approximation is presented in Appendix D with the main purpose of showing that if two processes occur in series, then the slower one takes control of the overall rate.

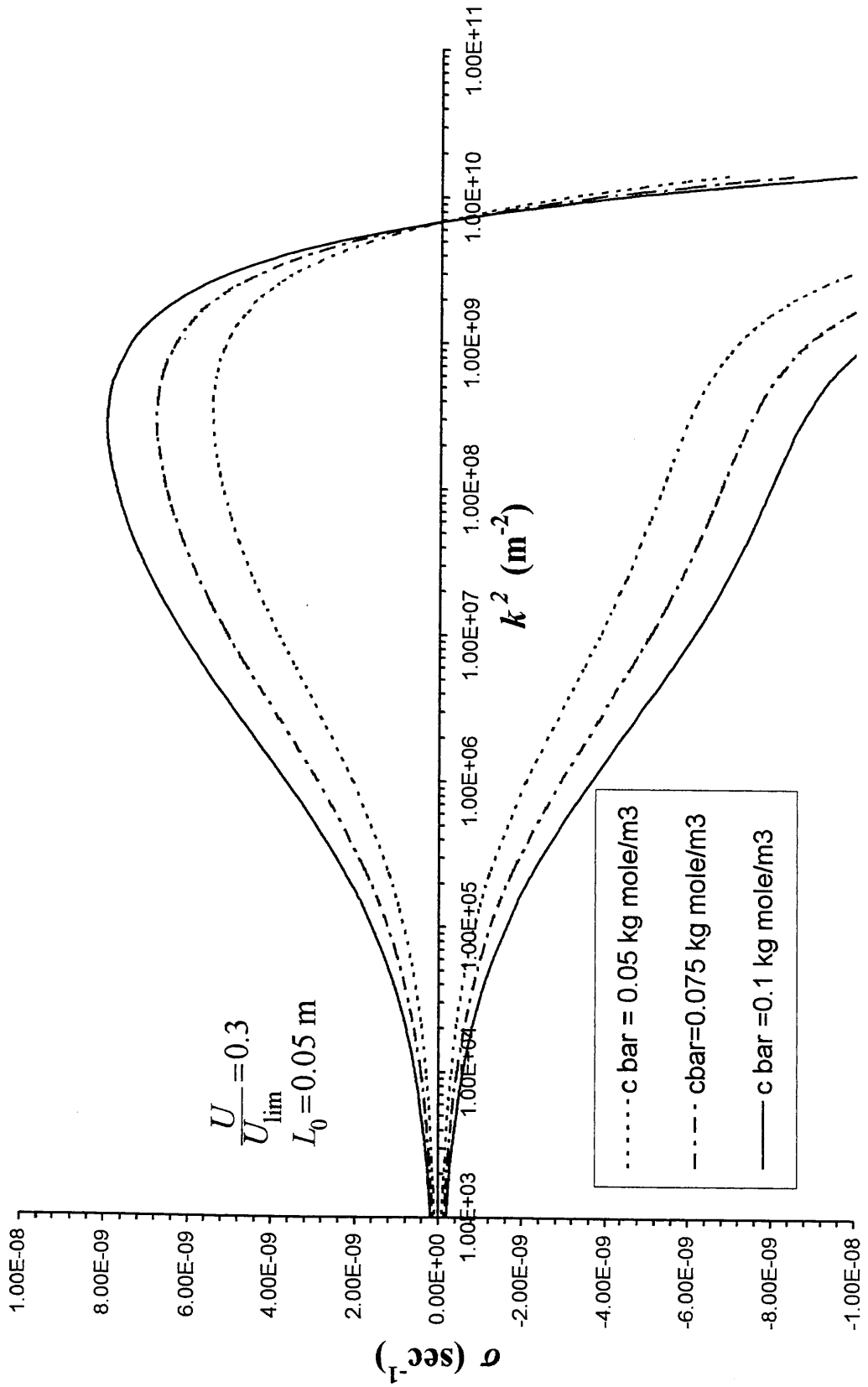


Figure 4-6. σ vs. k^2 relation for larger values of average ionic concentration.

Working through the simpler problem will lead to the following conclusion: scaling the equations properly and evaluating the order of magnitude for every factor multiplying a σ will determine when dropping σ from one part a problem and retaining it in another will be a good move.

Now let us apply what we have learned from the simpler problem on the electrodeposition problem to see if there is a valid reason to drop σ on the domain.

4.6.1 Scaling the Electrodeposition Problem to Study the Importance of the Different Growth Constants

To see if dropping σ from the domain makes a good approximation to the electrodeposition problem, our first step will be to scale our equations.

To scale the problem, let us define these dimensionless groups

$$c^* = \frac{c}{\bar{c}}, \quad t^* = \frac{t}{\bar{t}}, \quad \phi^* = \frac{z_1 F}{RT}\phi, \quad \nabla^* = L_0\nabla, \quad U^* = \frac{\bar{t}}{L_0}U, \quad u^* = \frac{\bar{t}}{L_0}u,$$

$$y^* = \frac{1}{L_0}y, \quad x^* = \frac{1}{L_0}x \text{ and } \nabla^{*2} = L_0^2\nabla^2$$

where $\bar{t}$,which represents a characteristic time, will be chosen later. Now, rewriting equations (4.1) and (4.2), the domain equations, after applying the scaling above will give

$$P\,\nabla^{*2}c^* + \nabla^{*2}\phi = 0 \tag{4.39}$$

and

$$\frac{L_0^2}{D}\frac{1}{\bar{t}}\frac{\partial c^*}{\partial t^*} = \nabla^{*2}c^* \tag{4.40}$$

Equation (4.39) will not introduce σ to the problem since time derivatives do not appear there. But σ will appear in the domain from equation (4.40) because of the term $\frac{\partial c^*}{\partial t^*}$.

Let us refer to $\frac{L_0^2}{D}\frac{1}{\bar{t}}$ as the dimensionless domain time scale t_D, that is

$$t_D = \frac{L_0^2}{D}\frac{1}{\bar{t}}$$

Now, t_D is the factor that multiplies $\frac{\partial c^*}{\partial t^*}$ in the domain equation. If we can prove that t_D is negligible compared to the time scales multiplying the other time derivatives appearing in the boundary equations, then we might be justified in dropping σ from the domain equation.

Let us now turn to the boundary equations. The scaled version of equation (4.4) is

$$\vec{n}\cdot\nabla^* c^* = \frac{-z_1 z_2 D_2 c_M}{z_1 D_1 - z_2 D_2}\frac{L_0^2}{D\,\bar{c}\,\bar{t}}\left[\vec{n}\cdot\vec{u}^* + \vec{n}\cdot\vec{U}^*\right] \tag{4.41}$$

where the time derivative will be introduced through $\vec{n}\cdot\vec{u}^*$ as $\frac{\partial Y}{\partial t}$ and the dimensionless time scale which multiplies the time derivative will be defined as t_{CB} where

$$t_{CB} = \frac{c_M z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\frac{L_0^2}{D\,\bar{c}\,\bar{t}}$$

The second boundary equation is equation (4.3), which contains the migration effect. Scaling this equation will give

$$P\,\vec{n}\cdot\nabla^* c^* + \vec{n}\cdot\nabla^*\phi^* = \frac{L_0^2}{\bar{c}}\frac{c_M z_1^2}{z_1 D_1 - z_2 D_2}\frac{1}{\bar{t}}\left[\vec{n}\cdot\vec{u}^* + \vec{n}\cdot\vec{U}^*\right] \tag{4.42}$$

where we define $t_{\phi B}$ as

$$t_{\phi B} = \frac{c_M}{\bar{c}}\frac{z_1^2}{z_1 D_1 - z_2 D_2}\frac{L_0^2}{\bar{t}}$$

The last equation at the boundary is the B-V equation. Scaling the B-V equation will give

$$\frac{-z_1 F c_M L}{i_0\ \overline{t}}\left[\vec{n}.\vec{u}^* + \vec{n}\cdot\vec{U}^*\right] = e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}-\frac{\gamma}{z_1Fc_M}2H\right]} - \frac{c}{\overline{c}}e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi-\Delta\phi_{EQ}-\frac{\gamma}{z_1Fc_M}2H\right]} \qquad (4.43)$$

which introduces the dimensionless time scale t_{BV}, viz.,

$$t_{BV} = \frac{z_1 F c_M L_0}{i_0}\frac{1}{\overline{t}}$$

Now, we can choose $\overline{t}$, the characteristic time, for our own convenience in comparing the orders of magnitude of the four dimensionless time scales obtained from the equations. Since we are focusing on the domain time scale, we choose $\overline{t}$ so that $t_D = 1$, hence $\overline{t}$ is given by

$$\overline{t} = \frac{L_0^2}{D},\quad t_D = 1 \text{ whence } t_D = 1$$

Now let us look at a typical case by choosing $L_0 = 0.005$ m and $\overline{c} = 0.1$ kg-mole/m^3 as our input variables. Then using values from Table 3-1 to get the diffusion coefficients etc., we can evaluate the other dimensionless time scales as follows

$$t_{CB} = \frac{c_M}{\overline{c}}\frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} \approx 17{,}000$$

$$t_{\phi B} = \frac{c_M}{\overline{c}}\frac{z_1^2 D}{z_1 D_1 - z_2 D_2} \approx 13{,}500$$

and

$$t_{BV} = \frac{z_1 F c_M D}{i_0 L_0} \approx 500$$

The values obtained above show clearly how small t_D is when compared to the other time scales. The dimensionless time scale obtained from the B-V equation is two orders of magnitude larger than t_D and the other two from the boundary equations are

four orders of magnitude larger. This result is just what we were hoping to get. The values of the time scales tell us clearly that dropping σ from the domain is the right thing to do if we want to simplify the problem when seeking an explicit σ vs. k^2 relation and it also tells us that the CRE approximation ought to be good.

Thus, the definitions of the dimensionless time scales can be used to decide when the approximation of dropping σ from the domain is a good or a bad move. Increasing the diffusion coefficients and decreasing the average ionic concentration will enlarge the values of the boundary time scales making dropping σ from the domain a more realistic approximation.

It was mentioned at the beginning of this chapter that the value of a growth constant is an indication on how fast a perturbation will die with time. So, the physical interpretation of saying that σ in the domain is small and can be dropped compared to the other $\sigma's$, is that the perturbations at the domain will die faster than those at the boundaries. In addition, from a physical point of view, the trends mentioned above that encourage neglecting the domain perturbations agree with common sense. For example, increasing the diffusion coefficients will make it easier for perturbations in the domain to spread and die out faster. Furthermore, increasing the average ion concentration makes migration more effective and hence acts like D.

The last thing we want to comment on, before leaving this topic and turning to solve the equations after dropping the domain perturbation, is the dimensionless time scale of the B-V equation t_{BV}. The value of this time scale is the nearest to the domain time scale and it is very sensitive to the distance between the electrodes and the exchange current density which is a function of the average electrolytic concentration. For large L_0

and i_0, t_{BV} could also be neglected. This is not a new finding. In fact, if t_{BV} is dropped then the B-V equation will turn into the CRE equation and this is what we did in the previous chapter. So under some circumstances one even can drop the time constant from the B-V equation in addition to the σ that appears in the domain equation without worrying about the accuracy of the result. This discovery will be made use of later in chapter 6 where the nonlinear stability is studied and we will be in need of every approximation that will simplify the complicated calculations. But for now, we will satisfy ourselves by dropping σ from the domain and reworking the problem to get an explicit formula for σ vs. k^2. This is our next goal.

4.6.2 Getting σ Explicitly in Terms of k^2 by Setting $\sigma = 0$ on the Domain

By going back to equation (4.14) and setting σ to zero, so that m will be equal to k, the positive square root of k^2, and reworking the problem by following the same steps one will get these equations

$$\hat{c}_1^A = -\frac{\sigma}{k}\frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\frac{c_M}{D}\left[\hat{Y}_1^C \operatorname{csch}(kL_0) - \hat{Y}_1^A \coth(kL_0)\right] \tag{4.44}$$

$$\hat{c}_1^C = -\frac{\sigma}{k}\frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\frac{c_M}{D}\left[\hat{Y}_1^C \coth(kL_0) - \hat{Y}_1^A \operatorname{csch}(kL_0)\right] \tag{4.45}$$

$$\hat{\phi}_1^A = \frac{\sigma}{k}\frac{RT}{z_1 F}\frac{c_M}{\bar{c}}\frac{z_1^2}{D_1(z_1 - z_2)}\left[\hat{Y}_1^C \operatorname{csch}(kL_0) - \hat{Y}_1^A \coth(kL_0)\right] \tag{4.46}$$

and

$$\hat{\phi}_1^C = \frac{\sigma}{k}\frac{RT}{z_1 F}\frac{c_M}{\bar{c}}\frac{z_1^2}{D_1(z_1 - z_2)}\left[\hat{Y}_1^C \coth(kL_0) - \hat{Y}_1^A \operatorname{csch}(kL_0)\right] \tag{4.47}$$

and we can notice how dropping σ from the domain makes the right hand side of each equation a multiple of σ. Now having found $\hat{c}_1^A$, $\hat{\phi}_1^A$, $\hat{c}_1^C$ and $\hat{\phi}_1^C$ we can substitute these results into equations (4.18) and (4.21) to get

$$-\frac{z_1 F c_M}{i_0}\sigma\hat{Y}_1^A = \left[\left[1-\beta\right]e^{\left[1-\beta\right]\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}+\frac{c_0^A}{\bar{c}}\beta e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}\right]\left[\frac{z_1F}{RT}\right]$$
$$\times\left[-\frac{\sigma}{k}\frac{RT}{z_1F}\frac{c_M}{\bar{c}}\frac{z_1^2}{D_1\left(z_1-z_2\right)}\left[\hat{Y}_1^C\operatorname{csch}\left(kL_0\right)-\hat{Y}_1^A\coth\left(kL_0\right)\right]+\hat{Y}_1^A\frac{d}{dy_0}\Delta\phi_0^A+\frac{\gamma}{z_1Fc_M}k^2\hat{Y}_1^A\right]$$
$$-\frac{e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}}{\bar{c}}\left[-\frac{\sigma}{k}\frac{z_1z_2D_2}{z_1D_1-z_2D_2}\frac{c_M}{D}\left[\hat{Y}_1^C\operatorname{csch}\left(kL_0\right)-\hat{Y}_1^A\coth\left(kL_0\right)\right]+\hat{Y}_1^A\frac{dc_0^A}{dy_0}\right]$$

and

$$+\frac{z_1 F c_M}{i_0}\sigma\hat{Y}_1^C = \left[\left[1-\beta\right]e^{\left[1-\beta\right]\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{EQ}\right]}+\frac{c_0^C}{\bar{c}}\beta e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{EQ}\right]}\right]\left[\frac{z_1F}{RT}\right]$$
$$\times\left[-\frac{\sigma}{k}\frac{RT}{z_1F}\frac{c_M}{\bar{c}}\frac{z_1^2}{D_1\left(z_1-z_2\right)}\left[\hat{Y}_1^C\coth\left(kL_0\right)-\hat{Y}_1^A\operatorname{csch}\left(kL_0\right)\right]+\hat{Y}_1^C\frac{d}{dy_0}\Delta\phi_0^C-\frac{\gamma}{z_1Fc_M}k^2\hat{Y}_1^C\right]$$
$$-\frac{e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{EQ}\right]}}{\bar{c}}\left[-\frac{\sigma}{k}\frac{z_1z_2D_2}{z_1D_1-z_2D_2}\frac{c_M}{D}\left[\hat{Y}_1^C\coth\left(kL_0\right)-\hat{Y}_1^A\operatorname{csch}\left(kL_0\right)\right]+\hat{Y}_1^C\frac{dc_0^C}{dy_0}\right]$$

These two equations, the perturbed B-V equations are linear, homogenous, algebraic equations in $\hat{Y}_1^A$ and $\hat{Y}_1^C$ and they can be written as

$$\begin{pmatrix}B_{11} & B_{12}\\ B_{21} & B_{22}\end{pmatrix}\begin{pmatrix}\hat{Y}_1^A\\ \hat{Y}_1^C\end{pmatrix}=\begin{pmatrix}0\\0\end{pmatrix} \tag{4.48}$$

Now, a solution other than $\hat{Y}_1^A = 0 = \hat{Y}_1^C$ can be found if and only if

$$\det\begin{pmatrix}B_{11} & B_{12}\\ B_{21} & B_{22}\end{pmatrix} = B_{11}B_{22}-B_{12}B_{21} = 0$$

where

$$B_{11}=\left[\frac{\sigma}{k}\frac{c_M}{\bar{c}}\frac{z_1^2}{D_1(z_1-z_2)}\coth(kL_0)+\frac{\gamma}{c_M RT}k^2-\frac{z_1F}{RT}\frac{d\phi_0^A}{dy_0}\right]$$
$$\times\left[[1-\beta]e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}+\frac{c_0^A}{\bar{c}}\beta e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}\right]+\frac{z_1Fc_M}{i_0}\sigma$$
$$-\frac{e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}}{\bar{c}}\left[\frac{dc_0^A}{dy_0}+\frac{\sigma}{k}\frac{z_1z_2D_2}{z_1D_1-z_2D_2}\frac{c_M}{D}\coth(kL_0)\right]$$

$$B_{12}=-\left[\frac{\sigma}{k}\frac{c_M}{\bar{c}}\frac{z_1^2}{D_1(z_1-z_2)}\operatorname{csch}(kL_0)\right]\left[[1-\beta]e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}+\frac{c_0^A}{\bar{c}}\beta e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}\right]$$
$$+\frac{e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}}{\bar{c}}\frac{\sigma}{k}\frac{z_1z_2D_2}{z_1D_1-z_2D_2}\frac{c_M}{D}\operatorname{csch}(kL_0)$$

$$B_{21}=\left[\frac{\sigma}{k}\frac{c_M}{\bar{c}}\frac{z_1^2}{D_1(z_1-z_2)}\operatorname{csch}(kL_0)\right]\left[[1-\beta]e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{EQ}\right]}+\frac{c_0^C}{\bar{c}}\beta e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{EQ}\right]}\right]$$
$$-\frac{e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{EQ}\right]}}{\bar{c}}\frac{\sigma}{k}\frac{z_1z_2D_2}{z_1D_1-z_2D_2}\frac{c_M}{D}\operatorname{csch}(kL_0)$$

and

$$B_{22}=\left[-\frac{\sigma}{k}\frac{c_M}{\bar{c}}\frac{z_1^2}{D_1(z_1-z_2)}\coth(kL_0)-\frac{\gamma}{c_M RT}k^2-\frac{z_1F}{RT}\frac{d\phi_0^C}{dy_0}\right]$$
$$\times\left[[1-\beta]e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{EQ}\right]}+\frac{c_0^C}{\bar{c}}\beta e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{EQ}\right]}\right]-\frac{z_1Fc_M}{i_0}\sigma$$
$$-\frac{e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{EQ}\right]}}{\bar{c}}\left[\frac{dc_0^C}{dy_0}-\frac{\sigma}{k}\frac{z_1z_2D_2}{z_1D_1-z_2D_2}\frac{c_M}{D}\coth(kL_0)\right]$$

By setting $B_{11}B_{22}-B_{12}B_{21}$ to zero, an explicit relation between σ and k^2 can be obtained. This relation is a quadratic equation in σ whose solution is simply

$$\sigma=\frac{-b\pm\sqrt{b^2-4\,a\,c}}{2a} \tag{4.49}$$

where

$$a = \left\{ \left(\left[1-\beta\right] e^{\left[1-\beta\right]\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]} + \frac{c_0^C}{\overline{c}} \beta e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]} \right) \left(\frac{1}{k} \frac{c_M}{\overline{c}} \frac{z_1^2}{D_1\left(z_1 - z_2\right)} \coth(kL_0) \right) \right\}$$
$$+ \left\{ \left(\frac{e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]}}{\overline{c}} \right) \left(\frac{1}{k} \frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} \frac{c_M}{D} \coth(kL_0) \right) + \frac{z_1 F c_M}{i_0} \right\}$$
$$\times \left\{ \left(\frac{e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]}}{\overline{c}} \right) \left(\frac{1}{k} \frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} \frac{c_M}{D} \coth(kL_0) \right) - \frac{z_1 F c_M}{i_0} \right\}$$
$$\left\{ - \left(\left[1-\beta\right] e^{\left[1-\beta\right]\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]} + \frac{c_0^A}{\overline{c}} \beta e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]} \right) \left(\frac{1}{k} \frac{c_M}{\overline{c}} \frac{z_1^2}{D_1\left(z_1 - z_2\right)} \coth(kL_0) \right) \right\}$$
$$+ \left\{ \left(\left[1-\beta\right] e^{\left[1-\beta\right]\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]} + \frac{c_0^A}{\overline{c}} \beta e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]} \right) \left(\frac{1}{k} \frac{c_M}{\overline{c}} \frac{z_1^2}{D_1\left(z_1 - z_2\right)} \operatorname{csch}(kL_0) \right) \right\}$$
$$\left\{ - \left(\frac{e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]}}{\overline{c}} \right) \left(\frac{\sigma}{k} \frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} \frac{c_M}{D} \operatorname{csch}(kL_0) \right) \right\}$$
$$\times \left\{ \left(\left[1-\beta\right] e^{\left[1-\beta\right]\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]} + \frac{c_0^C}{\overline{c}} \beta e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]} \right) \left(\frac{1}{k} \frac{c_M}{\overline{c}} \frac{z_1^2}{D_1\left(z_1 - z_2\right)} \operatorname{csch}(kL_0) \right) \right\}$$
$$\left\{ - \left(\frac{e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]}}{\overline{c}} \right) \left(\frac{\sigma}{k} \frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} \frac{c_M}{D} \operatorname{csch}(kL_0) \right) \right\}$$

$$c = \left\{ \left(\left[1-\beta\right] e^{\left[1-\beta\right]\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]} + \frac{c_0^C}{\overline{c}} \beta e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]} \right) \left(\frac{z_1 F}{RT} \frac{d\phi_0^C}{dy_0} + \frac{\gamma}{c_M RT} k^2 \right) \right\}$$
$$\left\{ + \frac{e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]}}{\overline{c}} \frac{dc_0^C}{dy_0} \right\}$$
$$\times \left\{ \left(\left[1-\beta\right] e^{\left[1-\beta\right]\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]} + \frac{c_0^A}{\overline{c}} \beta e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]} \right) \left(\frac{z_1 F}{RT} \frac{d\phi_0^A}{dy_0} - \frac{\gamma}{c_M RT} k^2 \right) \right\}$$
$$\left\{ + \frac{e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]}}{\overline{c}} \frac{dc_0^A}{dy_0} \right\}$$

and

$$
\begin{aligned}
b = & \left\{ \left(\left[1-\beta\right] e^{\left[1-\beta\right]\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]} + \frac{c_0^C}{\overline{c}} \beta e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]} \right) \left(\frac{\gamma}{c_M RT} k^2 + \frac{z_1 F}{RT} \frac{d\phi_0^C}{dy_0} \right) + \right. \\
& \left. \frac{e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]}}{\overline{c}} \frac{dc_0^C}{dy_0} \right\} \\
& \times \left\{ \left(\frac{e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]}}{\overline{c}} \right) \left(\frac{1}{k} \frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} \frac{c_M}{D} \coth(kL_0) \right) - \frac{z_1 F c_M}{i_0} \right. \\
& \left. - \left(\left[1-\beta\right] e^{\left[1-\beta\right]\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]} + \frac{c_0^A}{\overline{c}} \beta e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]} \right) \left(\frac{1}{k} \frac{c_M}{\overline{c}} \frac{z_1^2}{D_1 \left(z_1 - z_2\right)} \coth(kL_0) \right) \right\} \\
& + \left\{ \left(\left[1-\beta\right] e^{\left[1-\beta\right]\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]} + \frac{c_0^C}{\overline{c}} \beta e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]} \right) \left(\frac{1}{k} \frac{c_M}{\overline{c}} \frac{z_1^2}{D_1 \left(z_1 - z_2\right)} \coth(kL_0) \right) \right. \\
& \left. + \left(\frac{e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]}}{\overline{c}} \right) \left(\frac{1}{k} \frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} \frac{c_M}{D} \coth(kL_0) \right) + \frac{z_1 F c_M}{i_0} \right\} \\
& \times \left\{ \left(\left[1-\beta\right] e^{\left[1-\beta\right]\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]} + \frac{c_0^A}{\overline{c}} \beta e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]} \right) \left(\frac{z_1 F}{RT} \frac{d\phi_0^A}{dy_0} - \frac{\gamma}{c_M RT} k^2 \right) \right. \\
& \left. + \frac{e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]}}{\overline{c}} \frac{dc_0^A}{dy_0} \right\}
\end{aligned}
$$

This is the relation obtained after dropping σ from the domain. Although it is not a simple relation, it is nonetheless clear how σ could be calculated explicitly for the input conditions including the wave number, k^2. It is also obvious that this quadratic equation will produce 2 values of σ for each value of k^2 so we are going to get two curves and we expect that these two curves will be approximate to the curves obtained before (i.e., one curve will pass through the neutral point and the other will give negative values of σ for every k^2 we input). The next thing to do is to compare the results obtained from this approximation with those obtained before.

4.6.3 Comparison Between the Results Obtained by Dropping and Keeping σ on the Domain

Here we will check how good the approximation of dropping σ from the domain equation is compared to the case where it is kept in tact. First, let us compare the results at different values of U/U_{lim}. Figures 4-7, 4-8 and 4-9 show σ vs. k^2 by the two methods where $\overline{c} = 0.1$ kg-mole/m^3, $L_0 = 0.05$ m and U/U_{lim} equals 0.3, 0.5 and 0.9 respectively. In all of the three figures it is very hard if not impossible to distinguish between the two curves. This tells us that this approximation is excellent for the whole range of currents used.

Let us now investigate the effect of changing the distance between the electrodes. Figures 4-10 is drawn at $U/U_{\text{lim}} = 0.3$, $\overline{c} = 0.1$ kg-mole/m^3 and $L_0 = 0.005$ m which can be compared to Figure 4-7. Again no difference at all can be noticed in the two figures for large or small values of L_0.

Finally, the effect of changing $\overline{c}$ is studied by fixing $U/U_{\text{lim}} = 0.01$, $L_0 = 0.05$ m and changing the values of $\overline{c}$. Figures 4-11, 4-12 and 4-13 are drawn for $\overline{c} = 0.1$ kg-mole/m^3, $\overline{c} = 1.0$ kg-mole/m^3 and $\overline{c} = 10.0$ kg-mole/m^3 respectively. The values that we set for $\overline{c}$ (i.e., 1.0 kg-mole/m^3 and 10.0 kg-mole/m^3) are extremely high values of concentration but we chose them in order to show that even for such high values of the average concentration we cannot distinguish between the two curves.

These figures present clear evidence that dropping σ from the domain is such an excellent approximation that has no effect on the precision of the results. And that the scaling given in section 4.6.1 was an excellent way to help us forecast this result even before doing the calculation and draw the figures.

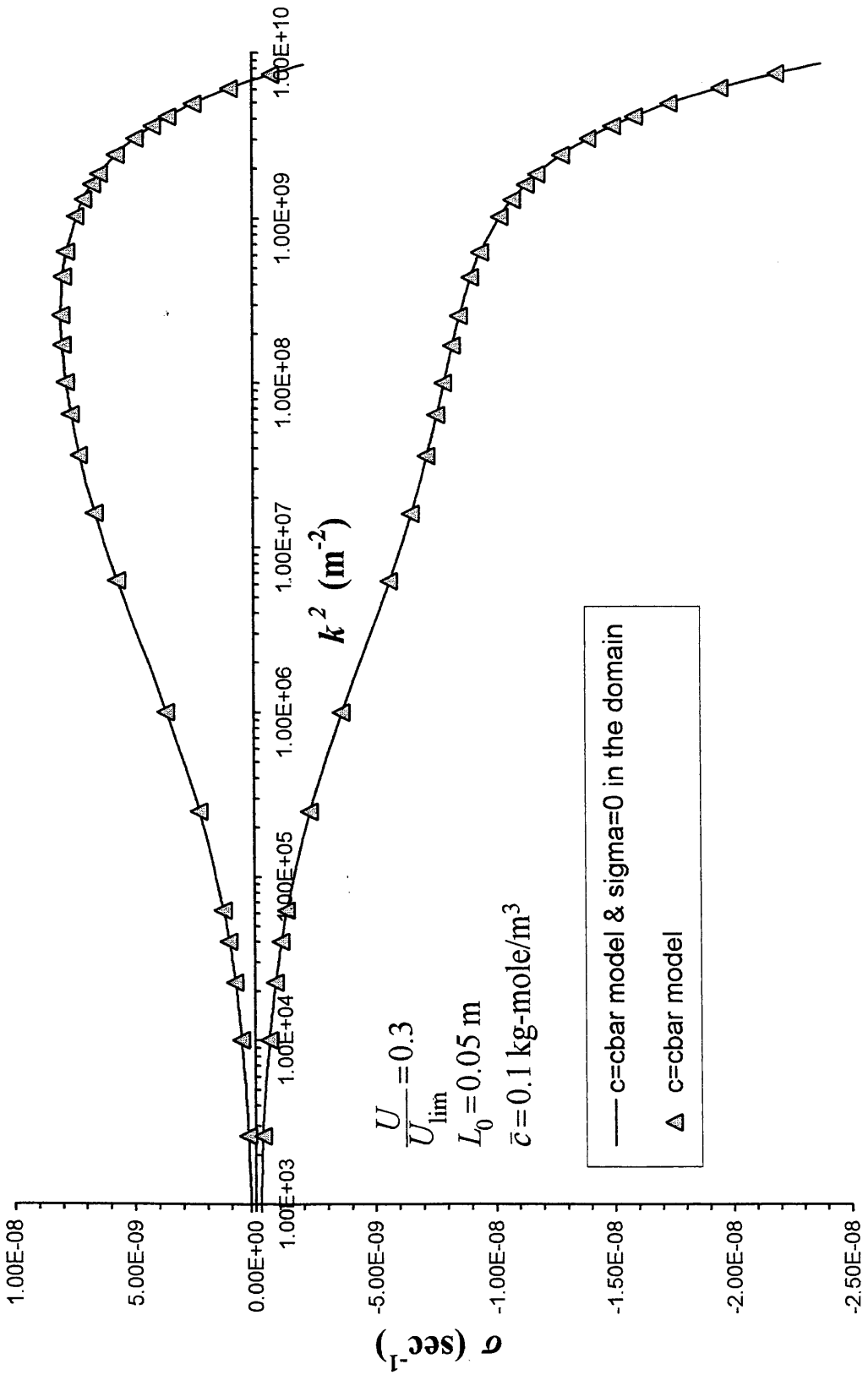


Figure 4-7. Effect of dropping σ from the domain at $U/U_{\text{lim}} = 0.3$.

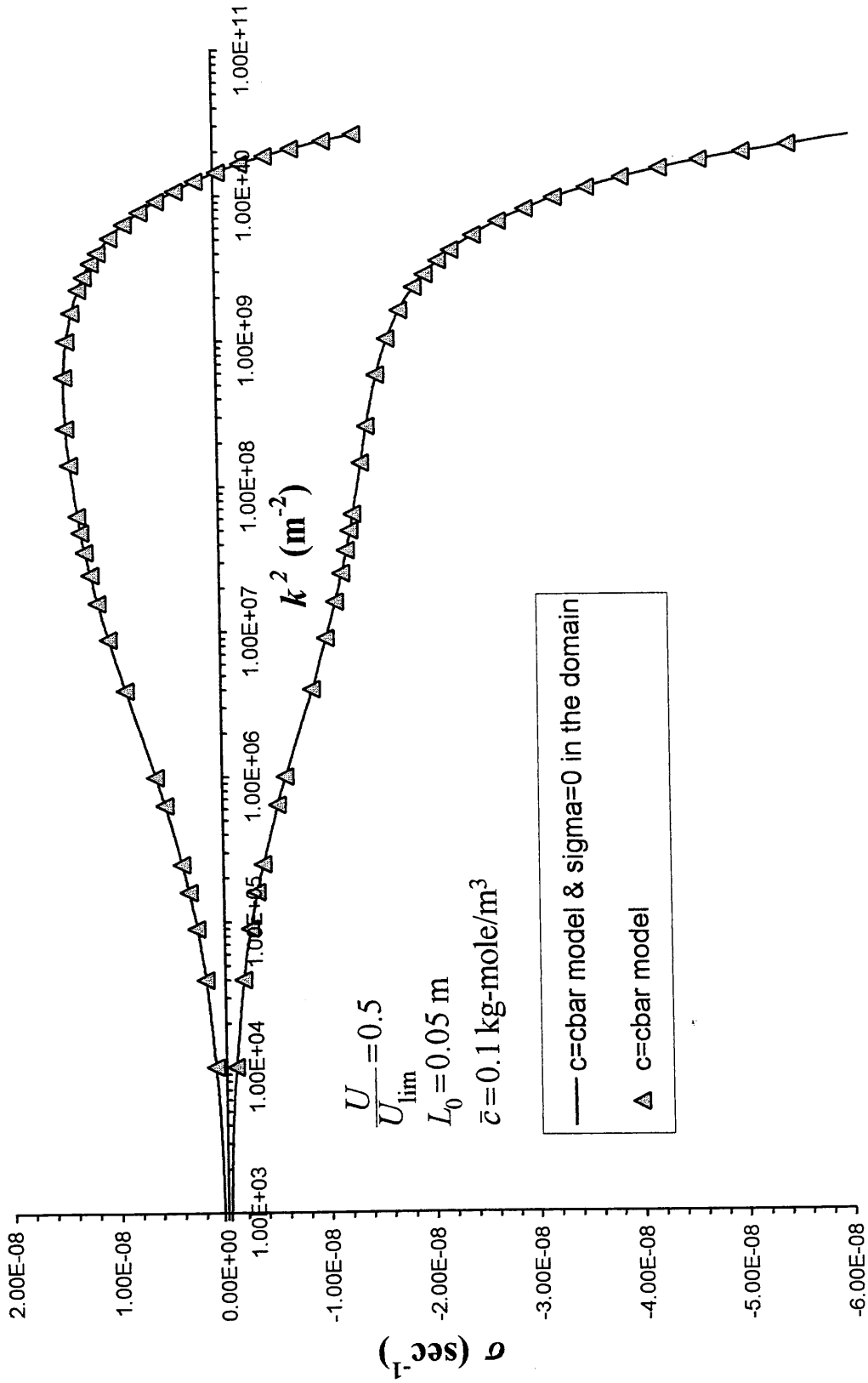


Figure 4-8. Effect of dropping σ from the domain at $U/U_{\text{lim}} = 0.5$.

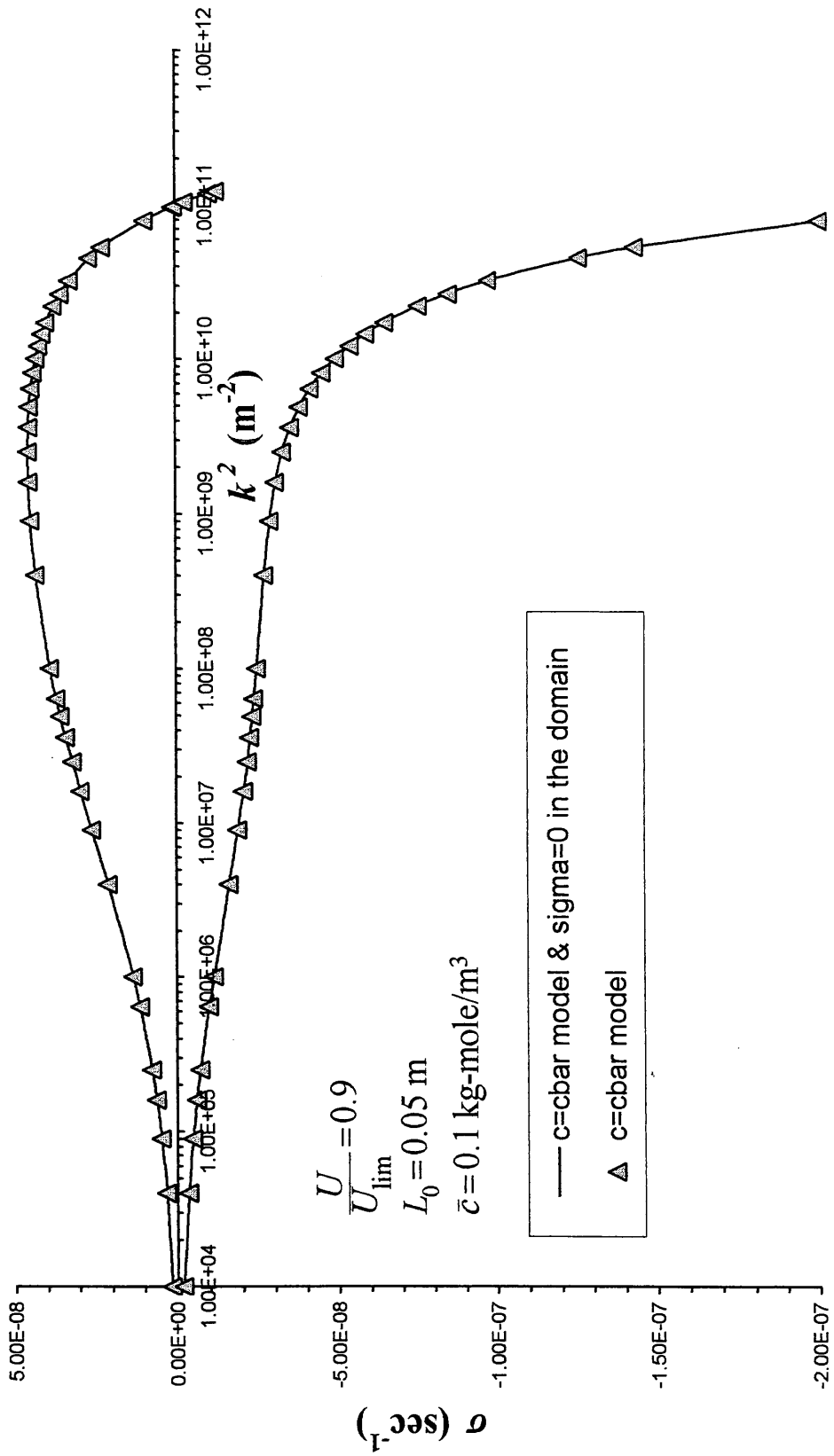


Figure 4-9. Effect of dropping σ from the domain at $U/U_{\text{lim}} = 0.9$.

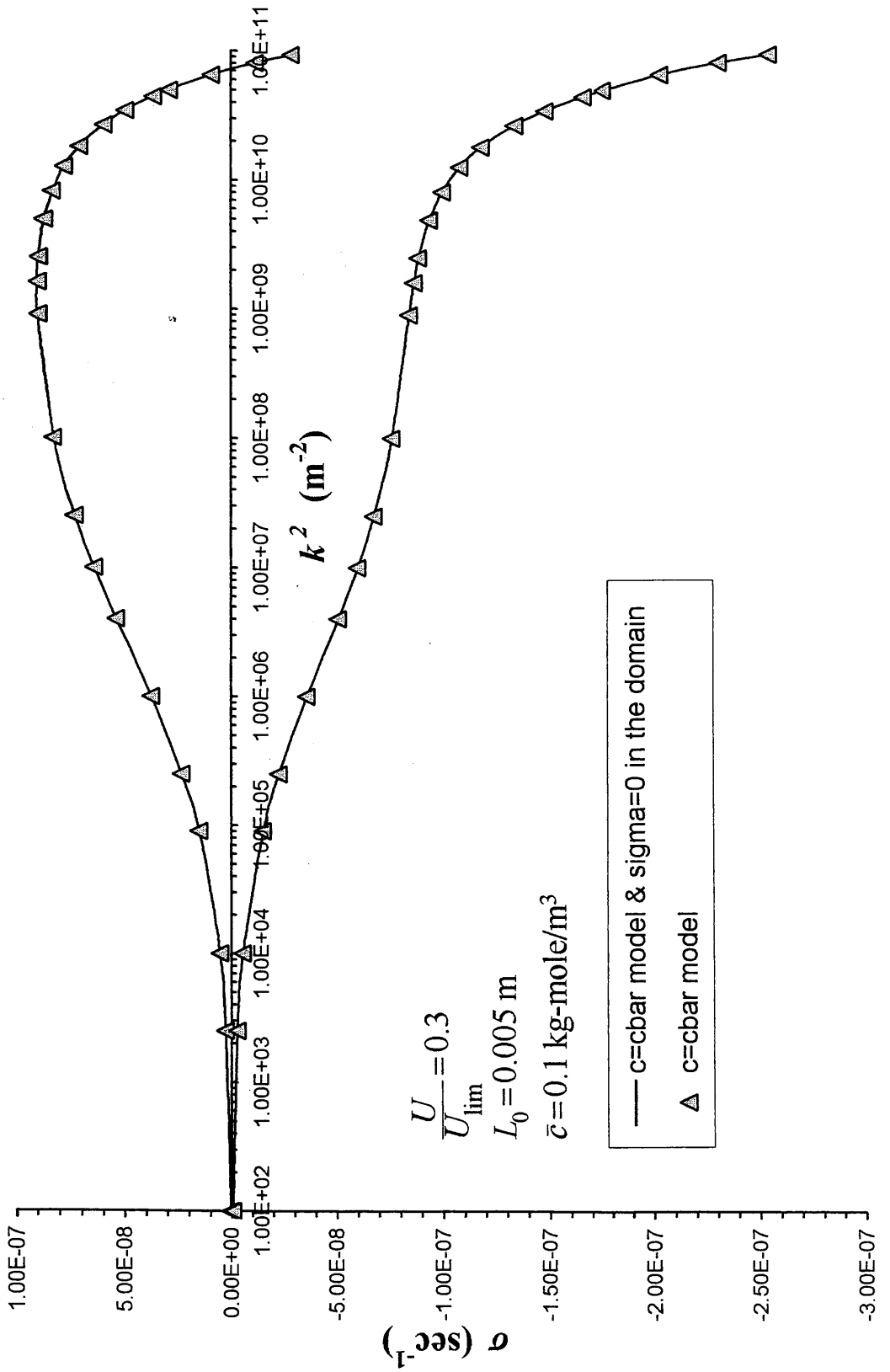


Figure 4-10. Effect of dropping σ from the domain for smaller electrode spacing.

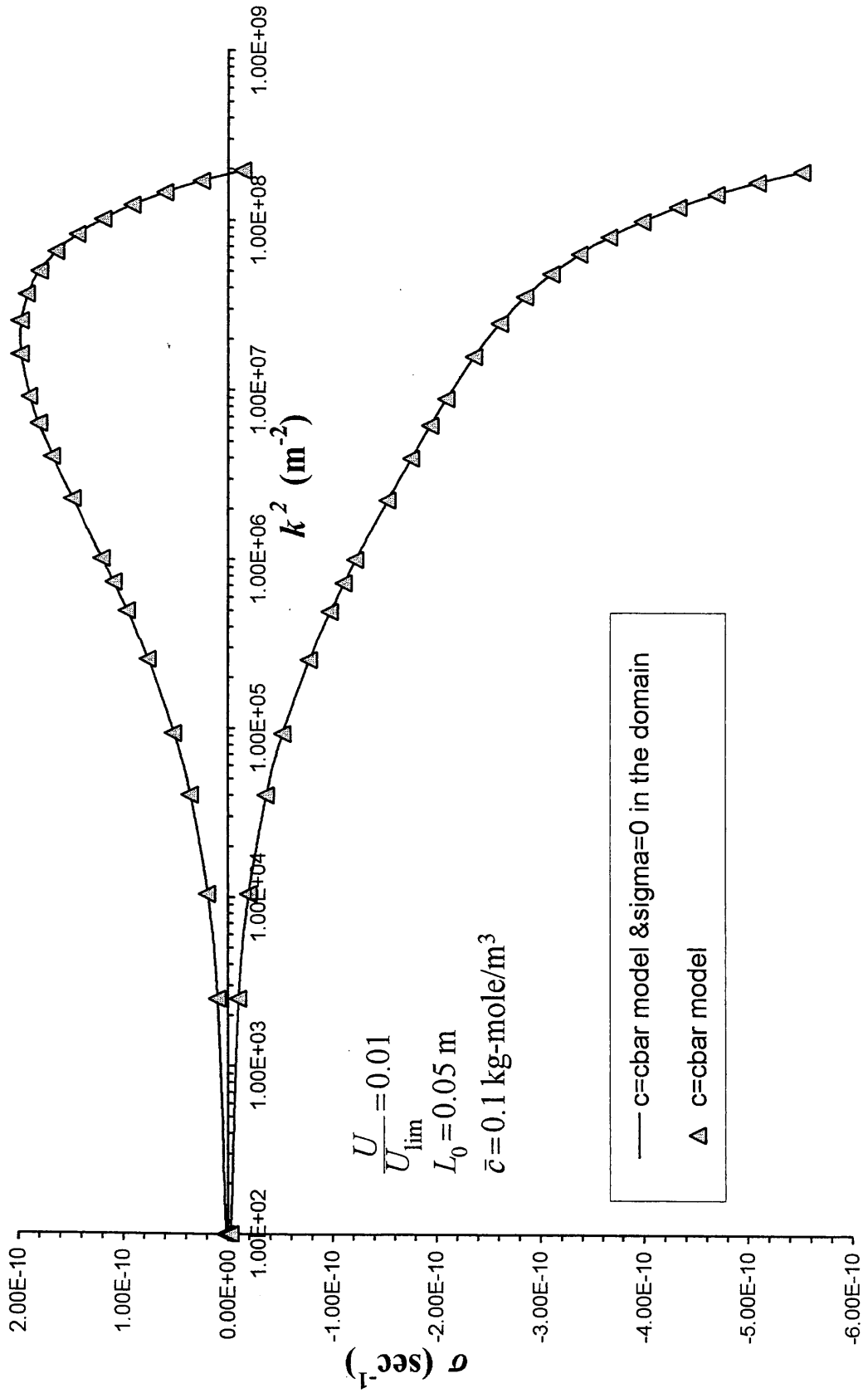


Figure 4-11. Effect of dropping σ from the domain for $\bar{c}$ = 0.1 kg-mole/m^3.

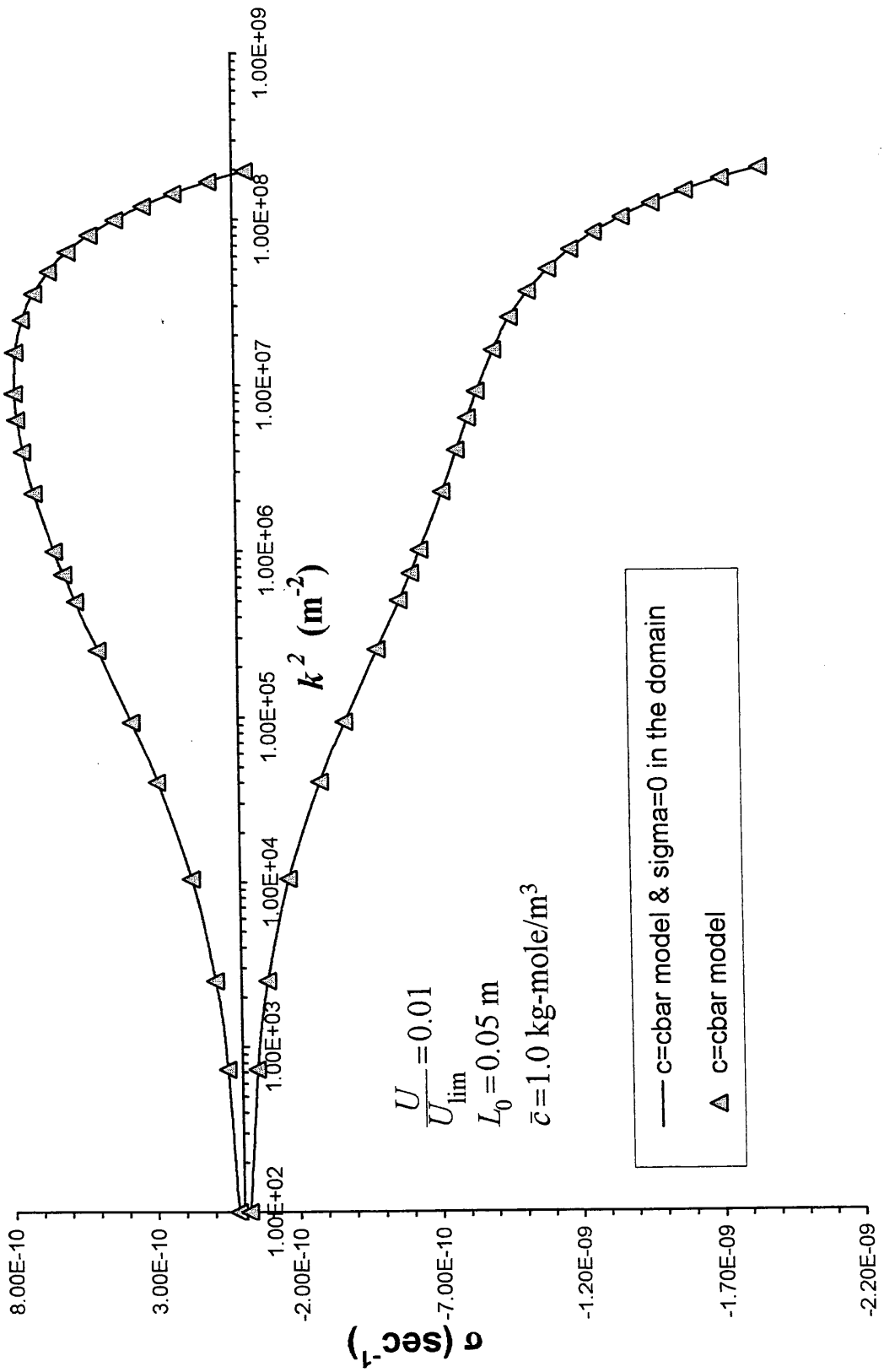


Figure 4-12. Effect of dropping σ from the domain for $\bar{c} = 1.0$ kg-mole/m^3.

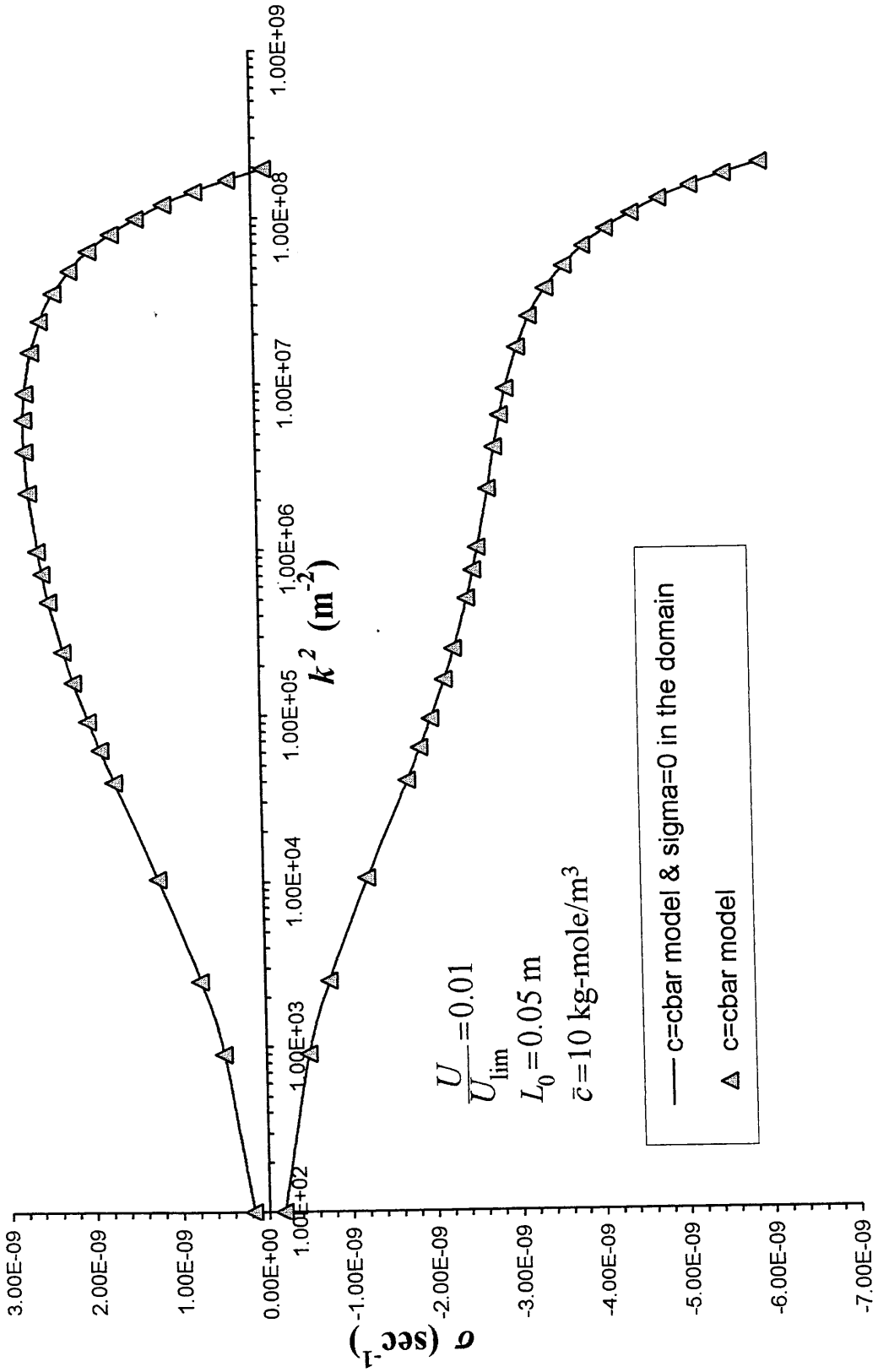


Figure 4-13. Effect of dropping σ from the domain for $\bar{c} = 10$ kg-mole/m^3.

4.6.4 Explaining the Behavior of the σ vs. k^2 Relation

Here we will combine all the approximations presented so far in order to simplify the relation between σ and k^2 so a person can trace the effect of the different input variables easily. We will use the CRE approximation along with putting $c = \overline{c}$ in the migration term and we will drop σ from the domain to achieve our simplest model. Even with all these approximations utilized, we are still going to get a quadratic equation in σ which will result in obtaining two roots which are the two predominant $\sigma's$ that we are going to draw.

To start, let us write the main equations required to achieve our target. First, the perturbed CRE equations i.e., equations (3.75) and (3.78) are

$$\frac{z_1F}{RT}\left[\Delta\hat{\phi}_1^A + \hat{Y}_1^A\frac{d}{dy_0}\Delta\phi_0^A + \frac{\gamma}{z_1Fc_M}k^2\hat{Y}_1^A\right] = e^{-\frac{z_1F}{RT}\left[\Delta\phi_0^A - \Delta\phi_{EQ}\right]}\left[\frac{\hat{c}_1^A}{\overline{c}} + \hat{Y}_1^A\frac{dc_0^A/dy_0}{\overline{c}}\right]$$

and

$$\frac{z_1F}{RT}\left[\Delta\hat{\phi}_1^C + \hat{Y}_1^C\frac{d}{dy_0}\Delta\phi_0^C - \frac{\gamma}{z_1Fc_M}k^2\hat{Y}_1^C\right] = e^{-\frac{z_1F}{RT}\left[\Delta\phi_0^C - \Delta\phi_{EQ}\right]}\left[\frac{\hat{c}_1^C}{\overline{c}} + \hat{Y}_1^C\frac{dc_0^C/dy_0}{\overline{c}}\right]$$

then the equations for $\hat{c}_1^A$, $\hat{c}_1^C$, $\hat{\phi}_1^A$ and $\hat{\phi}_1^C$ as given in this chapter, where the migration term approximation is used and where σ in the domain was set to zero, are

$$\hat{c}_1^A = -\frac{\sigma}{k}\frac{z_1z_2D_2}{z_1D_1 - z_2D_2}\frac{c_M}{D}\left[\hat{Y}_1^C\operatorname{csch}(kL_0) - \hat{Y}_1^A\coth(kL_0)\right]$$

$$\hat{c}_1^C = -\frac{\sigma}{k}\frac{z_1z_2D_2}{z_1D_1 - z_2D_2}\frac{c_M}{D}\left[\hat{Y}_1^C\coth(kL_0) - \hat{Y}_1^A\operatorname{csch}(kL_0)\right]$$

$$\hat{\phi}_1^A = \frac{\sigma}{k}\frac{RT}{z_1F}\frac{c_M}{\overline{c}}\frac{z_1^2}{D_1(z_1 - z_2)}\left[\hat{Y}_1^C\operatorname{csch}(kL_0) - \hat{Y}_1^A\coth(kL_0)\right]$$

and

$$\hat{\phi}_1^C = \frac{\sigma}{k}\frac{RT}{z_1F}\frac{c_M}{\bar{c}}\frac{z_1^2}{D_1(z_1-z_2)}\left[\hat{Y}_1^C \coth(kL_0) - \hat{Y}_1^A \operatorname{csch}(kL_0)\right]$$

Now in order to solve for $\hat{Y}_1^A$, $\hat{Y}_1^C$ and σ, the expressions for $\hat{c}_1^A$, $\hat{c}_1^C$, $\hat{\phi}_1^A$ and $\hat{\phi}_1^C$ are substituted in equations (3.75) and (3.78). The result of such a substitution is

$$\left[\frac{\gamma}{c_M RT}k^2 - \frac{dc_0/dy_0}{c_0^A} - \frac{z_1F}{RT}\frac{d\phi_0}{dy_0} + \frac{\sigma}{k}\coth(kL_0)(J-N^A)\right]\hat{Y}_1^A + \frac{\sigma}{k}\operatorname{csch}(kL_0)(N^A-J)\hat{Y}_1^C = 0 \tag{4.50}$$

and

$$-\frac{\sigma}{k}\operatorname{csch}(kL_0)(J-N^C)\hat{Y}_1^A + \left[\frac{\gamma}{c_M RT}k^2 + \frac{dc_0/dy_0}{c_0^C} + \frac{z_1F}{RT}\frac{d\phi_0}{dy_0} - \frac{\sigma}{k}\coth(kL_0)(N^C-J)\right]\hat{Y}_1^C = 0 \tag{4.51}$$

where $J = \frac{c_M}{\bar{c}}\frac{z_1^2}{D_1(z_1-z_2)} > 0$, $N^A = \frac{z_1z_2D_2}{z_1D_1-z_2D_2}\frac{c_M}{D}\frac{1}{c_0^A} < 0$ and $N^C = \frac{z_1z_2D_2}{z_1D_1-z_2D_2}\frac{c_M}{D}\frac{1}{c_0^C} < 0$.

Equations (4.50) and (4.51) are linear, homogenous, algebraic equations in $\hat{Y}_1^A$ and $\hat{Y}_1^C$ and they can be written as

$$\begin{pmatrix} E_{11} & E_{12} \\ E_{21} & E_{22} \end{pmatrix}\begin{pmatrix} \hat{Y}_1^A \\ \hat{Y}_1^C \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{4.52}$$

where the matrix $\begin{pmatrix} E_{11} & E_{12} \\ E_{21} & E_{22} \end{pmatrix}$ can be written as

$$\begin{pmatrix} \frac{\gamma}{c_M RT}k^2 - \frac{dc_0/dy_0}{c_0^A} - \frac{z_1F}{RT}\frac{d\phi_0}{dy_0} + \frac{\sigma}{k}\coth(kL_0)(J-N^A) & \frac{\sigma}{k}\operatorname{csch}(kL_0)(N^A-J) \\ -\frac{\sigma}{k}\operatorname{csch}(kL_0)(J-N^C) & \frac{\gamma}{c_M RT}k^2 + \frac{dc_0/dy_0}{c_0^C} + \frac{z_1F}{RT}\frac{d\phi_0}{dy_0} - \frac{\sigma}{k}\coth(kL_0)(N^C-J) \end{pmatrix}$$

The way we usually handle such a situation to find a relation between σ and k^2 is to look for a solution other than $\hat{Y}_1^A = 0 = \hat{Y}_1^C$ by setting $\det\begin{pmatrix} E_{11} & E_{12} \\ E_{21} & E_{22} \end{pmatrix} = 0$. This will generate a quadratic equation in σ as a function of the input variables. This equation can be written as

$$\sigma = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \tag{4.53}$$

where

$$a = \frac{1}{k^2}\left(J - N^A\right)\left(N^C - J\right)\left[\coth^2\left(kL_0\right) - \operatorname{csch}^2\left(kL_0\right)\right]$$

$$b = \frac{\gamma k}{c_M RT}\coth\left(kL_0\right)\left[\left(N^C - J\right) - \left(J - N^A\right)\right]$$

and

$$c = -\frac{\gamma^2 k^4}{\left(c_M RT\right)^2} + \frac{\gamma k^2}{c_M RT}\frac{U}{U_{\lim}}\frac{2}{L_0}\overline{c}\left(\frac{1}{c_0^C} - \frac{1}{c_0^A}\right) + \frac{4\overline{c}}{L_0^2}\frac{\left(U/U_{\lim}\right)^2}{1-\left(U/U_{\lim}\right)^2}\left[\overline{c} + 3 - \left(U/U_{\lim}\right)^2\right]$$

This is the simplest relation between σ and k^2 we obtained so far, however, it is not so obvious how the input variables contribute to such a relation. Using this equation to draw σ vs. k^2 will result in getting two curves corresponding to the most dangerous growth constants that we will draw later.

In trying to determine where from these curves arrive, we argue that one of these two curves has to do with the anode dynamics and the other with cathode dynamics. To show if this is true let us pretend that the cathode dynamics are frozen so $\vec{n}^C \cdot \vec{u}^C$ or σ coming from the cathode equations is set to zero. This will leave only one σ appearing in our solution which is due to the anode dynamics and which we will call σ^A. Then we

will assume that the anode is frozen and seek an expression for the growth constant related to the cathode dynamics (i.e., σ^C).

First, to find $\hat{c}_1^A$ when the dynamics of the electrodes are decoupled, we will use the domain equation for $\hat{c}_1$ viz.,

$$\left[\frac{d^2}{dy_0^2} - k^2\right]\hat{c}_1 = 0 \tag{4.54}$$

in addition to

$$D\frac{d\hat{c}_1}{dy_0} = -\frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} c_M \sigma \hat{Y}_1^A$$

which is valid at the anode where $y_0 = 0$, given as equation (4.16), and

$$\frac{d\hat{c}_1}{dy_0} = 0 \tag{4.55}$$

which is obtained from equation (4.19) after setting $\sigma\hat{Y}_1^C = 0$ (i.e., ignoring the cathode dynamics). Solving for $\hat{c}_1^A$ using these equation will lead to this expression

$$\hat{c}_1^A = \frac{\sigma}{k}\frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\frac{c_M}{D}\hat{Y}_1^A \coth(kL_0) \tag{4.56}$$

Then when solving for $\hat{\phi}_1^A$ we have the following three equations

$$\left[\frac{d^2}{dy_0^2} - k^2\right]\hat{\phi}_1 = 0 \tag{4.57}$$

$$P\frac{d\hat{c}_1}{dy_0} + \frac{z_1 F}{RT}\bar{c}\frac{d\hat{\phi}_1}{dy_0} = \frac{c_M z_1^2}{z_1 D_1 - z_2 D_2}\sigma\hat{Y}_1^A \tag{4.58}$$

and

$$P\frac{d\hat{c}_1}{dy_0} + \frac{z_1 F}{RT}\bar{c}\frac{d\hat{\phi}_1}{dy_0} = 0 \tag{4.59}$$

And the solution to the $\hat{\phi}_1^A$ is

$$\hat{\phi}_1^A = -\frac{\sigma}{k}\frac{RT}{z_1 F}\frac{c_M}{\bar{c}}\frac{z_1^2}{D_1(z_1 - z_2)}\hat{Y}_1^A \coth(kL_0) \tag{4.60}$$

Substituting for $\hat{c}_1^A$ and $\hat{\phi}_1^A$ in equation (3.75) will lead to

$$\sigma^A = \frac{-\frac{\gamma}{c_M RT}k^2 + \frac{dc_0/dy_0}{c_0^A} + \frac{z_1 F}{RT}\frac{d\phi_0}{dy_0}}{\frac{1}{k}\coth(kL_0)(J - N^A)} \tag{4.61}$$

Then to get σ^C, set $\sigma\hat{Y}_1^A = 0$ and follow the same moves to get

$$\sigma^C = \frac{-\frac{\gamma}{c_M RT}k^2 - \frac{dc_0/dy_0}{c_0^C} - \frac{z_1 F}{RT}\frac{d\phi_0}{dy_0}}{\frac{1}{k}\coth(kL_0)(J - N^C)} \tag{4.62}$$

Now if the numerical values of σ^A and σ^C are similar to the values of the two predominant eigenvalues obtained after applying all the approximations, we can identify the source of each curve and have the simplest relation describing the σ vs. k^2 relation. Figure 4-14 presents a comparison between σ vs. k^2 relation obtained from the quadratic equation, i.e., equation (4.53), and that obtained from equations (4.61) and (4.62). It is clear how the results are very close which confirms our prediction that one of these two $\sigma's$ comes from the anode while the second originates from the cathode.

Now the denominator in equation (4.61) is always positive, while the numerator is always negative which resulted in σ_A being always less than zero. It is clear from the equation that the surface tension, the concentration gradient and the electrical potential gradient all stabilize the anode (i.e., they have negative signs) which is in agreement with the picture argument given in chapter 1.

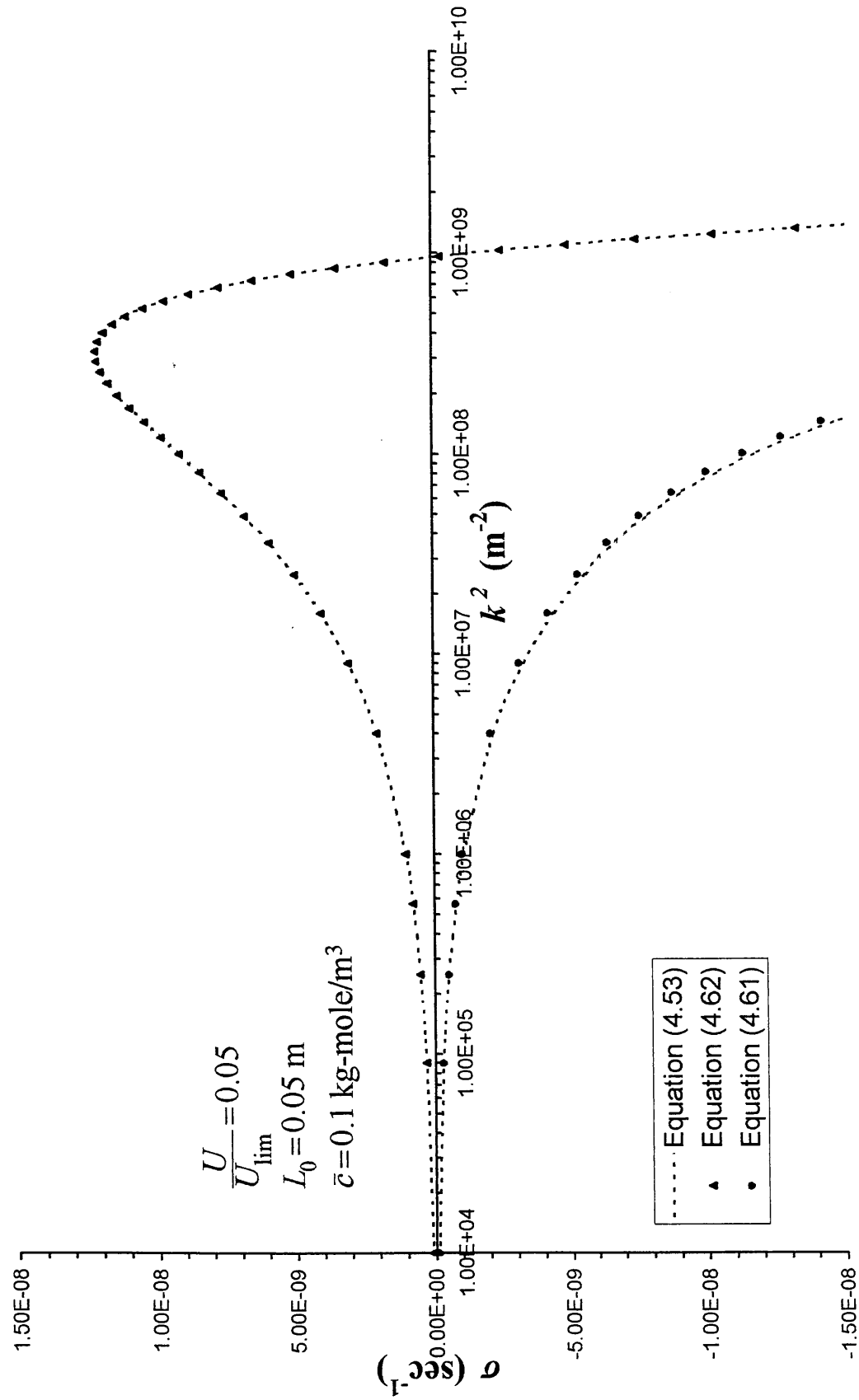


Figure 4-14. The relation between σ and k^2 from equations (4.53), (4.61) and (4.62).

The denominator in equation (4.62) is again positive leaving the numerator to determine the sign of σ^C. It is obvious that the surface tension term, which is negative, is stabilizing while the other terms namely; the concentration and the electrical potential gradients are both positive and destabilizing. So it is clear from equation (4.62) why the behavior of the curve corresponds to the largest eigenvalue is totally different from the other curve. Knowing the origin of these curves explains why the largest eigenvalue becomes more unstable as we increase U/U_{lim} and $\overline{c}$ or decrease L_0 which all destabilize the cathode. On the other hand, increase U/U_{lim} and $\overline{c}$ or decrease L_0 will all stabilize the anode, and this explains the behavior of the growth constants given in the first six figures of this chapter.

A strange behavior of the σ^C curve is that it goes up (i.e., the positive value of σ increases) as the wave number increases while we expected that increasing the wave number should always make the system more stable. This is the result of the wave number that appears in the term $\frac{1}{k}\coth(kL_0)$, which originated from the term $\frac{d^2c_1}{dx_0^2}$ (i.e., from transverse diffusion) that brings this destabilizing effect.

At one stage, one might be interested in comparing the rate at which the perturbation is growing namely, σY_1^C resulting from u, to the velocity of the front, U. This cannot be done in this chapter since finding Y_1^C is not possible using the first order perturbation method. Unfortunately, even if we go to the 2nd order calculation, which are presented in chapter 6, or the 3rd order we will not be able to provide this kind of information because Y_1^C that could be found at third order will correspond to steady state where σ is equal to zero.

In conclusion, we have learned several things about the electrodeposition problem in this chapter. First, we were successful in finding the relation between σ and k^2 and the shape of the curves describing this relation tells us a lot about the physics of the problem. We believe now that the curve that corresponds to the largest eigenvalue comes from the cathode while the second curve resulted from the dynamics at the anode. Second, we were able to identify the role of transverse diffusion which has a destabilizing effect. Third, we have learned that finding σ is the first step if someone is interested in finding the rate of the perturbation growth compared to the velocity of the front but we have already explained why we cannot do this at this stage. Fourth, some workers such as Mullins and Sekerka (1964) might expect to see the patterns forming at the wave number that corresponds to the maximum growth rate which is one of the things we learned from our calculations in this chapter. Finally, we have learned that a simple model that contains all the approximations used so far is useful over a wide range of conditions not just at the critical point so it can be used as a basis for subsequent calculations as those in chapter 6.

In the next chapter we will evaluate the migration term approximation by solving the whole problem without implementing any of the approximations used so far in this and the previous chapter.

CHAPTER 5
THE SOLUTION FOR THE GROWTH CONSTANT

In this chapter a way of solving the problem without approximations is presented. So we are going to accept all the primitive assumptions used in writing the model, but are not going to invoke any of the approximations used earlier as we will solve the whole eigenvalue problem. The main objective of this chapter is therefore to present the solution to the electrodeposition model in order to test the approximation used to simplify the migration term and to check if the results obtained by S&B are in agreement with our results.

Here we will follow the same steps as in the earlier two chapters. We start with the non linear equations presented in chapter 2 then a base solution will be found without approximations such as CRE or setting $c = \overline{c}$ in the migration term as we did in chapters 3 and 4 respectively. Next, the stability of the base solution will be examined via a linear perturbation analysis again with the aim of getting the relation between σ and k^2. The results obtained here will then be compared with the results obtained earlier in chapter 4 to see under what conditions the approximation is valid. Finally the results from this chapter will be compared with work by S&B where the eigenvalue problem was solved by difference approximation for selected values of the input variables. This will be done to check if the results obtained numerically by S&B are in agreement with ours.

Since this chapter completes the work started in earlier chapters, a lot of the equations given here will be taken from those chapters. The equations that are taken over to this chapter will be given new numbers so the work here will be self-contained and it

will be easier for the reader to follow the solution without referring to three different chapters. So let us start this chapter by presenting the nonlinear equations of the electrodeposition model.

5.1 The Nonlinear Equations

Let us first write the equations that are valid on the domain namely equations (2.32) and (2.33). These two equations, after neglecting the effect of convection, can be written as follows

$$\frac{\partial c}{\partial t} = D\nabla^2 c \tag{5.1}$$

and

$$P\nabla^2 c + \frac{z_1 F}{RT}\nabla\cdot\left[c\nabla\phi\right] = 0 \tag{5.2}$$

where

$$D = \frac{D_1 D_2}{z_1 D_1 - z_2 D_2}\left[z_1 - z_2\right] \text{ and } P = \frac{z_1\left[D_1 - D_2\right]}{z_1 D_1 - z_2 D_2}.$$

Now the equations that are valid at the boundary (i.e., at each electrode) as mentioned earlier are (2.34), (2.35) and (2.38). These equations are

$$D\vec{n}\cdot\nabla c = \frac{-z_1 z_2 D_2 c_M}{z_1 D_1 - z_2 D_2}\left[\vec{n}\cdot\vec{u} + \vec{n}\cdot\vec{U}\right] \tag{5.3}$$

$$P\vec{n}\cdot\nabla c + \frac{z_1 F}{RT} c\vec{n}\cdot\nabla\phi = \frac{z_1^2 c_M}{z_1 D_1 - z_2 D_2}\left[\vec{n}\cdot\vec{u} + \vec{n}\cdot\vec{U}\right] \tag{5.4}$$

and

$$\vec{n}\cdot\vec{i} = -z_1 F c_M\left[\vec{n}\cdot\vec{u} + \vec{n}\cdot\vec{U}\right] = i_0\left[e^{[1-\beta]\frac{z_1 F}{RT}\left[\Delta\phi - \Delta\phi_{EQ} - \frac{\gamma}{z_1 F c_M}2H\right]} - \frac{c}{\overline{c}}e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi - \Delta\phi_{EQ} - \frac{\gamma}{z_1 F c_M}2H\right]}\right] \tag{5.5}$$

These nonlinear equations are taken directly from chapter 2. Let us now turn to writing the base solution as it was given in chapter 3.

5.2 The Base Solution

At steady state, equations (5.1) and (5.2) will become

$$D\frac{d^2c}{dy^2}=0 \tag{5.6}$$

and

$$\frac{d}{dy}\left[P\frac{dc}{dy}+c\frac{d}{dy}\left[\frac{z_1F}{RT}\phi\right]\right]=0 \tag{5.7}$$

hence $\frac{dc}{dy}$ and $c\frac{d}{dy}\left[\frac{z_1F}{RT}\phi\right]$ must remain constant through out the electrolytic solution. In addition equations (3.11) and (3.12) must hold at both electrodes, namely,

$$D\frac{dc}{dy}=\frac{-z_1z_2D_2}{z_1D_1-z_2D_2}c_MU \tag{5.8}$$

and

$$\frac{d}{dy}\left[\frac{z_1F}{RT}\phi\right]=\frac{z_1^2c_MU}{D_1\left[z_1-z_2\right]}\frac{1}{c} \tag{5.9}$$

and these equations determine the values of our two constants.

The B-V equation, which determines the rate of the electrode reactions in terms of the values of c and ϕ on the solution side of the electrodes, must hold at both the anode and the cathode. These equations, obtained from equation (5.5), are

$$i_y^A=-z_1Fc_MU=i_0\left[e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi^A-\Delta\phi_{EQ}\right]}-\frac{c^A}{\bar{c}}e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi^A-\Delta\phi_{EQ}\right]}\right] \tag{5.10}$$

and

$$-i_y^C = z_1 F c_M U = i_0 \left[e^{[1-\beta]\frac{z_1 F}{RT}\left[\Delta\phi^C - \Delta\phi_{EQ}\right]} - \frac{c^C}{\overline{c}} e^{-\beta\frac{z_1 F}{RT}\left[\Delta\phi^C - \Delta\phi_{EQ}\right]} \right] \tag{5.11}$$

Now the concentration profile is no different than what it was earlier. Solving for it introduces a third constant of integration which is evaluated in terms of the average concentration, $\overline{c}$, which is an input variable. It is given by equations (3.14), (3.15) and (3.16) namely

$$c = \overline{c} + \frac{-z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} c_M \frac{U}{D}\left[y - \frac{1}{2} L_0 \right] \tag{5.12}$$

where

$$c^A = \overline{c} - \frac{-z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} c_M \frac{U}{D}\frac{1}{2} L_0 \tag{5.13}$$

and

$$c^C = \overline{c} + \frac{-z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} c_M \frac{U}{D}\frac{1}{2} L_0 \tag{5.14}$$

Likewise the potential profile was given by equation (3.19) that is

$$\frac{z_1 F}{RT}\phi = \frac{z_1 F}{RT}\phi^A + \frac{z_1}{-z_2}\ln\frac{c}{c^A} \tag{5.15}$$

where $\phi^C - \phi^A$ can be determined, namely,

$$\frac{z_1 F}{RT}\left(\phi^C - \phi^A\right) = \frac{z_1}{-z_2}\ln\frac{c^C}{c^A} \tag{5.16}$$

but ϕ^A and ϕ^C remain unknown.

The role of the B-V equation at both electrodes in closing the problem will be to connect the voltage drop to the velocity of the surfaces. This is similar to what we have done in section 3.1.1 where we found

$$\frac{z_1 F}{RT}\left[V^A - V^C\right] = 2\ln\left(-\frac{1}{2}\frac{z_1 F c_M U}{i_0} + \frac{1}{2}\sqrt{\left(\frac{z_1 F c_M U}{i_0}\right)^2 + 4\frac{c^A}{\bar{c}}}\right) + \frac{z_1}{z_2}\ln\frac{c^C}{c^A}$$
$$-2\ln\left(\frac{1}{2}\frac{z_1 F c_M U}{i_0} + \frac{1}{2}\sqrt{\left(\frac{z_1 F c_M U}{i_0}\right)^2 + 4\frac{c^C}{\bar{c}}}\right) \tag{5.17}$$

where the value of β was selected to be one half in equations (5.10) and (5.11) and equation (5.16) was used in getting this equation which completes the base solution.

Now that we have the base solution, to find out if it is stable, our next step will be to write the perturbation equations, which are based on the nonlinear equations given in section 5.1.

5.3 The Perturbation Problem

The perturbation equations given here are taken directly from chapter 3 except for the perturbed B-V equations which are copied from chapter 4. As we know by now, these equations are the result of two steps, which are the linearization step and the separation of variables step. In the linearization step, we substituted the expansions of our variables to convert the nonlinear equations into a series of linear ones. Then in the next step we used separation of variables in order to solve the first order equations.

The first two equations are the perturbed domain equations. These equations were given in chapter 3 as equations (3.45) and (3.46) viz.,

$$D\left[\frac{d^2}{dy_0^2} - k^2\right]\hat{c}_1 = \sigma\hat{c}_1 \tag{5.18}$$

and

$$P\left[\frac{d^2}{dy_0^2}-k^2\right]\hat{c}_1+\frac{dc_0}{dy_0}\left[\frac{z_1F}{RT}\right]\frac{d\hat{\phi}_1}{dy_0}+c_0\left[\frac{z_1F}{RT}\right]\left[\frac{d^2}{dy_0^2}-k^2\right]\hat{\phi}_1$$
$$+\left[\frac{z_1F}{RT}\right]\frac{d\phi_0}{dy_0}\frac{d\hat{c}_1}{dy_0}+\left[\frac{z_1F}{RT}\right]\frac{d^2\phi_0}{dy_0^2}\hat{c}_1=0 \tag{5.19}$$

At the anode $\hat{c}_1$, $\hat{\phi}_1$ and $\hat{Y}_1^A$ must satisfy equations (3.55) and (3.56), viz.,

$$P\frac{d\hat{c}_1}{dy_0}+\hat{c}_1\left[\frac{z_1F}{RT}\right]\frac{d\phi_0}{dy_0}+c_0\left[\frac{z_1F}{RT}\right]\frac{d\hat{\phi}_1}{dy_0}=\frac{z_1^2}{z_1D_1-z_2D_2}c_M\sigma\hat{Y}_1^A \tag{5.20}$$

and

$$D\frac{d\hat{c}_1}{dy_0}=-\frac{z_1z_2D_2}{z_1D_1-z_2D_2}c_M\sigma\hat{Y}_1^A \tag{5.21}$$

as well as equation (4.18) viz.,

$$-\frac{z_1Fc_M}{i_0}\sigma\hat{Y}_1^A=\left[[1-\beta]e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}+\frac{c_0^A}{\overline{c}}\beta e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}\right]$$
$$\times\left[\frac{z_1F}{RT}\right]\left[\Delta\hat{\phi}_1^A+\hat{Y}_1^A\frac{d}{dy_0}\Delta\phi_0^A+\frac{\gamma}{z_1Fc_M}k^2\hat{Y}_1^A\right] \tag{5.22}$$
$$-e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^A-\Delta\phi_{EQ}\right]}\frac{\left[\hat{c}_1^A+\hat{Y}_1^A\frac{dc_0^A}{dy_0}\right]}{\overline{c}}$$

Equations (5.20) and (5.21) come from conservation laws while equation (5.22) comes from the B-V equation.

At the cathode, the perturbation equations (3.61) and (3.62) are

$$D\frac{d\hat{c}_1}{dy_0}=-\frac{z_1z_2D_2}{z_1D_1-z_2D_2}c_M\sigma\hat{Y}_1^C \tag{5.23}$$

and

$$P\frac{d\hat{c}_1}{dy_0}+\hat{c}_1\left[\frac{z_1F}{RT}\right]\frac{d\phi_0}{dy_0}+c_0\left[\frac{z_1F}{RT}\right]\frac{d\hat{\phi}_1}{dy_0}=\frac{z_1^2}{z_1D_1-z_2D_2}c_M\sigma\hat{Y}_1^C \tag{5.24}$$

while equation (4.21) is

$$\frac{z_1 F c_M}{i_0}\sigma\hat{Y}_1^C = \left[[1-\beta]e^{[1-\beta]\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{RQ}\right]} + \frac{c_0^C}{\overline{c}}\beta e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{RQ}\right]}\right]$$
$$\times\left[\frac{z_1F}{RT}\right]\left[\Delta\hat{\phi}_1^C + \hat{Y}_1^C\frac{d}{dy_0}\Delta\phi_0^C - \frac{\gamma}{z_1Fc_M}k^2\hat{Y}_1^C\right] \qquad (5.25)$$
$$-e^{-\beta\frac{z_1F}{RT}\left[\Delta\phi_0^C-\Delta\phi_{RQ}\right]}\frac{\left[\hat{c}_1^C + \hat{Y}_1^A\frac{dc_0^C}{dy_0}\right]}{\overline{c}}$$

Equations (5.18)-(5.25) construct our homogeneous eigenvalue problem. The eigenvalue is σ and the eigenfunctions are $\hat{c}_1$, $\hat{\phi}_1$, $\hat{Y}_1^A$ and $\hat{Y}_1^C$. Again beside our input variables, namely, $V^A - V^C$, L_0 and $\overline{c}$, the wave number k^2 is also going to be treated as an input to the problem. And the outputs that we want to find are $\hat{c}_1$, $\hat{\phi}_1$, $\hat{Y}_1^A$, $\hat{Y}_1^C$ and σ. Now we are ready to solve this eigenvalue problem to achieve our goal of finding σ vs. k^2 without making any of the approximations introduced in chapters 3 and 4.

5.4 The Stability of the Base Solution

In this section, our target will be to find the solution to the eigenvalue problem. On our way to achieve this goal, we will show how to transform equation (5.19) to a Bessel equation. This transformation will make it possible to solve the eigenvalue problem without the use of the finite difference method as applied by S&B.

Now we start by solving for $\hat{c}_1$ using equations (5.18), (5.21) and (5.23). The expression for $\hat{c}_1$ as found before using equation (5.18) is

$$\hat{c}_1 = A_1\, e^{m y_0} + B_1\, e^{-m y_0} \qquad (5.26)$$

where A_1 and B_1 can be found by applying the boundary conditions i.e., equations (5.21) and (5.23), to be

$$A_1 = \frac{-\frac{z_1 z_2 c_M}{mD_1(z_1 - z_2)}\sigma\left[\hat{Y}_1^C - e^{mL_0}\hat{Y}_1^A\right]}{e^{mL_0} - e^{-mL_0}} - \frac{z_1 z_2 c_M}{mD_1(z_1 - z_2)}\sigma\hat{Y}_1^A$$

and

$$B_1 = \frac{-\frac{z_1 z_2 c_M}{mD_1(z_1 - z_2)}\sigma\left[\hat{Y}_1^C - e^{mL_0}\hat{Y}_1^A\right]}{e^{mL_0} - e^{-mL_0}}$$

Finding $\hat{c}_1^A$ and $\hat{c}_1^C$ goes through as it did in chapter 4 with the result obtained when $\hat{c}_1$ is evaluated at $y_0 = 0$ and at $y_0 = L_0$. These results appear in chapter 4 as (4.23) and (4.24) and are written here as

$$\hat{c}_1^A = -\frac{\sigma}{m}\frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\frac{c_M}{D}\left[\hat{Y}_1^C \operatorname{csch}(mL_0) - \hat{Y}_1^A \coth(mL_0)\right] \tag{5.27}$$

and

$$\hat{c}_1^C = -\frac{\sigma}{m}\frac{z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\frac{c_M}{D}\left[\hat{Y}_1^C \coth(mL_0) - \hat{Y}_1^A \operatorname{csch}(mL_0)\right] \tag{5.28}$$

where $m = \sqrt{k^2 + \frac{\sigma}{D}}$.

So far we have repeated earlier work. But in going on we will deal with the $\hat{\phi}_1$ problem as it stands.

To solve for $\hat{\phi}_1$, we will start with equation (5.19) on the domain. However, before doing that let us remind the reader again why our problem is more difficult now than it was in chapters 3 or 4. In chapter 3, both $\hat{c}_1$ and $\hat{\phi}_1$ where found to be zero after setting σ to zero since we were interested in the neutral stability point. So this $\sigma = 0$ simplifies the problem greatly. On the other hand in chapter 4 the approximation $c = \overline{c}$ in the

migration term was very helpful in simplifying the $\hat{\phi}_1$ equation and instead of equation (5.19) we were working with a much simpler equation, equation (4.15), viz.,

$$P\left[\frac{d^2}{dy_0^2}-k^2\right]\hat{c}_1+\frac{z_1F}{RT}\bar{c}\left[\frac{d^2}{dy_0^2}-k^2\right]\hat{\phi}_1=0$$

whose solution was not difficult since it is a constant coefficient differential equation. On the other hand, equation (5.19) is a variable coefficient differential equation which is more difficult to solve.

Now to turn equation (5.19) into a form where we can find its solution easily we need to do some work. First multiply equation (5.19) by $\frac{RT}{z_1F}\frac{1}{c_0}$, then substitute $\frac{\sigma\hat{c}_1}{D}$ for $\left[\frac{d^2}{dy_0^2}-k^2\right]\hat{c}_1$, as given in equation (5.18), and rearrange to obtain the following equation

$$\frac{d^2\hat{\phi}_1}{dy_0^2}+\frac{dc_0/dy_0}{c_0}\frac{d\hat{\phi}_1}{dy_0}-k^2\hat{\phi}_1=r(y_0) \tag{5.29}$$

where $r(y_0)$ is given by the following expression

$$r(y_0)=-\frac{d\phi_0/dy_0}{c_0}\frac{d\hat{c}_1}{dy_0}-\frac{RT}{z_1F}\frac{P}{D}\sigma\frac{\hat{c}_1}{c_0}-\frac{d^2\phi_0}{dy_0^2}\frac{\hat{c}_1}{c_0} \tag{5.30}$$

Equation (5.29) is a non-homogeneous second order ordinary differential equation in $\hat{\phi}_1$ where the non-homogeneous part is given by $r(y_0)$. Note that all the expressions that appear in $r(y_0)$ are either known or can be easily calculated from the information in our hands.

Now we will do some manipulations to put equation (5.29) into a familiar form so that its solution will be easily found. First let us call $\frac{dc_0}{dy_0}$, a i.e., we will write

$$\frac{dc_0}{dy_0} = \frac{-z_1 z_2 D_2}{z_1 D_1 - z_2 D_2}\frac{c_M}{D}U = \text{constant} = a\text{, where } a \text{ is always negative} \qquad (5.31)$$

then the expression for c_0 i.e., equation (5.12) can be written

$$c_0 = ay_0 + \bar{c} - \frac{L_0}{2}a \qquad (5.32)$$

Let us go one step further and call the constant $\bar{c} - \frac{L_0}{2}a$, which appears in equation (5.32), b and rewrite equation (5.32) as

$$c_0 = ay_0 + b\text{, where } b \text{ is always positive} \qquad (5.33)$$

then equation (5.29) can be written in terms of the new constants a and b in the following form

$$\frac{d^2\hat{\phi}_1}{dy_0^2} + \frac{a}{ay_0 + b}\frac{d\hat{\phi}_1}{dy_0} - k^2\hat{\phi}_1 = r(y_0) \qquad (5.34)$$

It is our job now to try to solve this equation. In order to do this, let us introduce the variable η via

$$\eta = -\frac{k}{a}(ay_0 + b) \qquad (5.35)$$

where η is always positive and $\eta = -\frac{k}{a}b$ when $y_0 = 0$ and $\eta = -\frac{k}{a}(aL_0 + b)$ when $y_0 = L_0$. So the range of η is $-\frac{k}{a}b < \eta < -\frac{k}{a}(aL_0 + b)$ and it runs opposite to y_0 (i.e., when y_0 is small η is large and vise versa).

After introducing η to our problem, we want to write equation (5.34) in terms of our new variable. First let us write

$$\hat{\phi}_1(y_0) = \hat{\phi}_1\left(-\frac{\eta}{k} - \frac{b}{a}\right) = f(\eta) \text{ and } r(y_0) = g(\eta)$$

Then notice that

$$d\eta = -k\, dy_0 \text{ or } \frac{d\eta}{dy_0} = -k$$

hence $\frac{d\hat{\phi}_1}{dy_0}$ can be written, by using the chain rule, as

$$\frac{d\hat{\phi}_1}{dy_0} = \frac{df}{d\eta}\frac{d\eta}{dy_0} = -k\frac{df}{d\eta}$$

and finally the chain rule can be used again to get $\frac{d^2\hat{\phi}_1}{dy_0^2}$ in terms of $\frac{d^2 f}{d\eta^2}$ in the following way

$$\frac{d^2\hat{\phi}_1}{dy_0^2} = \frac{d}{dy_0}\left[\frac{d\hat{\phi}_1}{dy_0}\right] = \frac{d}{d\eta}\left[\frac{df}{dy_0}\right]\frac{d\eta}{dy_0} = \frac{d}{d\eta}\left[-k\frac{df}{d\eta}\right][-k] \text{ or } \frac{d^2\hat{\phi}_1}{dy_0^2} = k^2\frac{d^2 f}{d\eta^2}$$

Now substituting for $ay_0 + b$, $\frac{d\hat{\phi}_1}{dy_0}$, $\frac{d^2\hat{\phi}_1}{dy_0^2}$ and $r(y_0)$ in equation (5.34) will lead to the following equation in f as a function of η

$$\frac{d^2 f}{d\eta^2} + \frac{1}{\eta}\frac{df}{d\eta} - f = \frac{g(\eta)}{k^2} \tag{5.36}$$

This equation can be recognized as a Bessel's equation and the general solution to the homogeneous equation can be written as (Mickley *et al.*, 1957)

$$f_h = A_2 I_0(\eta) + B_2 K_0(\eta) \tag{5.37}$$

where A_2 and B_2 are two constants to be determined by using the boundary conditions.

Now the solution to equation (5.29) is the sum of the general solution to the homogeneous equation and a particular solution. Using the method of variation of parameters, a particular solution to the non-homogeneous equation can be written as follows

$$f_p = -I_0(\eta)\int_{\eta_1}^{\eta}\frac{K_0(\eta)g(\eta)}{W\,k^2}d\eta + K_0(\eta)\int_{\eta_1}^{\eta}\frac{I_0(\eta)\,g(\eta)}{W\,k^2}\,d\eta \tag{5.38}$$

where W is the Wronskian which equals to $-\frac{1}{\eta}$ (Watson, 1944).

Now after substituting for W in equation (5.38), the solution to equation (5.36), which is the sum of the general solution to the homogeneous equation and a particular solution, is

$$f = f_h + f_p = A_2 I_0(\eta) + B_2 K_0(\eta) + I_0(\eta)\int_{\eta_1}^{\eta}\eta\frac{K_0(\eta)g(\eta)}{k^2}d\eta - K_0(\eta)\int_{\eta_1}^{\eta}\eta\frac{I_0(\eta)\,g(\eta)}{k^2}\,d\eta \tag{5.39}$$

This is the solution to equation (5.36) which is a function of η. Writing this equations as a function of y_0 will reintroduce $\hat{\phi}_1$ to the problem which can be found as

$$\begin{aligned}\hat{\phi}_1 = {} & A_2 I_0\left(-\frac{k}{a}(ay_0+b)\right) + B_2 K_0\left(-\frac{k}{a}(ay_0+b)\right) + \\ & \frac{I_0\left(-\frac{k}{a}(ay_0+b)\right)}{a}\int_0^{y_0}(ay_0+b)K_0\left(-\frac{k}{a}(ay_0+b)\right)r\,dy_0 - \\ & \frac{K_0\left(-\frac{k}{a}(ay_0+b)\right)}{a}\int_0^{y_0}(ay_0+b)I_0\left(-\frac{k}{a}(ay_0+b)\right)r\,dy_0\end{aligned} \tag{5.40}$$

Equation (5.40) gives the general solution to the domain equation i.e., to equation (5.19), where r and a are given by equations (5.30) and (5.31) while b is equal to $\overline{c} - \frac{L_0}{2}a$. This solution is more complicated than the corresponding solution given as equation (4.38) in chapter 4 where the assumption $c = \overline{c}$ was applied in the migration term. For comparison, equation (4.25) is

$$\hat{\phi}_1 = A_2 e^{k y_0} + B_2 e^{-k y_0} - \frac{P}{\overline{c}} \frac{RT}{z_1 F} A_1 e^{m y_0} - \frac{P}{\overline{c}} \frac{RT}{z_1 F} B_1 e^{-m y_0}$$

where A_1 and B_1 are the constants that appear in $\hat{c}_1$ and they are the same in both equations while A_2 and B_2 are not the same in these two equations. Finding A_2 and B_2 previously was easy because equation (4.25), which resulted from the constant coefficient differential equation is simple to deal with. Now with the variable coefficient differential equation i.e., equation (5.19), which lead us to equation (5.40), the constants A_2 and B_2 cannot be obtained easily and this contributes to the complication of the problem.

To find the constants A_2 and B_2, we turn to the boundary conditions, equations (5.20) and (5.24) where we see that $\frac{d\hat{\phi}_1}{dy_0}$ appears. This can be obtained by differentiating equation (5.40) and evaluate it at the anode and at the cathode. The results are

$$\frac{d\hat{\phi}_1^A}{dy_0} = -k\, A_2 I_1\left(-\frac{k}{a}b\right) + k\, B_2 K_1\left(-\frac{k}{a}b\right) \qquad (5.41)$$

and

$$\frac{d\hat{\phi}_1^C}{dy_0} = -k\ A_2 I_1\left(-\frac{k}{a}(aL_0+b)\right) + k\ B_2 K_1\left(-\frac{k}{a}(aL_0+b)\right) -$$
$$k\frac{I_1\left(-\frac{k}{a}(aL_0+b)\right)}{a}\int_0^{L_0}(ay_0+b)K_0\left(-\frac{k}{a}(ay_0+b)\right)\,r\,dy_0 - \qquad (5.42)$$
$$k\frac{K_1\left(-\frac{k}{a}(aL_0+b)\right)}{a}\int_0^{L_0}(ay_0+b)I_0\left(-\frac{k}{a}(ay_0+b)\right)\,r\,dy_0$$

Now by substituting equations (5.41) and (5.42) back into equations (5.20) and (5.24) we can get the constants A_2 and B_2 as

$$A_2 = \frac{\frac{z_1^2}{z_1D_1 - z_2D_2}c_M\sigma\hat{Y}_1^C - P\frac{d\hat{c}_1^C}{dy_0} - \hat{c}_1^C\left[\frac{z_1F}{RT}\right]\frac{d\phi_0^C}{dy_0}}{kc_0^C\left[\frac{z_1F}{RT}\right]\left[\frac{K_1\left(-\frac{k}{a}(aL_0+b)\right)}{K_1\left(-\frac{k}{a}b\right)}I_1\left(-\frac{k}{a}b\right) - I_1\left(-\frac{k}{a}(aL_0+b)\right)\right]}$$
$$+\frac{I_1\left(-\frac{k}{a}(aL_0+b)\right)\int_0^{L_0}(ay_0+b)K_0\left(-\frac{k}{a}(ay_0+b)\right)\,r\,dy_0}{a\left[\frac{K_1\left(-\frac{k}{a}(aL_0+b)\right)}{K_1\left(-\frac{k}{a}b\right)}I_1\left(-\frac{k}{a}b\right) - I_1\left(-\frac{k}{a}(aL_0+b)\right)\right]}$$
$$+\frac{K_1\left(-\frac{k}{a}(aL_0+b)\right)\int_0^{L_0}(ay_0+b)I_0\left(-\frac{k}{a}(ay_0+b)\right)\,r\,dy_0}{a\left[\frac{K_1\left(-\frac{k}{a}(aL_0+b)\right)}{K_1\left(-\frac{k}{a}b\right)}I_1\left(-\frac{k}{a}b\right) - I_1\left(-\frac{k}{a}(aL_0+b)\right)\right]}$$
$$-\frac{\left(\frac{z_1^2}{z_1D_1 - z_2D_2}c_M\sigma\hat{Y}_1^A - P\frac{d\hat{c}_1^A}{dy_0} - \hat{c}_1^A\left[\frac{z_1F}{RT}\right]\frac{d\phi_0^A}{dy_0}\right)K_1\left(-\frac{k}{a}(aL_0+b)\right)}{kc_0^A\left[\frac{z_1F}{RT}\right]K_1\left(-\frac{k}{a}b\right)\left[\frac{K_1\left(-\frac{k}{a}(aL_0+b)\right)}{K_1\left(-\frac{k}{a}b\right)}I_1\left(-\frac{k}{a}b\right) - I_1\left(-\frac{k}{a}(aL_0+b)\right)\right]}$$

and

$$B_2 = \frac{\dfrac{z_1^2}{z_1D_1 - z_2D_2} c_M \sigma \hat{Y}_1^A - P\dfrac{d\hat{c}_1^A}{dy_0} - \hat{c}_1^A\left[\dfrac{z_1F}{RT}\right]\dfrac{d\phi_0^A}{dy_0}}{kc_0^A\left[\dfrac{z_1F}{RT}\right]K_1\left(-\dfrac{k}{a}b\right)}$$

$$+\frac{I_1\left(-\dfrac{k}{a}b\right)}{K_1\left(-\dfrac{k}{a}b\right)} \frac{\dfrac{z_1^2}{z_1D_1 - z_2D_2} c_M \sigma \hat{Y}_1^C - P\dfrac{d\hat{c}_1^C}{dy_0} - \hat{c}_1^C\left[\dfrac{z_1F}{RT}\right]\dfrac{d\phi_0^C}{dy_0}}{kc_0^C\left[\dfrac{z_1F}{RT}\right]\left[\dfrac{K_1\left(-\dfrac{k}{a}(aL_0+b)\right)}{K_1\left(-\dfrac{k}{a}b\right)} I_1\left(-\dfrac{k}{a}b\right) - I_1\left(-\dfrac{k}{a}(aL_0+b)\right)\right]}$$

$$+\frac{I_1\left(-\dfrac{k}{a}b\right)}{K_1\left(-\dfrac{k}{a}b\right)} \frac{I_1\left(-\dfrac{k}{a}(aL_0+b)\right)\displaystyle\int_0^{L_0}(ay_0+b)K_0\left(-\dfrac{k}{a}(ay_0+b)\right) r\, dy_0}{a\left[\dfrac{K_1\left(-\dfrac{k}{a}(aL_0+b)\right)}{K_1\left(-\dfrac{k}{a}b\right)} I_1\left(-\dfrac{k}{a}b\right) - I_1\left(-\dfrac{k}{a}(aL_0+b)\right)\right]}$$

$$+\frac{I_1\left(-\dfrac{k}{a}b\right)}{K_1\left(-\dfrac{k}{a}b\right)} \frac{K_1\left(-\dfrac{k}{a}(aL_0+b)\right)\displaystyle\int_0^{L_0}(ay_0+b)I_0\left(-\dfrac{k}{a}(ay_0+b)\right) r\, dy_0}{a\left[\dfrac{K_1\left(-\dfrac{k}{a}(aL_0+b)\right)}{K_1\left(-\dfrac{k}{a}b\right)} I_1\left(-\dfrac{k}{a}b\right) - I_1\left(-\dfrac{k}{a}(aL_0+b)\right)\right]}$$

$$-\frac{I_1\left(-\dfrac{k}{a}b\right)}{K_1\left(-\dfrac{k}{a}b\right)} \frac{\left(\dfrac{z_1^2}{z_1D_1 - z_2D_2} c_M \sigma \hat{Y}_1^A - P\dfrac{d\hat{c}_1^A}{dy_0} - \hat{c}_1^A\left[\dfrac{z_1F}{RT}\right]\dfrac{d\phi_0^A}{dy_0}\right)K_1\left(-\dfrac{k}{a}(aL_0+b)\right)}{kc_0^A\left[\dfrac{z_1F}{RT}\right]K_1\left(-\dfrac{k}{a}b\right)\left[\dfrac{K_1\left(-\dfrac{k}{a}(aL_0+b)\right)}{K_1\left(-\dfrac{k}{a}b\right)} I_1\left(-\dfrac{k}{a}b\right) - I_1\left(-\dfrac{k}{a}(aL_0+b)\right)\right]}$$

It is clear how the expressions for the constants A_2 and B_2 are lengthy and complicated even though we did not substitute in them the expressions for some of the variables such as r, $\hat{c}_1^A$, $\hat{c}_1^C$ etc. Now after getting A_2 and B_2, let us go on showing how we will continue to solve our eigenvalue problem.

At this stage, since both A_2 and B_2 are found, we can evaluate $\hat{\phi}_1$ at both electrodes namely, $\hat{\phi}_1^A$ and $\hat{\phi}_1^C$ which can be obtained from equation (5.40) at $y_0 = 0$, the anode, and at $y_0 = L_0$, the cathode. The results are

$$\hat{\phi}_1^A = A_2 I_0\left(-\frac{k}{a}\, b\right) + B_2 K_0\left(-\frac{k}{a}\, b\right) \tag{5.43}$$

and

$$\begin{aligned}\hat{\phi}_1^C = {} & A_2 I_0\left(-\frac{k}{a}(aL_0+b)\right) + B_2 K_0\left(-\frac{k}{a}(aL_0+b)\right) \\ & + \frac{I_0\left(-\frac{k}{a}(aL_0+b)\right)}{a} \int_0^{L_0} (ay_0+b) K_0\left(-\frac{k}{a}(ay_0+b)\right) r\, dy_0 \\ & - \frac{K_0\left(-\frac{k}{a}(aL_0+b)\right)}{a} \int_0^{L_0} (ay_0+b) I_0\left(-\frac{k}{a}(ay_0+b)\right) r\, dy_0\end{aligned} \tag{5.44}$$

Now all the equations of the eigenvalue problem have been used except the two B-V equations i.e., equations (5.22) and (5.25). In these two equations, $\hat{c}_1^A$, $\hat{c}_1^C$, $\hat{\phi}_1^A$ and $\hat{\phi}_1^C$ appear and they are in terms of $\hat{Y}_1^A$, $\hat{Y}_1^C$ and σ which have not been determined yet. So substituting for $\hat{c}_1^A$, $\hat{c}_1^C$, $\hat{\phi}_1^A$ and $\hat{\phi}_1^C$ in the B-V equations will result in having two linear, homogeneous equations in terms of $\hat{Y}_1^A$, $\hat{Y}_1^C$. They can be written

$$A_{11}\hat{Y}_1^A + A_{12}\hat{Y}_1^C = 0 \tag{5.45}$$

and

$$A_{21}\hat{Y}_1^A + A_{22}\hat{Y}_1^C = 0 \tag{5.46}$$

where A_{11}, A_{12}, A_{21} and A_{22} are different from previous chapters but they will be playing the same rule. To get a solution other than $\hat{Y}_1^A = \hat{Y}_1^C = 0$, we set the determinant of the coefficients of $\hat{Y}_1^A$ and $\hat{Y}_1^C$ to zero i.e.,

$$\det\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} = A_{11}A_{22} - A_{12}A_{21} = 0 \tag{5.47}$$

The expressions for A_{11}, A_{12}, A_{21} and A_{22} are very lengthy and we are not going to write them here. Now once the variables and the properties of the system are set, in addition to setting k^2, the only unknown that we will be solving for is σ that will turn the determinant to zero. This is not an easy thing to do since the resulted equation will be implicit in σ. So the way to deal with this equation is to solve it like any complicated equation with an implicit variable that is to use trial and error. By this we mean that we are going to plot $A_{11}A_{22} - A_{12}A_{21}$ as a function of σ and see where it is zero. These $\sigma's$ will be the roots of our problem. However, we do not have to go through all of this work because we already have good guesses where they are from the approximate model. The next section will present the results of performing this calculation of finding σ.

5.5 Results and Discussion

Here we will compare the results obtained in this chapter with those presented in chapter 4. In this comparison we will draw figures showing σ vs. k^2 over a wide range of the input conditions. This will be done to investigate under what conditions the approximation will give good results and to see whether we can use the simple chapter 4 results in our later work which will be complicated enough without chapter 5 complications. Then we will compare the results obtained by our method to those

obtained by S&B which presented the results of a difference approximation for a selected set of physical properties and a range of input variables.

5.5.1 Comparison of the Results in Chapters 4 and 5

In this section we will compare the results of chapters 4 and 5 by presenting graphs of σ vs. k^2 as they depend on the input variables. Our input variables are as usual U/U_{lim}, $\overline{c}$ and L_0 and we will start with the effect of changing the current on the relation between σ and k^2.

5.5.1.1 The Comparison for Different Values of U/U_{lim}

Figure 5-1 shows a comparison between the two models for the following input conditions: $U/U_{\text{lim}} = 0.1$, $L_0 = 0.05$ m and $\overline{c} = 0.1$ kg mole/m^3. In this figure and all the figures to come, the solid line will represent chapter 5 results and the dashed line will represent the approximate obtained in chapter 4.

It is clear from Figure 5-1 that the results from chapters 4 and 5 are in qualitative and quantitative agreement and the approximation is reasonable over the whole range of k^2 which is true for both the first and the second eigenvalue. The approximation misses the critical point slightly and under predicts the maximum growth rate a little.

To see what will happen at larger values of U/U_{lim}, Figure 5-2 is drawn for the values of L_0 and $\overline{c}$ used in Figure 5-1 and for $U/U_{\text{lim}} = 0.3$. The approximation is not quiet as good at this higher current but the general behavior of the whole figure is no different than Figure 5-1. Going to higher currents, Figure 5-3 is drawn for $U/U_{\text{lim}} = 0.5$ while keeping L_0 and $\overline{c}$ the same. Now the approximation to the first eigenvalue begins to breakdown but the approximation to the second eigenvalue remains reasonable.

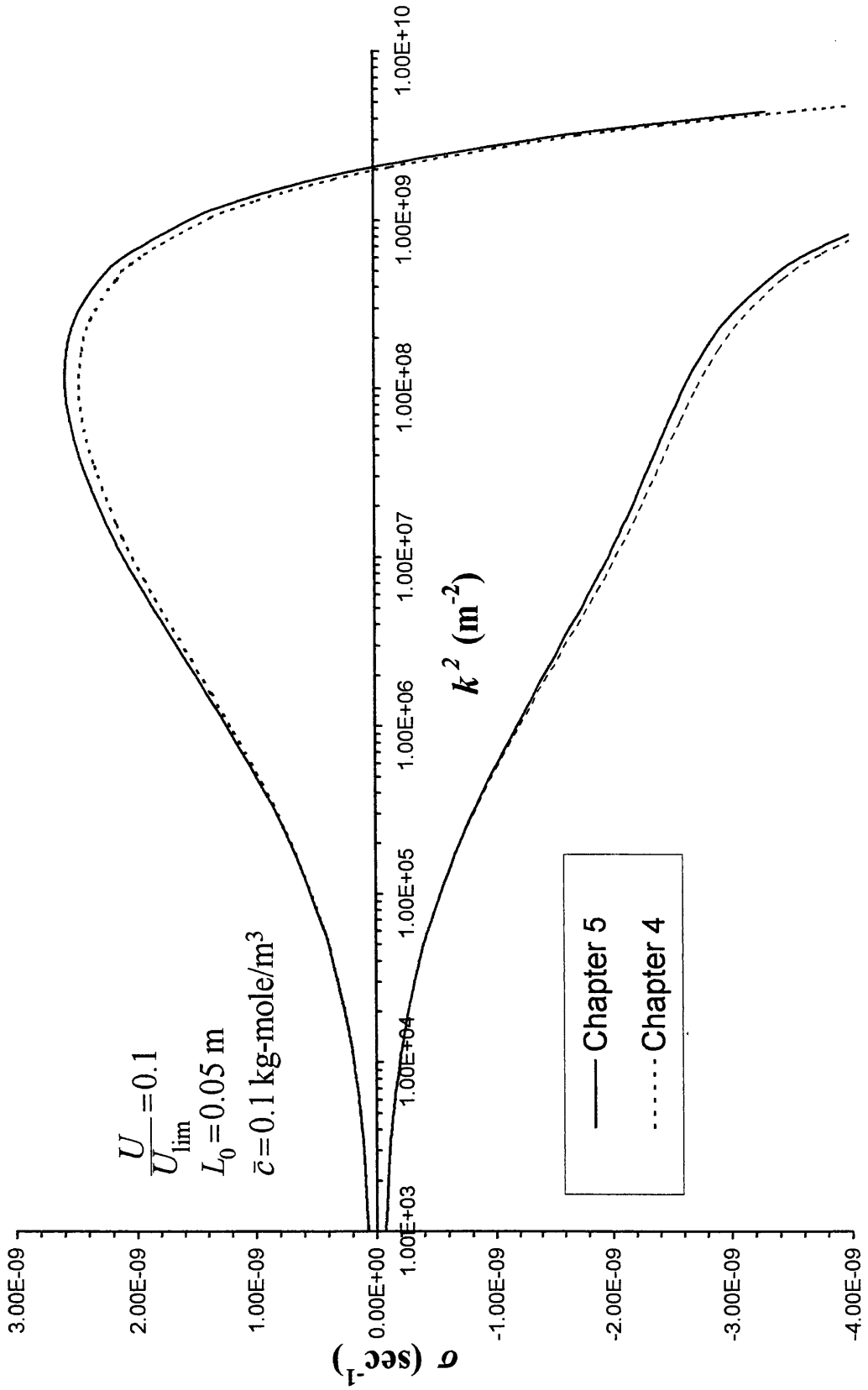


Figure 5-1. Evaluation of the approximation at $U/U_{lim} = 0.1$.

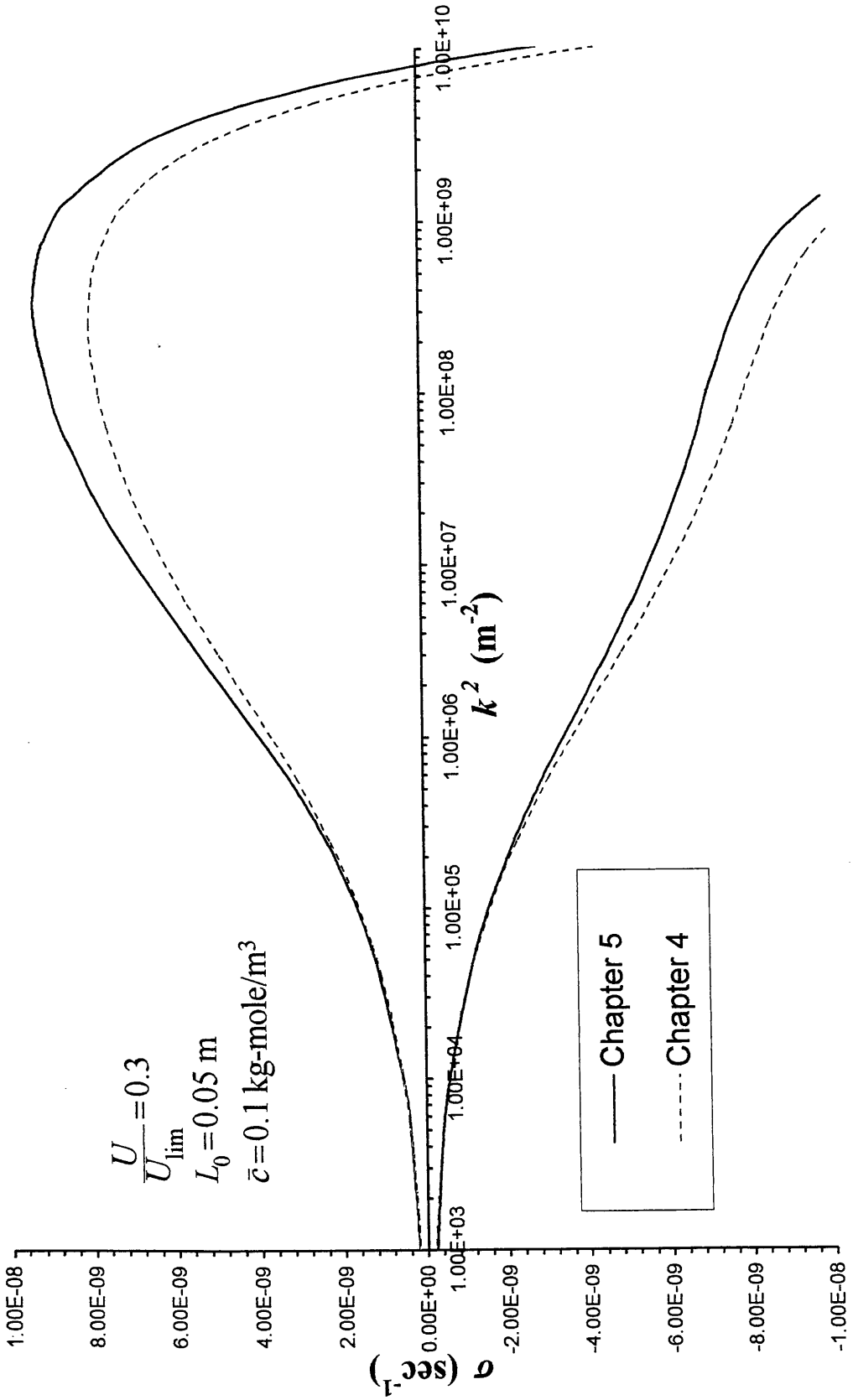


Figure 5-2. Evaluation of the approximation at $U/U_{\lim} = 0.3$.

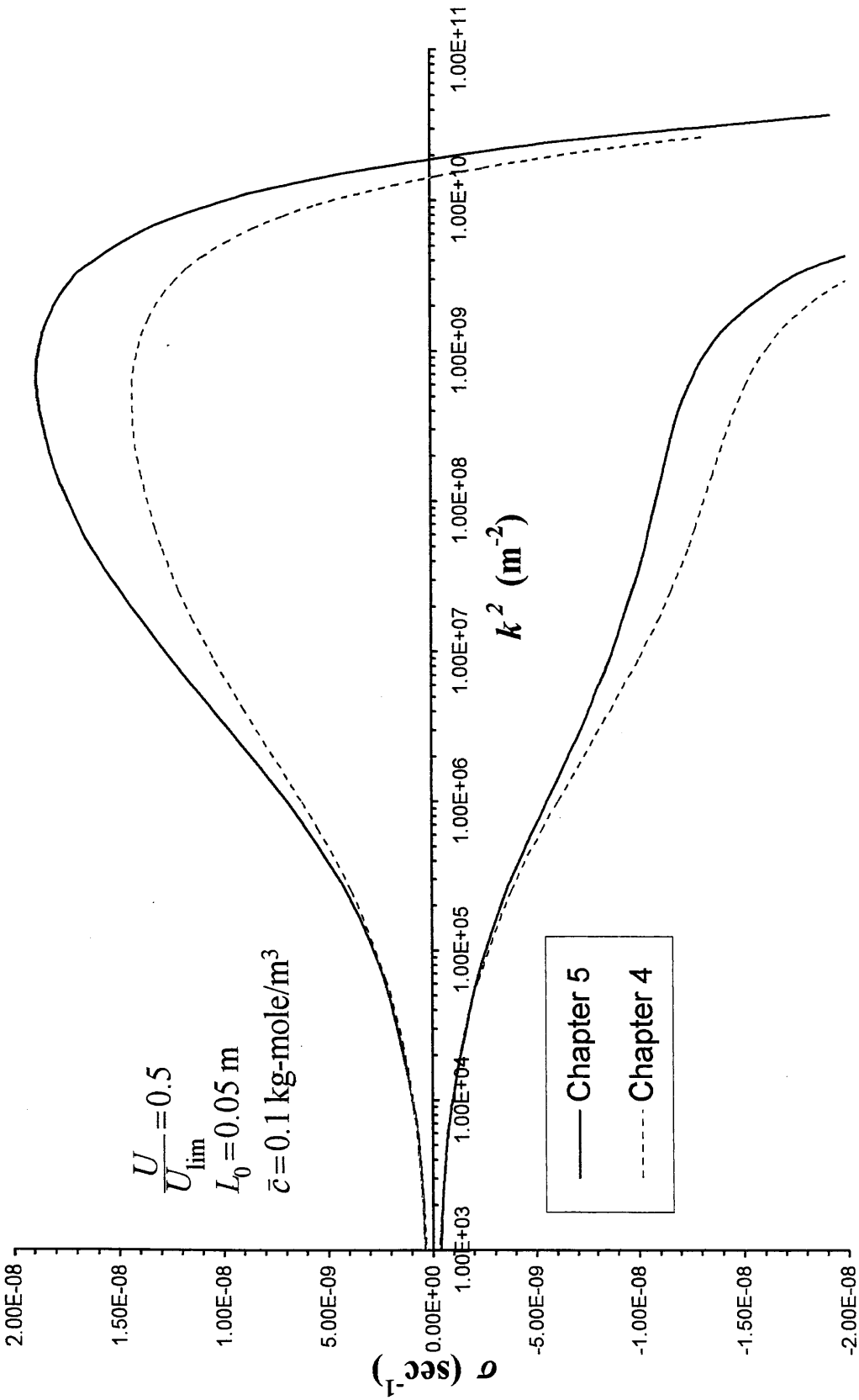


Figure 5-3. Evaluation of the approximation at $U/U_{lim} = 0.5$.

Now if one traces $U/U_{\lim}$ keeping the electrode spacing and the average ionic concentration fixed then he can look at the three figures successively. The figures show that the system will be more unstable at higher currents than it is at lower ones. That is the larger the value of $U/U_{\lim}$ the more positive the growth constant and the larger the value of the critical wave number. It is also true that at a given k^2, the larger the positive value of the first eigenvalue, the more negative the second eigenvalue.

We should not be surprised that the approximation becomes weaker as $U/U_{\lim}$ becomes larger. This is because increasing the current will make the migration term more important so any change in the input variables that will increase the effect of migration will work against the $c=\overline{c}$ approximation since this approximation only appears in the migration term. Also by looking to the base solution we can predict this result and we can tell if the approximate model will under predict or over predict the instability. This can be done by looking to the expressions for the electrical potential gradient in the approximate and in the full model. In the full model, the expression for the electrical potential gradient when written as a function of $U/U_{\lim}$ at the cathode as it appears in chapter 3 is

$$\frac{d}{dy_0}\left[\frac{z_1F}{RT}\phi_0\right]^C = \frac{z_1}{z_2}\frac{2}{L_0}\frac{U/U_{\lim}}{1-U/U_{\lim}}$$

while that for the approximate model from chapter 4 is

$$\frac{d}{dy_0}\left[\frac{z_1F}{RT}\phi_0\right]^C = \frac{z_1}{z_2}\frac{2}{L_0}\frac{U}{U_{\lim}}$$

By looking to these two equations it is clear that increasing $U/U_{\lim}$ will increase the potential gradient in both cases. Moreover, it is obvious that for any value of $U/U_{\lim}$ the full model will always give a higher electrical potential gradient than the approximate

and as U/U_{lim} grows larger this effect becomes more significant. So the conclusion of studying the effect of U/U_{lim} is that qualitatively, the approximation makes sense, however, quantitatively, the approximation grows weaker as U/U_{lim} grows larger.

This is the first promising result in favor of the approximation used in chapter 4. We want now to continue the comparison at different values of the electrode spacing namely at different values of L_0.

5.5.1.2 The Comparison at Different Values of L_0

Here we will study the effect of changing the electrode spacing while fixing both U/U_{lim} and $\bar{c}$. Figure 5-4 is drawn for $U/U_{lim} = 0.3$, $\bar{c} = 0.1$ kg mole/m^3 and $L_0 = 0.005$ m. The case where $L_0 = 0.05$ m and for the same U/U_{lim} and $\bar{c}$ has already been presented as Figure 5-2. The validity of the approximation appears not to depend strongly on L_0 in the range of L_0 tested. To make sure that this conclusion is valid for even smaller L_0's, Figure 5-5 is drawn for the same values of U/U_{lim} and $\bar{c}$ in Figures 5-2 and 5-4 and for $L_0 = 0.002$ m and it seems to be similar to those figures. The approximation appears to be reasonable over a fair range of L_0.

Now when looking to Figures 5-2, 5-4 and 5-5 to follow how changing L_0 while keeping U/U_{lim} and $\bar{c}$ will affect the σ vs. k^2 relation, we see that larger values of L_0 have the same effect as smaller values of U/U_{lim} on both the first and the second eigenvalue as we obtained earlier in chapter 4.

Now we turn to the effect of changing the average ionic concentration.

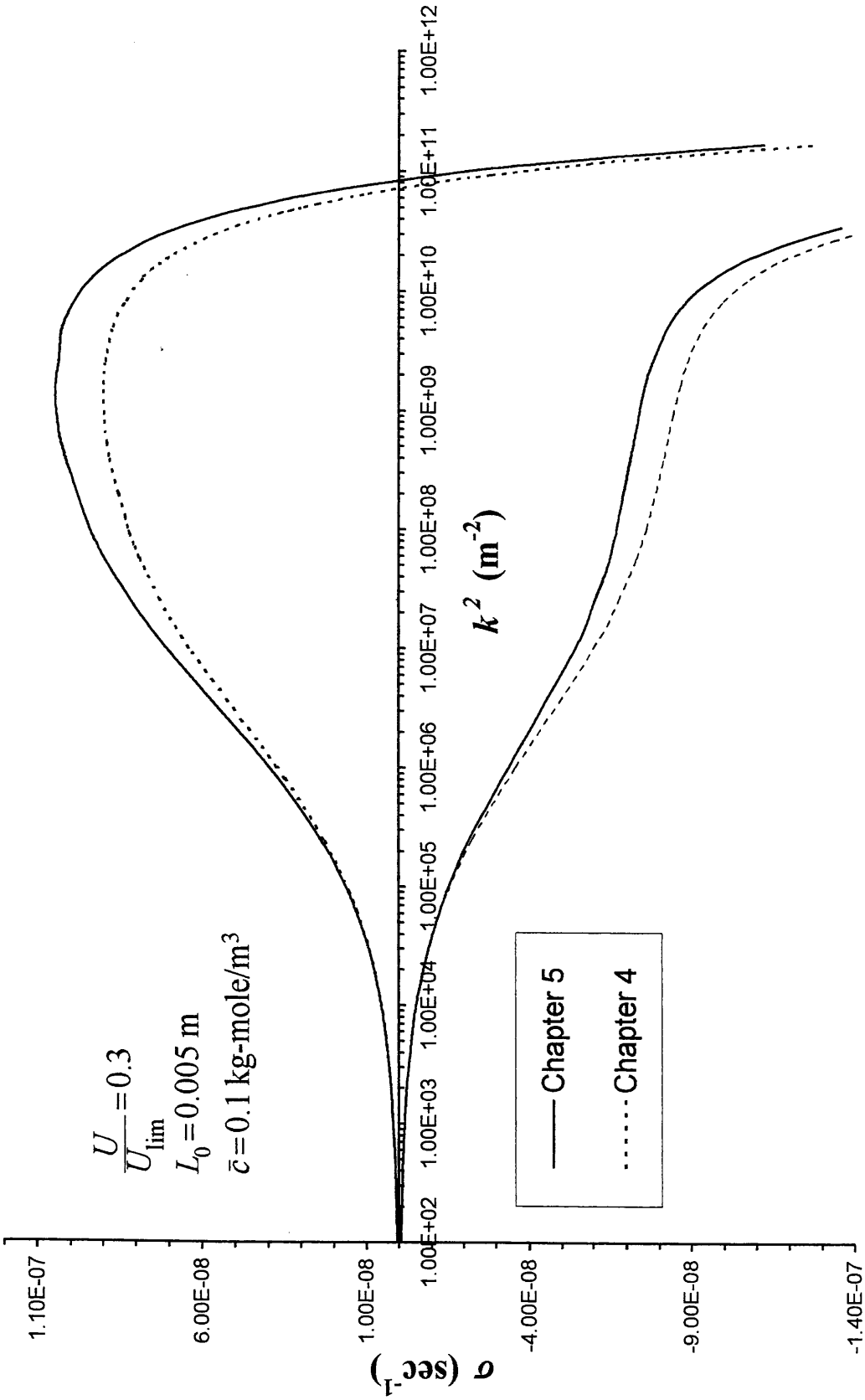


Figure 5-4. Evaluation of the approximation at $L_0 = 0.005$ m.

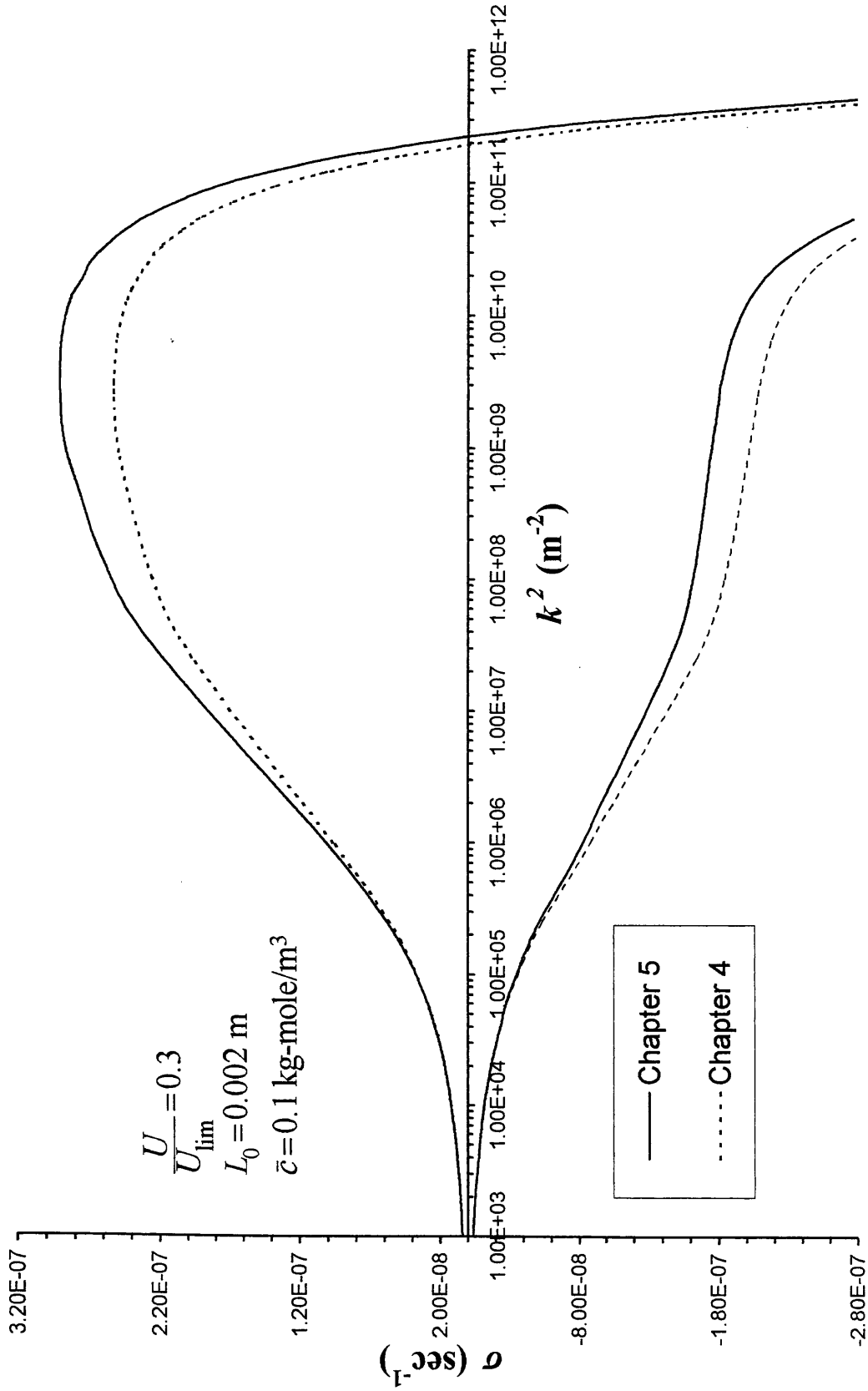


Figure 5-5. Evaluation of the approximation at $L_0 = 0.002$ m.

5.5.1.3 The Comparison for Different $\bar{c}$

The effect of changing $\bar{c}$ is studied by drawing figures at the same U/U_{lim} and L_0 but at different $\bar{c}$. Figure 5-6 is drawn for $U/U_{\text{lim}} = 0.3$, $L_0 = 0.05$ m and $\bar{c} = 0.01$ kg mole/m^3 where $\bar{c}$ is now one-tenth the average ionic concentration of Figure 5-2. The figures show that decreasing $\bar{c}$ makes the approximation a little better. The trend continues as $\bar{c}$ decreases. Figure 5-7 is drawn for $U/U_{\text{lim}} = 0.3$, $\bar{c} = 0.005$ kg mole/m^3 and $L_0 = 0.05$ m. This figure shows the approximation to be just slightly better than the previous figure and suggests that while the approximation is reasonable at all concentrations studied, the error does not disappear as $\bar{c}$ goes to zero.

Now if we want to trace $\bar{c}$ holding both U/U_{lim} and L_0 constant we shall look to Figures 5-2, 5-6 and 5-7. First, notice that the curve with the larger $\bar{c}$ is the more unstable because it gives larger positive $\sigma's$ even though both of the curves are passing through the same neutral stability point (i.e., they have the same $k^2_{critical}$). Moreover, the curves for the second eigenvalue show that the one with the higher concentration is more negative than the one with the lower concentration. These are results that we are familiar with from the previous chapter.

The conclusion from the comparison between chapters 4 and 5 results can be summarized as follows. First, the approximate model did not harm the qualitative behavior when studying the effect of any of the input variables. Second, when looking to the quantitative results, it is obvious that increasing U/U_{lim} has the worst effect in breaking down the approximation since changing $\bar{c}$ and L_0 did not harm the approximation by much. This is an excellent achievement supporting the approximate

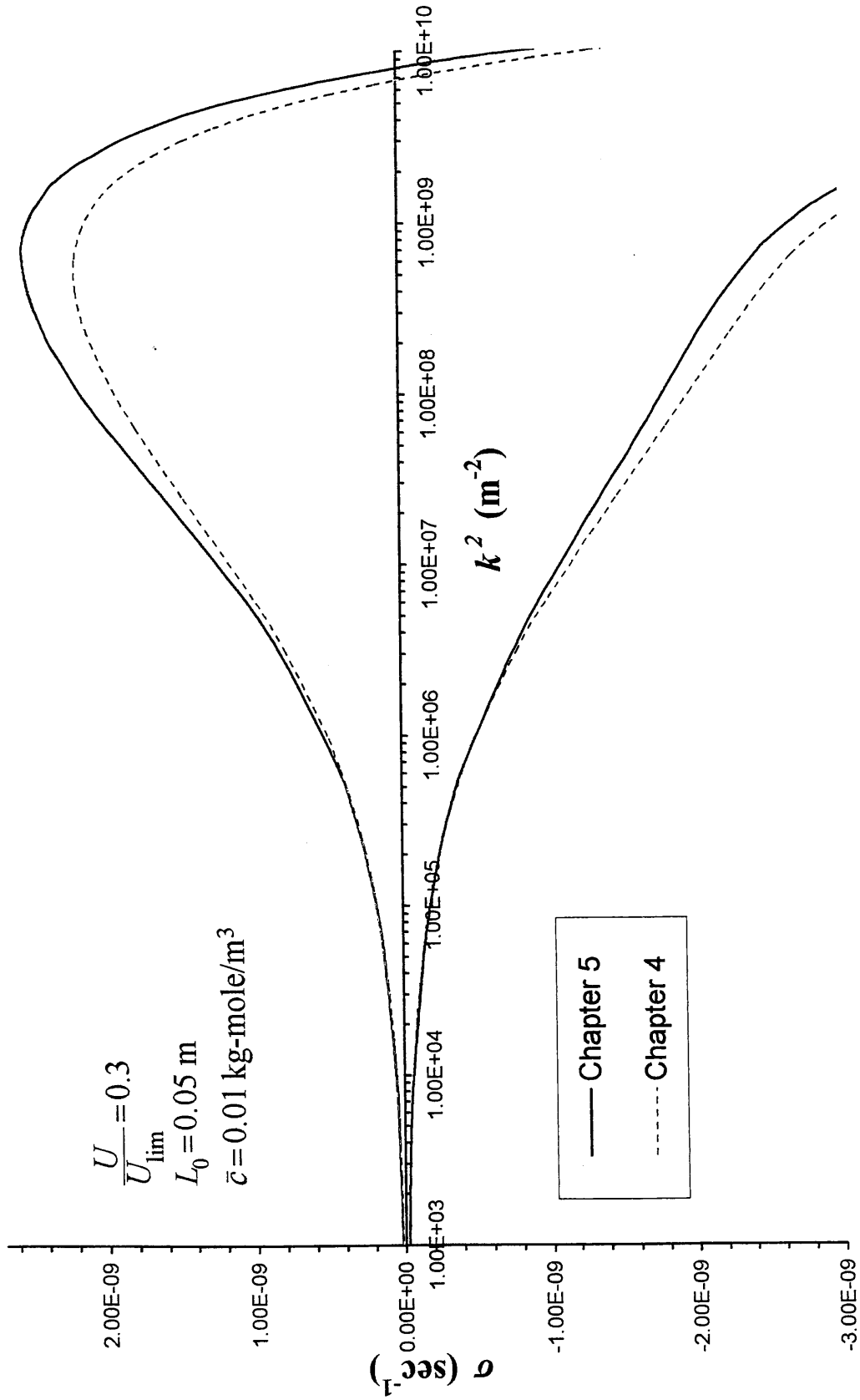


Figure 5-6. Evaluation of the approximation at $\bar{c} = 0.01$ kg-mole/m^3.

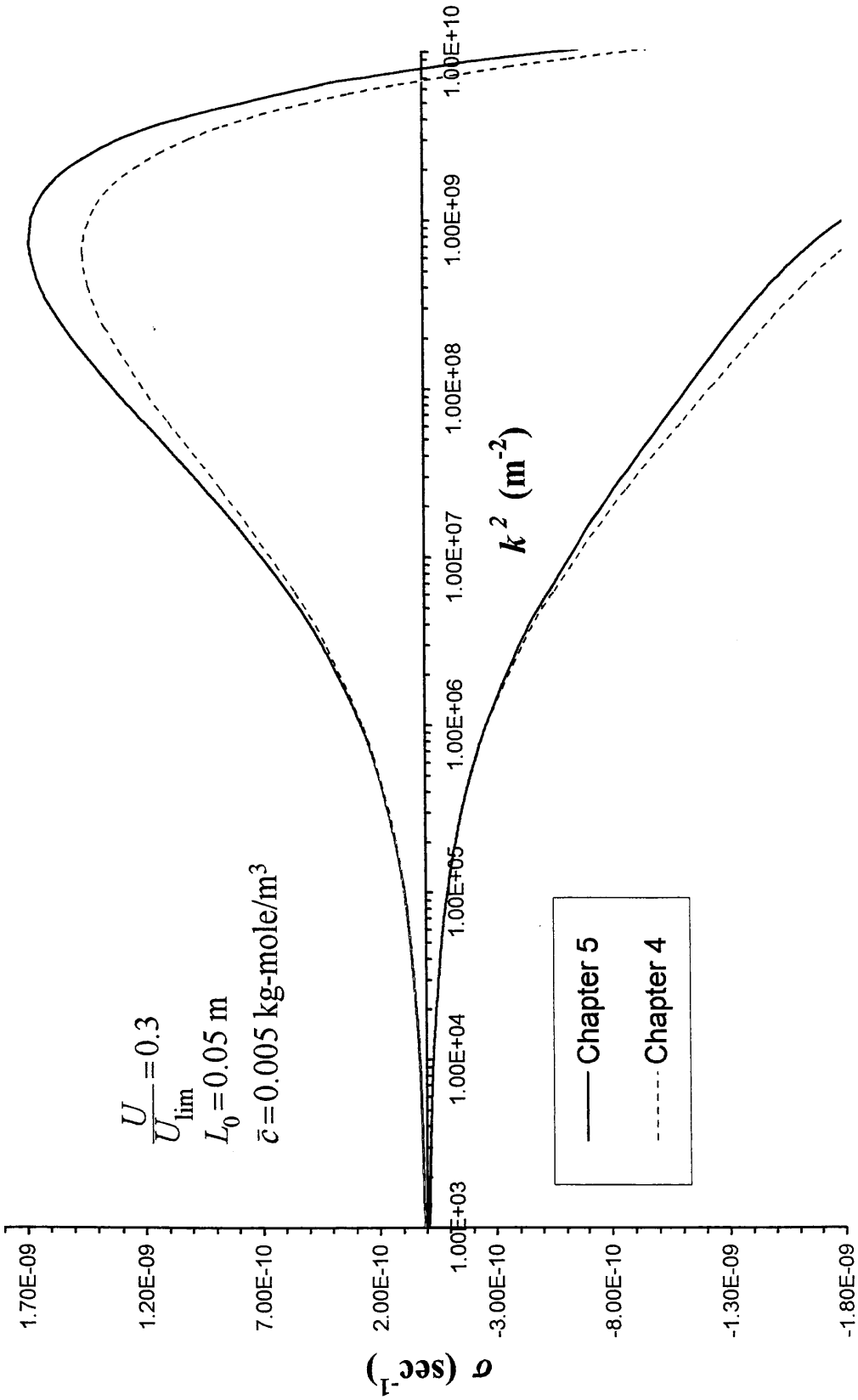


Figure 5-7. Evaluation of the approximation at $\bar{c} = 0.005$ kg-mole/m^3.

model and showing that using it later in the complicated calculations is a wise move under the restriction of making the calculations for small values of $U/U_{\lim}$.

The last topic to be discussed in this chapter is to compare our chapter 5 results with previous work by S&B.

5.5.2 Comparison with Previous Work by S&B

In this section we want to show the reader that we get the same results as those obtained by S&B where they solved the problem by finite difference approximation.

S&B did not use the copper/copper sulphate system to get their results instead they scaled the problem, then they assigned values to their dimensionless groups based on typical values of the input conditions for small cells with $L_0 \approx 0.002$ m. The one particular case that we will use to compare our results with theirs corresponds to the following values of the non-dimensional parameters:

$\frac{\gamma}{c_M RTL_0} = 10^{-4}$, $Z = \frac{z_1}{|z_2|} = 1$, $\frac{D_1}{D_2} = 1.1$, $\frac{i_0 L_0}{2FD_1\bar{c}(1+Z)} = 0.1$, $\beta = 0.5$ and

$\frac{2c_M D_1(1+Z)\bar{c}}{Dz_1} = 0.04$, where $D = \frac{D_1 D_2 (z_1 - z_2)}{D_1 z_1 - D_2 z_2}$ which is similar to what we are using in our work.

Figure 5-8 presents a graph of $\log \frac{J}{1-J}$ vs. $\log k$ given by S&B. where J stands for what we called $U/U_{\lim}$ and k denotes the scaled wave number which equals kL_0 in our notation. In addition, the numbers assigned to each curve are the values of the non-dimensional growth rate which is given by $\sigma L_0^2 / D$. This figure looks different from the figures we presented earlier as here each curve belongs to a single non-dimensional σ; however, it predicts the same behavior that we have obtained. Figure 5-8 shows that for

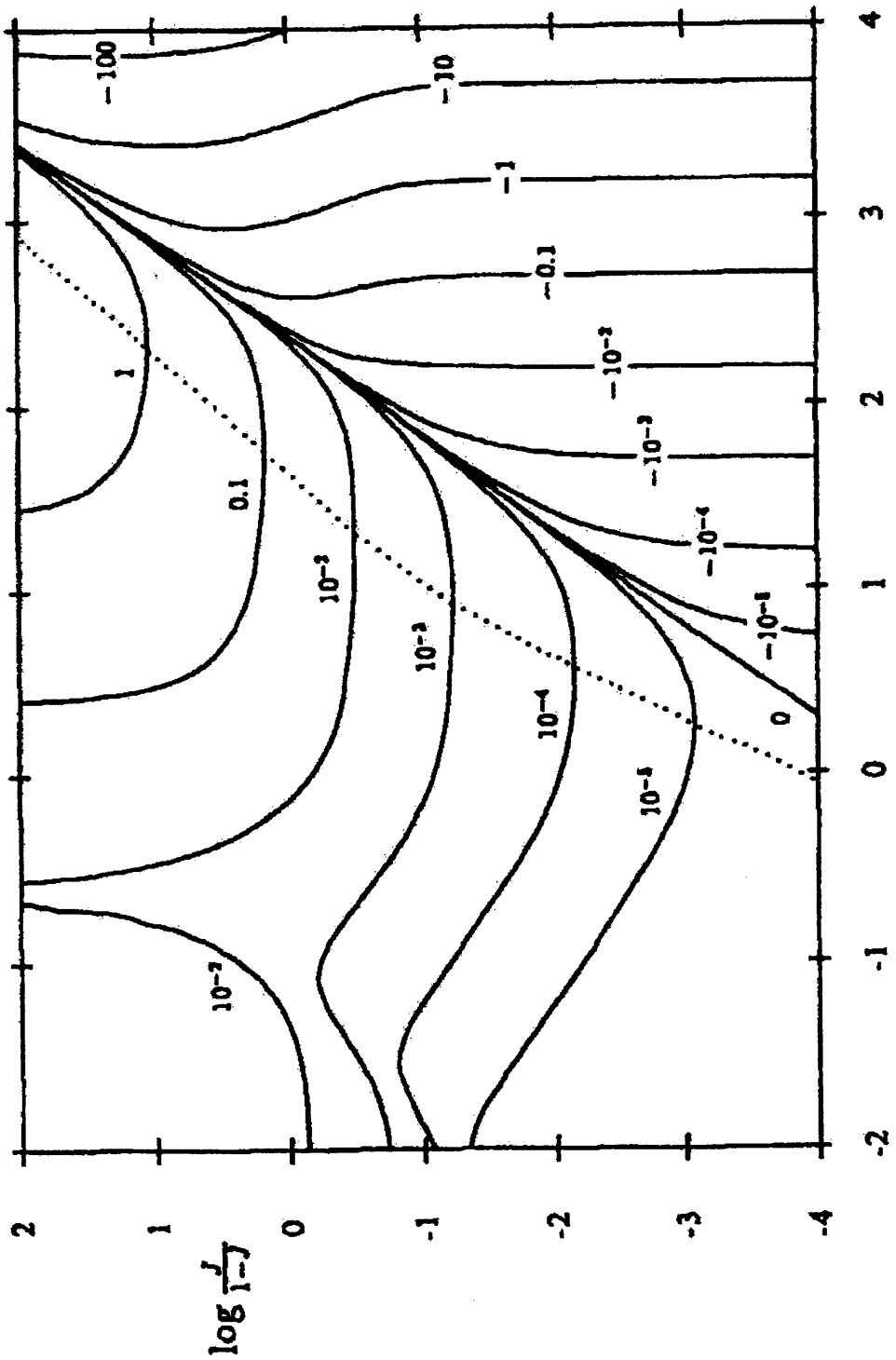


Figure 5-8. Contours of the non-dimensional growth constant given by S&B (Sundström and Bark, 1995).

every value of the current no matter how small, there will a positive growth constant and if the current is small then the growth rate will be also small and vise versa. This is what we found when we studied the effect of changing the current on the σ vs. k^2 curve.

Now the purpose of giving Figure 5-8 is to compare it to the results of our approach, which simplifies the problem and thereby avoids the need for a finite difference solution to the eigenvalue problem. To do this, we choose three curves from the figure and try to duplicate them in Figure 5-9. These curves belong to the non-dimensional growth rate of 10^{-5}, 10^{-4} and 10^{-3}. Figure 5-9 then shows $\log \frac{U/U_{\lim}}{1-U/U_{\lim}}$ vs. $\log kL_0$ drawn for three values of $\sigma L_0^2 / D$. Even though reading these two figures will not be so precise, one can roughly see by comparing Figures 5-8 and 5-9 at the same value of the growth constant, that these three curves agree with each other which means that S&B results and our results are in good agreement.

Let us summarize what we have done in this chapter. First, we obtained the solution to the electrodeposition problem without the approximations used in the previous two chapters. By converting the electrical potential equation to a Bessel form, we avoid the finite difference work of S&B while confirming that our results are in agreement. We also made a comparison between the results obtained in chapter 4, where c was replaced with $\bar{c}$ in the migration term, with those obtained in this chapter. The approximation seems to be acceptable as long as $U/U_{\lim}$ is not too large.

What we have done so far in this dissertation was to present and validate a number of approximations that will help in making the problem easier for subsequent work. In chapter 3, we presented the CRE approximation which simplify the kinetics of the

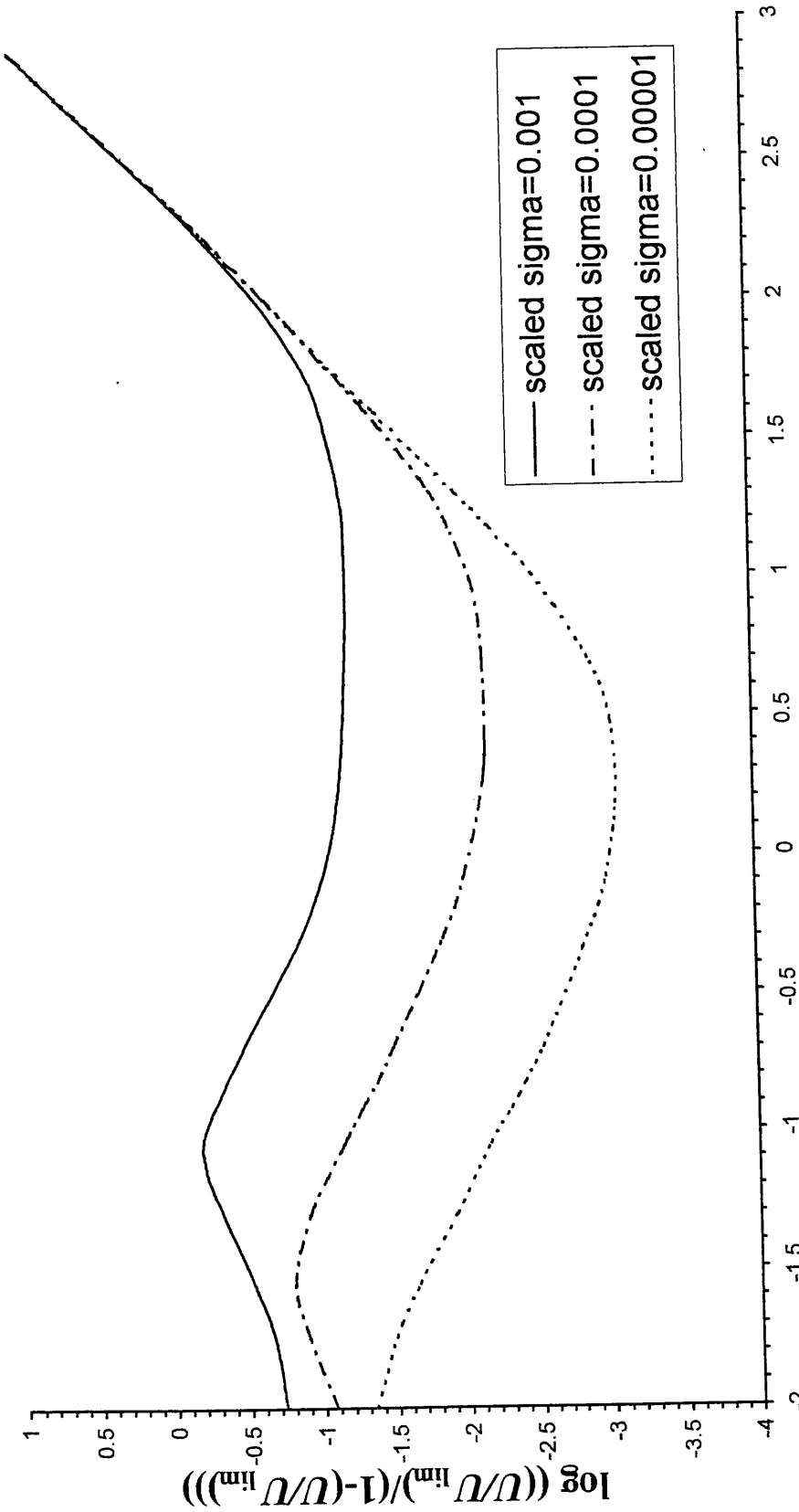


Figure 5-9. Results obtained by our approach for three different values of the scaled growth constant.

problem leading mainly to a simpler base relation between the voltage drop and the current or the velocity of the surface. Then in the previous chapter, we presented the main approximation to simplify the transport by replacing c with $\overline{c}$ in the migration term with the aim of solving the eigenvalue problem analytically. Along with this approximation, we proposed dropping the growth constant from the domain so we can simplify σ vs. k^2 relation in order to be able to arrive to a simple relation from which tracing the effect of the different variables and understanding the behavior of the curves can be achieved.

Even though we found all the previous approximations to be successful, we chose to solve the full model, which turned out to be very complicated in this chapter without implementing the CRE or dropping σ from the domain. This was for different reasons. First, since we were evaluating the migration term approximation, we did not want to enjoin this with any other approximation. Second, One of our objectives of this chapter was to show that we are able to solve the complete model without the need for finite differencing as S&B did and we showed that our results and theirs are really close. The final reason is that even if we implemented these two approximations we would still get a variable coefficient differential equation that will require approximate methods to evaluate the integrals appearing in the particular solution. Hence these two approximations will not help much unless we combine them with the migration term approximation when solving the eigenvalue problem.

It is in the next chapter that we will combine the CRE and the migration term approximation since the calculations will be complicated enough even with these two approximations in use. As we already know that these two approximations break down at

higher currents, the work in the next chapter will be applicable to lower currents and it will lose its validity as the current approaches its limiting value.

The main concern of chapter 6 will be to predict what we might see when running an experiment. It is noteworthy that in the previous chapters we were looking for the critical wavelength for any value of the control variable. However, in chapter 6, we will show how to decide what the critical value of the control variable in a physical cell is. Then we will go beyond the critical conditions and carry our calculations further to see if there is something that can be measured which will lead us to predict the initiation of the instability once we crossed the critical point of the control variable.

CHAPTER 6
WEAKLY NONLINEAR CALCULATIONS

In chapter 5 the σ vs. k^2 relation was obtained by solving the eigenvalue problem without introducing any approximations other than the assumptions presented in chapter 2. The main problem was that a differential equation with a variable coefficient was obtained. We were successful in overcoming this difficulty by putting the equation in Bessel's function form which then reduced the problem to integrations which were then carried out by approximate methods.

Also in chapter 5 we compared the results with those obtained in chapter 4, where the migration term was approximated and found that the approximation worked beautifully in getting both qualitative and quantitative agreement with the full model. Moreover, in chapter 3 we have also shown that another approximation, namely CRE, was reasonable. This chapter will be the place where all the knowledge we gathered in the previous chapters will help us perform further studies which involve weakly nonlinear calculations. It is really the purpose of all the approximations presented in this dissertation to simplify the model so that it can be used here to get some idea of nonlinear effects.

But then we might ask ourselves what is in this chapter that is so important that it must be preceded by five full chapters explaining what the problem is and how to use different approximations to simplify it. The importance of this chapter lies in its practical application since these calculations will explain what to expect during an experiment and it will show how the total current in the electrodeposition cell will respond if the voltage

drop is increased through its critical value. This calculation will therefore help us predict the detection of the onset of the instability experimentally. Moreover, it will help us get a good idea on how to design and run an electrodeposition experiment which will be a topic of the last chapter.

We know that for every set of input conditions there is a critical k^2 which is not zero. So every set of conditions is unstable. In this chapter we are going to study what might happen in an experiment and will refer to critical voltages. The reader might be surprised to hear us talking about this because, from the previous chapters, it seems that every voltage is unstable. But, in fact, every critical voltage generates an unstable range of wave numbers and a stable ranges of wave numbers.

In an electrodeposition experiment, the cell cannot be stable unless the displacements to which it is unstable (i.e., the displacements corresponding to wave numbers less than $k_{critical}$) can be prevented from being imposed on the cell. The easiest way to do this is to control the width of the cell. Let W_0 denotes this width. Then W_0 determines the allowable wave numbers and in the case of homogeneous Neumann side wall conditions, which are going to be used in this chapter, the allowable wave numbers are $n\pi/W_0$, $n = 1, 2, \cdots$ and hence the smallest and most dangerous, allowable wave number is π/W_0.

To introduce a control variable, let the width of the cell be fixed at some finite value. This fixes the allowable wave numbers, the smallest or most dangerous lying to the right of zero. Then, start with the cell at equilibrium and begin to increase the potential difference across the cell. This moves the critical wave number upward from zero, but as long as it lies to the left of the most dangerous wave number, the cell remains stable.

However, as the potential difference applied across the cell continues its increase, sooner or later it will reach a value at which the critical wave number will just become equal to the least allowable wave number. This will be the critical value of $V^A - V^C$ i.e., $\left(V^A - V^C\right)_{critical}$. Increasing $V^A - V^C$ beyond this value will produce at least one displacement to which the cell is unstable. In this way, the potential difference across the cell can be viewed as a control variable by virtue of the fact that the long wavelength displacements to which the cell is unstable are screened out by setting W_0 to some finite value.

This discussion on how to run an experiment is important to our work in this chapter as from now on we will be talking about critical voltage drop and critical current whereas in the previous chapters we were talking about critical wave number.

The linear stability analysis presented in the earlier chapters can only give the onset conditions for the instability of the electrode surfaces. It cannot predict what we see in experiments, as experiments are always conducted, at least slightly, in the nonlinear regime. Hence nonlinear calculations are required to determine the behavior beyond the neutral stability point but the calculations we present will be valid only in a small region very close to the onset conditions as we only go to second order, one order higher than the linear or the first order results presented so far.

The plan of this chapter will be as follows. First, the nonlinear equations will be written after taking into account both the CRE and the migration term approximations. Next the nonlinear equations will be scaled to reduce the number of variables appearing in them and to make the equations look simpler to aid in our work. This scaling was not

introduced earlier because it is easier to think physically about the problem in terms of unscaled variables.

After getting the scaled equations, a steady one-dimensional base solution will be found followed by the first order calculations to determine its stability. Now in the first order problem, our interest will not be to find the critical wave number as in the previous chapters. The objective of solving the first order problem in this chapter will be to find the critical voltage not the critical wave number, since the critical wave number is known once the side wall conditions are set. So the first-order calculations will be patterned after the work in chapters 3, 4 and 5 and leads to expressions for the critical voltage drop and the critical current. Once the critical conditions are determined, we will ask what might be seen as this point is crossed. Going beyond the critical voltage requires us to perform nonlinear calculations and by this is meant going to higher orders in ε, not that we ever have to solve nonlinear equations. When performing the calculations, the potential difference will be moved from the critical by an amount $\frac{1}{2}\varepsilon^2$ and the response to this is investigated.

Earlier, when we were looking for the stability of the base solution to small disturbances, ε meant the amplitude of the perturbation. Now, since we are interested in constructing the solution as a result of the instability, ε is the departure of the control variable, namely, the voltage drop from its critical value.

The total current drawn by the cell, which is easily measurable by an ammeter, will be our indication of interesting things that might result when a surface loses its planarity and acquires a wiggly shape. So let us start by presenting the nonlinear equations of the electrodeposition model.

6.1 The Nonlinear Equations

The first step is to write the nonlinear equations on the domain and at the two boundaries. This is the practice we have followed since the third chapter in order to make every chapter self-contained. Here we will make use of all the approximations presented earlier such as CRE and putting $\overline{c}$ in place of c in the migration term. The first way this chapter differs from earlier chapters is that in this chapter the cell will have a finite width. That is to say there will be boundaries in the transverse direction and homogeneous Neumann conditions will be assumed to hold there.

The equations that hold through the electrolytic solution (i.e., between $Y^A(x,t) \le y \le Y^C(x,t)$ and $0 \le x \le W_0$) are

$$\frac{\partial c}{\partial t} = D\,\nabla^2 c \tag{6.1}$$

and

$$P\,\nabla^2 c + \frac{z_1 F}{RT}\,\overline{c}\,\nabla^2 \phi = 0 \tag{6.2}$$

Then at the anode and at the cathode surfaces, c and ϕ must satisfy

$$D\,\vec{n}\cdot\nabla c = \frac{-z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} c_M \left[\vec{n}\cdot\vec{u} + \vec{n}\cdot\vec{U}\right] \tag{6.3}$$

$$P\,\vec{n}\cdot\nabla c + \frac{z_1 F}{RT}\overline{c}\,\vec{n}\cdot\nabla\phi = \frac{c_M z_1^2}{z_1 D_1 - z_2 D_2}\left[\vec{n}\cdot\vec{u} + \vec{n}\cdot\vec{U}\right] \tag{6.4}$$

where $D = \dfrac{D_1 D_2 (z_1 - z_2)}{z_1 D_1 - z_2 D_2}$, $P = \dfrac{z_1 (D_1 - D_2)}{z_1 D_1 - z_2 D_2}$ and the current density and the velocity of the surface are related by

$$\vec{n}\cdot\vec{i} = -z_1 F c_M \left[\vec{n}\cdot\vec{u} + \vec{n}\cdot\vec{U}\right] \tag{6.5}$$

where $\vec{U} = U\vec{j}$.

Moreover, at the anode and cathode surfaces c and ϕ must be related by the reaction equilibrium condition which can be written as

$$\frac{c^A}{\overline{c}} = e^{\frac{z_1 F}{RT}\left[\Delta\phi^A - \Delta\phi_{EQ} - \frac{\gamma}{z_1 F c_M} 2H^A\right]} \tag{6.6}$$

at the anode, while at the cathode it is given by

$$\frac{c^C}{\overline{c}} = e^{\frac{z_1 F}{RT}\left[\Delta\phi^C - \Delta\phi_{EQ} - \frac{\gamma}{z_1 F c_M} 2H^C\right]} \tag{6.7}$$

where $\Delta\phi^A = V^A - \phi^A$, $\Delta\phi^C = V^C - \phi^C$, and the shape of the surfaces, denoted by Y^A and Y^C, appears inside the local speed (i.e., $\vec{n}\cdot\vec{u}$) and in the curvature terms, namely, $2H^A$ and $2H^C$ as we know from our previous work.

The last two equations express the facts that both the volume of the electrolytic solution and its average ion concentration remains constant in time as required by local electrical neutrality. A word argument for this was given in chapter 2 when local electrical neutrality was introduced. Here we will turn these ideas into equations.

These equations will be written for a two-dimensional cell with the third dimension being into the plane of the paper. The two conditions, constant volume and constant average ion concentration require that

$$\int_0^{W_0}\int_{Y^A}^{Y^C} dydx = V(\text{volume}) = \text{constant} \tag{6.8}$$

and

$$\int_0^{W_0}\int_{Y^A}^{Y^C} c\, dydx = \overline{c}\ V = \text{constant} \tag{6.9}$$

These are the main nonlinear equations that need to be solved. But before solving these equations, we will scale the problem to reduce the number of variables and make the equations more convenient for further work.

6.2 The Scaled Nonlinear Equations

In order to scale the nonlinear equations, the following scaled variables will be introduced

$$c^* = \frac{c}{\bar{c}},\quad t^* = \frac{D}{L_0^2}t,\quad \phi^* = \frac{z_1 F}{RT}\phi,\quad U^* = \frac{L_0}{D}U,\quad u^* = \frac{L_0}{D}u,\quad \nabla^* = \nabla L_0,\quad \nabla^{*2} = \nabla^2 L_0^2,$$

$$2H^* = 2H\,L_0,\quad \gamma^* = \frac{\gamma}{L_0 c_M RT},\quad x^* = \frac{x}{L_0},\quad y^* = \frac{y}{L_0},\quad Y^* = \frac{Y}{L_0},\quad W_0^* = \frac{W_0}{L_0},\quad i^* = \frac{L_0}{Dz_1 F c_M} i$$

where the stars denote dimensionless variables or parameters.

In addition we need the expression for the limiting current that was obtained previously, namely,

$$U_{\lim} = \frac{2}{L_0}\frac{z_1 D_1 - z_2 D_2}{z_1 z_2 D_2} D \frac{\bar{c}}{c_M}$$

This expression was obtained from the solution to the base problem and we introduce it here and use it in writing the scaled equations. The scaled version of $U_{\lim}$ will be

$$U_{\lim}^* = 2\frac{\bar{c}}{c_M}\frac{z_1 D_1 - z_2 D_2}{z_1 z_2 D_2} \tag{6.10}$$

The reason we introduce the scaled limiting current is that it will appear in the boundary conditions and it will simplify the form of these equations when it is used.

Using the scaling introduced above, the domain equations will be written as

$$\frac{\partial c^*}{\partial t^*} = \nabla^{*2} c^* \tag{6.11}$$

and

$$P\,\nabla^{*2}c^{*}+\nabla^{*2}\phi^{*}=0 \tag{6.12}$$

The scaled equations that must hold at the two electrode surfaces, i.e., the result of scaling equations (6.3) (6.4) and (6.5), are

$$\vec{n}\cdot\nabla^{*}c^{*}=-\frac{2}{U^{*}_{\lim}}\left[\vec{n}\cdot\vec{u}^{*}+\vec{n}\cdot\vec{U}^{*}\right] \tag{6.13}$$

$$\vec{n}\cdot\nabla^{*}\phi^{*}=\frac{-2\,Z}{U^{*}_{\lim}}\left[\vec{n}\cdot\vec{u}^{*}+\vec{n}\cdot\vec{U}^{*}\right] \tag{6.14}$$

and

$$\vec{n}\cdot\vec{i}^{\,*}=-\left[\vec{n}\cdot\vec{u}^{*}+\vec{n}\cdot\vec{U}^{*}\right] \tag{6.15}$$

where $Z=\frac{z_1}{|z_2|}$ and Z is a positive number.

The scaled reaction equilibrium conditions at the anode and at the cathode are

$$c^{*A}=e^{\Delta\phi^{*A}-\Delta\phi^{*}_{EQ}-\gamma^{*}2H^{*A}} \tag{6.16}$$

and

$$c^{*C}=e^{\Delta\phi^{*C}-\Delta\phi^{*}_{EQ}-\gamma^{*}2H^{*C}} \tag{6.17}$$

while the scaled integral conditions are

$$\int_{0}^{W_0^{*}}\int_{Y^{A^{*}}}^{Y^{C^{*}}} dy^{*}dx^{*}=\text{ constant} \tag{6.18}$$

and

$$\int_{0}^{W_0^{*}}\int_{Y^{A^{*}}}^{Y^{C^{*}}} c^{*}\,dy^{*}dx^{*}=\text{constant} \tag{6.19}$$

We mentioned earlier that we will be working in this chapter with a cell having side walls. This implies boundaries in the transverse direction, and homogeneous Neumann conditions to be valid on the sidewalls such as:

$\frac{dc^*}{dx^*} = 0$ at $x^* = 0,\ W_0^*$, which implies that no solute crosses the walls.

$\frac{d\phi^*}{dx^*} = 0$ at $x^* = 0,\ W_0^*$, which implies that the walls are made of insulator material.

$\frac{dY^*}{dx^*} = 0$ at $x^* = 0,\ W_0^*$, which implies that the metal solution interface contacts the sidewalls in right angels.

Now having the scaled nonlinear equations, we are ready to start the weakly nonlinear calculations but we do not want to carry along these star superscripts, so they will be dropped henceforth.

6.3 The Weakly Nonlinear Calculations

Now it is our job to translate what is written at the beginning of this chapter about running an electrodeposition experiment into equations that can be used to investigate what might happen as $\left(V^A - V^C\right)$ passes $\left(V^A - V^C\right)_{critical}$. Let us say, in our experiment, that we have just increased the voltage drop an amount $\frac{1}{2}\varepsilon^2$ above the critical voltage drop that is to say

$$\left(V^A - V^C\right) = \left(V^A - V^C\right)_c + \frac{1}{2}\varepsilon^2 \quad \text{or} \quad \left(V^A - V^C\right) - \left(V^A - V^C\right)_c = \frac{1}{2}\varepsilon^2 \qquad (6.20)$$

and once V^A is set as a reference (i.e., taking it to be constant that is not going to be perturbed) this equation will be written as

$$-V^C + V_c^C = \frac{1}{2}\varepsilon^2 \quad \text{or} \quad V^C = V_c^C - \frac{1}{2}\varepsilon^2 \tag{6.21}$$

where the subscript c stands for the critical value and $\frac{1}{2}\varepsilon^2$ denotes the increment in the voltage drop.

Then to account for the change in the velocity of the surface, or the current, once the critical point is passed, the following equation can be written

$$U = U_0 + \frac{1}{2}\varepsilon^2\, U_2 \tag{6.22}$$

The calculations in this chapter will be carried to second order; consequently, we are going to stop at U_2.

The expansions of c and ∇c will follow the method given in Appendix B. They are

$$c = c_0 + \varepsilon\left(c_1 + Y_1\frac{\partial c_0}{\partial y_0}\right) + \frac{1}{2}\varepsilon^2\left(c_2 + 2Y_1\frac{\partial c_1}{\partial y_0} + Y_1^2\frac{\partial^2 c_0}{\partial y_0^2} + Y_2\frac{\partial c_0}{\partial y_0}\right) \tag{6.23}$$

and

$$\nabla c = \nabla_0 c_0 + \varepsilon\left(\nabla_0 c_1 + Y_1\frac{\partial \nabla_0 c_0}{\partial y_0}\right) + \frac{1}{2}\varepsilon^2\left(\nabla_0 c_2 + 2Y_1\frac{\partial \nabla_0 c_1}{\partial y_0} + Y_1^2\frac{\partial^2 \nabla_0 c_0}{\partial y_0^2} + Y_2\frac{\partial \nabla_0 c_0}{\partial y_0}\right) \tag{6.24}$$

and likewise for the expansions of ϕ and $\nabla\phi$.

In addition to these equations, the expansions of the surface, the surface normal and the curvature of the surface at the anode are given by

$$Y^A = Y_0^A + \varepsilon Y_1^A + \frac{1}{2}\varepsilon^2 Y_2^A \tag{6.25}$$

$$\vec{n}^A \text{ (without denominator)} = \left[\vec{j} - \frac{\partial}{\partial x_0}\left(Y_0^A + \varepsilon Y_1^A + \frac{1}{2}\varepsilon^2 Y_2^A\right)\vec{i}\right] \tag{6.26}$$

and

$$2H^A = \frac{\partial^2 Y_0^A}{\partial x_0^2} + \varepsilon \frac{\partial^2 Y_1^A}{\partial x_0^2} + \frac{1}{2}\varepsilon^2 \frac{\partial^2 Y_2^A}{\partial x_0^2} \tag{6.27}$$

whereas at the cathode they are

$$Y^A = Y_0^C + \varepsilon Y_1^C + \frac{1}{2}\varepsilon^2 Y_2^C \tag{6.28}$$

$$\vec{n}^C \text{ (without denominator)} = \left[-\vec{j} + \frac{\partial}{\partial x_0}\left(Y_0^C + \varepsilon Y_1^C + \frac{1}{2}\varepsilon^2 Y_2^C \right)\vec{i} \right] \tag{6.29}$$

and

$$2H^C = -\frac{\partial^2 Y_0^C}{\partial x_0^2} - \varepsilon \frac{\partial^2 Y_1^C}{\partial x_0^2} - \frac{1}{2}\varepsilon^2 \frac{\partial^2 Y_2^C}{\partial x_0^2} \tag{6.30}$$

where the explanation on how to arrive at equations (6.27) and (6.30) is given in Appendix E. Finally the expansions of the integral conditions are

$$\int_0^{W_0}\int_{Y^A}^{Y^C} dy dx = \int_0^{W_0}\int_0^1 dy_0 dx_0 + \varepsilon \int_0^{W_0}\int_0^1 \frac{dy_1}{dy_0} dy_0 dx_0 + \frac{1}{2}\varepsilon^2 \int_0^{W_0}\int_0^1 \frac{dy_2}{dy_0} dy_0 dx_0 = \text{constant} \tag{6.31}$$

and

$$\begin{aligned} &\int_0^{W_0}\int_{Y^A}^{Y^C} c\, dy dx = \int_0^{W_0}\int_0^1 c_0\, dy_0 dx_0 + \varepsilon \int_0^{W_0}\int_0^1 \left[c_1 + \frac{d}{dy_0}(c_0 y_1) \right] dy_0 dx_0 \\ &+ \frac{1}{2}\varepsilon^2 \int_0^{W_0}\int_0^1 \left[c_2 + \frac{d}{dy_0}(c_0 y_2) + \frac{d}{dy_0}(c_1 y_1) + \frac{d}{dy_0}\left(\frac{dc_0}{dy_0} y_1^2 \right) \right] dy_0 dx_0 = \text{constant} \end{aligned} \tag{6.32}$$

where Appendix F explains how to arrive at these equations starting from equations (6.18) and (6.19). The next step will be to get a base solution for this set of nonlinear equations.

6.3.1 The Base Solution

Finding a one dimensional steady base solution in the new scaling can be obtained by substituting equations (6.23)-(6.32) into the nonlinear equations and it is done just as it was earlier when the base solutions were found in chapters 3, 4 and 5. According to this scaling the spacing between the electrodes will run from $y = 0$ to $y = 1$. The two equations on the domain at steady state assuming variation in the y direction are

$$\frac{d^2 c_0}{dy_0^2} = 0 \tag{6.33}$$

and

$$\frac{d^2 \phi_0}{dy_0^2} = 0 \tag{6.34}$$

These equations will be solved subject to equations (6.13) and (6.14) which are valid at both electrodes, namely,

$$\frac{dc_0}{dy_0} = -2\frac{U_0}{U_{\text{lim}}} \quad \text{at } y = 0 \quad \text{and at } y = 1 \tag{6.35}$$

and

$$\frac{d\phi_0}{dy_0} = -2\,Z\,\frac{U_0}{U_{\text{lim}}} \quad \text{at } y = 0 \quad \text{and at } y = 1 \tag{6.36}$$

The relation between the current density and the velocity of the surface based on equation (6.15) will be

$$i = -U_0 \tag{6.37}$$

which is a direct relation showing that the variable U_0 is just a different way of talking about the electrical current density in the cell under steady, one-dimensional conditions.

Now the base concentration profile across the cell can be found to be

$$c_0 = (-2y_0 + 1)\frac{U_0}{U_{\lim}} + 1 \tag{6.38}$$

whence at the anode, where $y = 0$ and the concentration is denoted c_0^A, we have

$$c_0^A = 1 + \frac{U_0}{U_{\lim}} \tag{6.39}$$

while at the cathode, where $y = 1$ and the concentration is denoted c_0^C, we have

$$c_0^C = 1 - \frac{U_0}{U_{\lim}} \tag{6.40}$$

The variation of the electrical potential across the cell is obtained by integrating equation (6.36) and when the result is evaluated at the anode, the constant of integration will turn to be ϕ_0^A, hence we have

$$\phi_0 = -2\,Z\,\frac{U_0}{U_{\lim}} y_0 + \phi_0^A \tag{6.41}$$

where ϕ_0^A cannot be found at this point, but the difference $\phi_0^C - \phi_0^A$ is known and it is

$$\phi_0^C - \phi_0^A = -2\,Z\,\frac{U_0}{U_{\lim}} \tag{6.42}$$

Now U_0 is not known, unless it is taken to be the control variable. But taking $V^A - V^C$ to be the control variable, we can determine U_0, the velocity of the two surfaces in the laboratory frame, and all the remaining base variables by using the chemical reaction equilibrium conditions at the two planar surfaces, viz.,

$$c_0^A = e^{\Delta\phi_0^A - \Delta\phi_{RQ}} \tag{6.43}$$

at the anode and

$$c_0^C = e^{\Delta\phi_0^C - \Delta\phi_{RQ}} \tag{6.44}$$

at the cathode. Now using these equations in addition to equation (6.42), we arrive at the following equation

$$V^A - V^C = \ln\frac{c_0^A}{c_0^C} + 2Z\frac{U_0}{U_{\lim}} \tag{6.45}$$

then substituting for c_0^A and c_0^C from equations (6.39) and (6.40) the following formula for U_0 as a function of $V^A - V^C$ can be obtained

$$V^A - V^C = \ln\frac{1+\dfrac{U_0}{U_{\lim}}}{1-\dfrac{U_0}{U_{\lim}}} + 2Z\frac{U_0}{U_{\lim}} \tag{6.46}$$

Having a steady one-dimensional base solution, the next step is to proceed to find the steady first order solution.

6.3.2 The Steady First Order Solution

Our interest is now very specific. We want to fix all the input variables and then carry out a first order calculation in order to identify critical conditions. This calculation needs to be done only at steady state and hence no terms arise from $\frac{\partial c}{\partial t}$ and $\vec{n}\cdot\vec{u}$ in our eigenvalue problem.

Now let us start the calculations of the first order problem. First, the equations on the reference domain for c_1 and ϕ_1 are

$$\nabla_0^2 c_1 = 0 \tag{6.47}$$

and

$$\nabla_0^2 \phi_1 = 0 \tag{6.48}$$

Now let us turn to equation (6.13) and work at the anode. First to make our equations better looking we will redefine $\frac{\vec{U}}{U_{\lim}}$ by just $\vec{U}$ or in scalar form $U = \frac{U}{U_{\lim}}$ where $0 < U < 1$. We have

$$\vec{n}^A \cdot \nabla c = -2\, \vec{n}^A \cdot \vec{U} \tag{6.49}$$

and when the first order expansion is substituted in this equation, we obtain

$$\begin{aligned} &\left(\vec{j} - \left(\frac{\partial Y_0^A}{\partial x_0} + \varepsilon \frac{\partial Y_1^A}{\partial x_0}\right)\vec{i}\right) \cdot \left\{\frac{\partial c_0}{\partial x_0}\vec{i} + \frac{\partial c_0}{\partial y_0}\vec{j} + \varepsilon\left[\frac{\partial c_1}{\partial x_0}\vec{i} + \frac{\partial c_1}{\partial y_0}\vec{j} + Y_1^A \frac{\partial}{\partial y_0}\left(\frac{\partial c_0}{\partial x_0}\vec{i} + \frac{\partial c_0}{\partial y_0}\vec{j}\right)\right]\right\} \\ &= -2\left(\vec{j} - \left(\frac{\partial Y_0}{\partial x_0} + \varepsilon \frac{\partial Y_1^A}{\partial x_0}\right)\vec{i}\right) \cdot (U_0)\vec{j} \end{aligned} \tag{6.50}$$

which simplifies due to

$\frac{\partial Y_0^A}{\partial x_0} = 0$ since Y_0^A is a constant, and is, in fact, zero.

$\frac{\partial c_0}{\partial x_0} = 0$ since c_0 is not a function of x_0.

and

$\frac{\partial^2 c_0}{\partial y_0^2} = 0$ due to the base domain equation.

to

$$\frac{dc_0}{dy_0} + \varepsilon \frac{dc_1}{dy_0} = -2\, U_0 \tag{6.51}$$

But from the base solution we have $\frac{dc_0}{dy_0} = -2\, U_0$ hence at the anode we obtain

$$\frac{dc_1}{dy_0} = 0 \text{ at } y_0 = 0, \text{ or } \frac{dc_1^A}{dy_0} = 0 \tag{6.52}$$

By following the same steps when equation (6.13) is perturbed at the cathode we obtain

$$\frac{dc_1}{dy_0} = 0 \text{ at } y_0 = 1, \text{ or } \frac{dc_1^C}{dy_0} = 0 \tag{6.53}$$

Now working on equation (6.14) and following a similar approach we get the following two equations, first at the anode

$$\frac{d\phi_1}{dy_0} = 0 \text{ at } y_0 = 0, \text{ or } \frac{d\phi_1^A}{dy_0} = 0 \tag{6.54}$$

and then at the cathode

$$\frac{d\phi_1}{dy_0} = 0 \text{ at } y_0 = 1, \text{ or } \frac{d\phi_1^C}{dy_0} = 0 \tag{6.55}$$

Equations (6.52) and (6.53) imply that c_1= constant . Likewise, equations (6.54) and (6.55) imply that ϕ_1= constant and hence $c_1^A = c_1^C = c_1$ and $\phi_1^A = \phi_1^C = \phi_1$.

Let us now turn to the equilibrium condition at the anode and at the cathode. First, at the anode, where V^A is taken to be constant, and $\varepsilon\ 2H_1^A = \varepsilon \frac{d^2 Y_1^A}{dx_0^2}$, the nonlinear equation to first order will be

$$c_0^A + \varepsilon\left(c_1 + Y_1^A \frac{dc_0}{dy_0}\right) = e^{-\phi_0^A - \varepsilon\phi_1 - \varepsilon Y_1^A \frac{d\phi_0^A}{dy_0} - \Delta\phi_{EQ} - \varepsilon\gamma \frac{d^2 Y_1^A}{dx_0^2}} \tag{6.56}$$

which can be written

$$c_0^A + \varepsilon\left(c_1 + Y_1^A \frac{dc_0}{dy_0}\right) = e^{\Delta\phi_0^A - \Delta\phi_{EQ}}\ e^{\varepsilon\left(-\phi_1 - Y_1^A \frac{d\phi_0^A}{dy_0} - \gamma \frac{d^2 Y_1^A}{dx_0^2}\right)} \tag{6.57}$$

and then recalling that $e^{\Delta\phi_0^A - \Delta\phi_{eq}} = c_0^A$ and by setting $\varepsilon\left(-\phi_1^A - Y_1^A\frac{d\phi_0}{dy_0} - \gamma\frac{d^2Y_1^A}{dx_0^2}\right) = x$ and using the Taylor series expansion of $e^x = 1 + x$, the perturbation equation at the anode will be obtained. It is

$$\frac{c_1}{c_0^A} + \frac{dc_0/dy_0}{c_0^A}Y_1^A = -\phi_1 - \frac{d\phi_0}{dy_0}Y_1^A - \gamma\frac{d^2Y_1^A}{dx_0^2} \tag{6.58}$$

and it can be written

$$\frac{d^2Y_1^A}{dx_0^2} + \frac{1}{\gamma}\left(\frac{dc_0/dy_0}{c_0^A} + \frac{d\phi_0}{dy_0}\right)Y_1^A = -\frac{1}{\gamma}\left(\phi_1 + \frac{c_1}{c_0^A}\right) \tag{6.59}$$

where the right-hand side is a constant.

Now we turn to the reaction equilibrium condition at the cathode in order to find Y_1^C. First note that the expansion for the curvature at the cathode will be $\varepsilon\ 2H_1^C = -\varepsilon\frac{d^2Y_1^C}{dx_0^2}$. Then substituting this into equation (6.17) and repeating the steps used at the anode, we can get the following differential equation for Y_1^C

$$\frac{d^2Y_1^C}{dx_0^2} - \frac{1}{\gamma}\left(\frac{dc_0/dy_0}{c_0^C} + \frac{d\phi_0}{dy_0}\right)Y_1^C = -\frac{1}{\gamma}\left(\phi_1 + \frac{c_1}{c_0^C}\right) \tag{6.60}$$

By looking at equations (6.59) and (6.60) it is clear that these two equations have four unknowns namely Y_1^A, Y_1^C, c_1 and ϕ_1. So we still need two more equations to be able to solve for all the unknowns. These two equations are the integral conditions concerned with the constant volume and the constant average ionic concentration which to first order are

$$\int_0^{W_0} Y_1^C dx_0 - \int_0^{W_0} Y_1^A dx_0 = 0 \tag{6.61}$$

and

$$\int_0^{W_0} c_1 dx_0 + \int_0^{W_0} c_0^C Y_1^C dx_0 - \int_0^{W_0} c_0^A Y_1^A dx_0 = 0 \tag{6.62}$$

where the details on how we get these equations are given in Appendix F.

Now at this stage we have all the equations required to solve the eigenvalue problem at the first order for Y_1^A, Y_1^C, c_1 and ϕ_1. It is obvious that this is a completely homogeneous eigenvalue problem that has the solution $Y_1^A = Y_1^C = c_1 = \phi_1 = 0$. But this is the trivial solution and we want to see if there is another solution such that this is not true. To do this let us suggest a solution of the following form

$$c_1 = \hat{c}_1(y_0)\cos kx_0 \tag{6.63}$$

$$\phi_1 = \hat{\phi}_1(y_0)\cos kx_0 \tag{6.64}$$

$$Y_1^A = \hat{Y}_1^A \cos kx_0 \tag{6.65}$$

and

$$Y_1^C = \hat{Y}_1^C \cos kx_0 \tag{6.66}$$

Now in order to solve for Y_1^A, Y_1^C, c_1 and ϕ_1 we have to consider two cases, the first corresponds to $k = 0$ and the second corresponds to the case where k is not zero. Let us first see if $k = 0$ is a valid choice. If k was set to zero then equations (6.63)-(6.66) will show that Y_1^A, Y_1^C, c_1 and ϕ_1 are all constants and equations (6.59), (6.60), (6.61) and (6.62) will turn into

$$\left(\frac{dc_0/dy_0}{c_0^A}+\frac{d\phi_0}{dy_0}\right)Y_1^A=-\left(\phi_1+\frac{c_1}{c_0^A}\right) \tag{6.67}$$

$$\left(\frac{dc_0/dy_0}{c_0^C}+\frac{d\phi_0}{dy_0}\right)Y_1^C=\left(\phi_1+\frac{c_1}{c_0^C}\right) \tag{6.68}$$

$$Y_1^A=Y_1^C \tag{6.69}$$

and

$$c_1+c_0^CY_1^C-c_0^AY_1^A=0 \tag{6.70}$$

Let us now use equation (6.69) and call $Y_1^A=Y_1^C=Y_1$ so we will have three unknowns, namely, Y_1, c_1 and ϕ_1 that we want to find. First, add equations (6.67) to equation (6.68) to get

$$\left[\frac{dc_0}{dy_0}\left(\frac{c_0^A+c_0^C}{c_0^Ac_0^C}\right)+2\frac{d\phi_0}{dy_0}\right]Y_1=\left(\frac{c_0^A-c_0^C}{c_0^Ac_0^C}\right)c_1 \tag{6.71}$$

then equation (6.70) can be rearranged such as

$$\left(c_0^A-c_0^C\right)Y_1=c_1 \tag{6.72}$$

It is known from the base solution that $\frac{dc_0}{dy_0}$ and $\frac{d\phi_0}{dy_0}$ are negative quantities while c_0^A and c_0^C are both positive with $c_0^A>c_0^C$. Now equation (6.71) shows that Y_1 and c_1 have different signs, while equation (6.72) shows the opposite. So the only way that these two constants have similar and different signs is that they are both equal to zero which also lead to ϕ_1 is zero as well. This is a solution that we already know so this rule out the $k=0$ possibility.

So knowing that k cannot be zero, the solution to the c and ϕ problems will proceed as was in chapter 3 and will lead to the result $c_1 = \phi_1 = 0$ as before in chapter 3. So finding both c_1 and ϕ_1 to be zero, equation (6.59) for Y_1^A will be

$$\frac{d^2Y_1^A}{dx_0^2} + \frac{1}{\gamma}\left(\frac{dc_0/dy_0}{c_0^A} + \frac{d\phi_0}{dy_0}\right)Y_1^A = 0 \tag{6.73}$$

then substituting $Y_1^A = \hat{Y}_1^A \cos kx_0$ in this equation will lead to

$$\left[-k^2 + \frac{1}{\gamma}\left(\frac{dc_0/dy_0}{c_0^A} + \frac{d\phi_0}{dy_0}\right)\right]Y_1^A = 0 \tag{6.74}$$

which implies that $Y_1^A = 0$ since the term multiplying it is negative that cannot be zero. This leaves us with only Y_1^C to be determined. Going to equation (6.60) and putting $c_1 = \phi_1 = 0$ will result in getting

$$\frac{d^2Y_1^C}{dx_0^2} - \frac{1}{\gamma}\left(\frac{dc_0/dy_0}{c_0^C} + \frac{d\phi_0}{dy_0}\right)Y_1^C = 0 \tag{6.75}$$

and then after the substitution for Y_1^C by $\hat{Y}_1^C \cos kx_0$ one will get

$$\left[-k^2 - \frac{1}{\gamma}\left(\frac{dc_0/dy_0}{c_0^C} + \frac{d\phi_0}{dy_0}\right)\right]Y_1^C = 0 \tag{6.76}$$

which has a solution other than $Y_1^C = 0$ if $k^2 = -\frac{1}{\gamma}\left(\frac{dc_0/dy_0}{c_0^C} + \frac{d\phi_0}{dy_0}\right)$ which is the critical wave number. Then equation (6.75) can be written as

$$\frac{d^2Y_1^C}{dx_0^2} + k^2Y_1^C = 0 \tag{6.77}$$

The solution to this equation is

$$Y_1^C = C_1 \sin kx_0 + D_1 \cos kx_0 \tag{6.78}$$

where both C_1 and D_1 are constants of integration that need to be determined and they are determined so as to satisfy the end conditions

$$\frac{dY_1^C}{dx_0} = 0 \quad \text{at } x_0 = 0 \tag{6.79}$$

and

$$\frac{dY_1^C}{dx_0} = 0 \quad \text{at } x_0 = W_0 \tag{6.80}$$

And to use these conditions, notice

$$\frac{dY_1^C}{dx_0} = C_1 k \cos kx_0 - D_1 k \sin kx_0 \tag{6.81}$$

Equation (6.79) implies $C_1 = 0$ while equation (6.80) requires

$$-D_1 k \sin kW_0 = 0 \tag{6.82}$$

where neither k nor W_0 can be zero nor can D_1 be zero because C_1 is already known to be zero hence we must have $kW_0 = n\pi$ or $k = \frac{n\pi}{W_0}$ where $n = 1, 2, 3, \ldots$ and hence the smallest and most dangerous allowable wave number is π/W_0.

Now setting

$$k^2_{critical} = -\frac{1}{\gamma}\left(\frac{dc_0/dy_0}{c_0^C} + \frac{d\phi_0}{dy_0}\right) = \left(\frac{\pi}{W_0}\right)^2$$

will result in finding the critical velocity of the surface, which we will call U_c that replaces U_0 henceforth and from which the critical voltage drop can be calculated.

What we have learned so far from the problem is that c_0 and ϕ_0 are known and depend on y_0 with $Y_0^A = 0$ and $Y_0^C = 1$. Moreover, c_1, ϕ_1 and Y_1^A are all zero while

$Y_1^C = D_1 \cos kx_0$. In addition we learned what the critical voltage drop and the velocity of the surface are and our job is to go to second order and see what we can learn about D_1.

6.3.3 The Second Order Problem

To learn about the response of the current as we increase the voltage drop beyond its critical value, we must go to second order, or perhaps even higher orders and see what we can learn about D_1. If we find that the current change differs from the base prediction on increasing the voltage drop we can take this as an experimental indication of a transition from a planar to a non-planar front.

At second order we have two unknowns which are D_1 and U_2. Finding these two unknowns will be our objective. We may or we may not find them both. In fact, it turns out that we cannot find them both but we will be able to relate them.

Now let us start the calculations of the second order problem. First, the equations on the reference domain for c_2 and ϕ_2 are

$$\nabla_0^2 c_2 = 0 \tag{6.83}$$

and

$$\nabla_0^2 \phi_2 = 0 \tag{6.84}$$

and the boundary conditions at the unperturbed sidewalls are

$$\frac{\partial c_2}{\partial x_0} = 0 \text{ at } x_0 = 0 \text{ and at } x_0 = W_0 \tag{6.85}$$

and

$$\frac{\partial \phi_2}{\partial x_0} = 0 \text{ at } x_0 = 0 \text{ and at } x_0 = W_0 \tag{6.86}$$

Now let us go to the electrode surfaces and find the conditions there to second order. Starting with equation (6.49) at the anode, we have

$$\left[\vec{j}\frac{\partial}{\partial x_0}\left(Y_0^A+\varepsilon Y_1^A+\frac{1}{2}\varepsilon^2 Y_2^A\right)\vec{i}\right]\cdot\left[\left(\nabla_0 c_0+\varepsilon\left(\nabla_0 c_1+Y_1\frac{\partial \nabla_0 c_0}{\partial y_0}\right)+\frac{1}{2}\varepsilon^2\left(\nabla_0 c_2+2Y_1^A\frac{\partial \nabla_0 c_1}{\partial y_0}+\left(Y_1^A\right)^2\frac{\partial^2 \nabla_0 c_0}{\partial y_0^2}+Y_2^A\frac{\partial \nabla_0 c_0}{\partial y_0}\right)\right)\right]=$$

$$-2\left[\vec{j}\frac{\partial}{\partial x_0}\left(Y_0^A+\varepsilon Y_1^A+\frac{1}{2}\varepsilon^2 Y_2^A\right)\vec{i}\right]\cdot\left[U_c+\frac{1}{2}\varepsilon^2 U_2\right]\vec{j} \tag{6.87}$$

whence equating the second order terms on the two sides of equation (6.87) and noticing that the terms in $\vec{i}$ play no rule we find

$$\frac{\partial c_2}{\partial y_0}=-2\ U_2 \tag{6.88}$$

which holds at $y_0=0$.

It is noteworthy that this problem simplified greatly because both c_1 and ϕ_1 turned to be zero and c_0 was just a function of y_0 If this was not the case and c_1 was a function of x_0 then we will have terms from $\vec{i}\cdot\nabla_0 c_1$, as shown in equation (6.87), and the problem will become more complicated.

Now considering the cathode, we also find, even though Y_1^C is not zero,

$$\frac{\partial c_2}{\partial y_0}=-2\ U_2 \text{ at } y_0=1 \tag{6.89}$$

Following the same procedure to find boundary conditions corresponding to ϕ_2, we get

$$\frac{\partial \phi_2}{\partial y_0}=-2\ Z\ U_2 \text{ at } y_0=0 \text{ and } y_0=1 \tag{6.90}$$

The solution to the c_2 problem can be found by using equations (6.83), (6.85), (6.88) and (6.89). It is

$$c_2 = -2\ U_2\ y_0 + \text{constant} \tag{6.91}$$

whence

$$c_2^A = c_2\left(y_0 = 0\right) = \text{constant} \tag{6.92}$$

and

$$c_2^C = c_2\left(y_0 = 1\right) = -2\ U_2 + c_2^A \tag{6.93}$$

The solution to the c_2 problem introduces one constant which we call c_2^A. Now turning to the ϕ_2 problem and using equations (6.84), (6.86) and (6.90), one can obtain the solution as

$$\phi_2 = -2\ Z\ U_2\ y_0 + \text{constant} \tag{6.94}$$

whence at the anode

$$\phi_2\left(y_0 = 0\right) = \phi_2^A = \text{constant} \tag{6.95}$$

which at the cathode

$$\phi_2\left(y_0 = 1\right) = \phi_2^C = -\ 2\ Z\ U_2 + \phi_2^A \tag{6.96}$$

At this point we have c_2 and ϕ_2 up to constants denoted c_2^A and ϕ_2^A. Let us turn to the reaction equilibrium condition at the anode and at the cathode and see what we can learn about Y_2^A and Y_2^C.

Now the expansion of the surface curvature to second order at the anode as given before is

$$2H^A = \varepsilon \frac{d^2Y_1}{dx_0^2} + \frac{1}{2}\varepsilon^2 \frac{d^2Y_2}{dx_0^2} \tag{6.97}$$

while at the cathode it is

$$2H^C = -\varepsilon \frac{d^2 Y_1^C}{dx_0^2} - \frac{1}{2}\varepsilon^2 \frac{d^2 Y_2^C}{dx_0^2} \tag{6.98}$$

To get the second order equation of Y_2^A let us turn to the CRE equation at the anode. All the variables that will appear in the coming equation are anode variables where the superscript $A's$ were dropped. The superscript $A's$ will appear in the final equation after we explain how we are going to simplify the equation. Now when V^A is set to a constant and after substituting the expansions of c, ϕ and $2H^A$ into equation (6.16), we find

$$c_0 + \varepsilon\left(c_1 + Y_1 \frac{dc_0}{dy_0}\right) + \frac{1}{2}\varepsilon^2\left(c_2 + 2Y_1 \frac{dc_1}{dy_0} + (Y_1)^2 \frac{d^2 c_0}{dy_0^2} + Y_2 \frac{dc_0}{dy_0}\right) = e^{-\left[\phi_0 + \varepsilon\left(\phi_1 + Y_1 \frac{d\phi_0}{dy_0}\right) + \frac{1}{2}\varepsilon^2\left(\phi_2 + 2Y_1 \frac{d\phi_1}{dy_0} + (Y_1)^2 \frac{d^2\phi_0}{dy_0^2} + Y_2 \frac{d\phi_0}{dy_0}\right)\right] - \Delta\phi_{EQ} - \gamma\left[2H_0 + \varepsilon \frac{d^2 Y_1}{dx_0^2} + \frac{1}{2}\varepsilon^2 \frac{d^2 Y_2}{dx_0^2}\right]} \tag{6.99}$$

and recognizing that $c_1 = \phi_1 = Y_1^A = 0$, then the equation to second order in ε is simply

$$c_0 + \frac{1}{2}\varepsilon^2\left(c_2 + Y_2 \frac{dc_0}{dy_0}\right) = c_0\, e^{-\frac{1}{2}\varepsilon^2\left(\phi_2 + Y_2 \frac{d\phi_0}{dy_0} + \gamma \frac{d^2 Y_2}{dx_0^2}\right)} \tag{6.100}$$

Now considering equation (6.100) to be solved for Y_2^A, let us set

$\frac{1}{2}\varepsilon^2\left(\phi_2 + Y_2 \frac{d\phi_0}{dy_0} + \gamma \frac{d^2 Y_2}{dx_0^2}\right) = x$ so $e^{-\frac{1}{2}\varepsilon^2\left(\phi_2 + Y_2 \frac{d\phi_0}{dy_0} + \gamma \frac{d^2 Y_2}{dx_0^2}\right)}$ can be written as e^{-x} which can be expanded to second order using the Taylor series expansion as $1 - x + \frac{1}{2}x^2$ and upon doing that and inserting the A superscript, equation (6.100), will turn into

$$c_2^A + Y_2^A \frac{dc_0}{dy_0} = -c_0^A\left(\phi_2^A + Y_2^A \frac{d\phi_0}{dy_0} + \gamma \frac{d^2 Y_2^A}{dx_0^2}\right) \tag{6.101}$$

which can be written

$$\frac{d^2Y_2^A}{dx_0^2}+\frac{1}{\gamma}\left(\frac{d\phi_0}{dy_0}+\frac{dc_0/dy_0}{c_0^A}\right)Y_2^A+\frac{1}{\gamma}\left(\frac{c_2^A}{c_0^A}+\phi_2^A\right)=0 \tag{6.102}$$

or setting $\frac{1}{\gamma}\left(\frac{d\phi_0}{dy_0}+\frac{dc_0/dy_0}{c_0^A}\right)=-K_A^2$,where K_A^2 is positive, will lead to

$$\frac{d^2Y_2^A}{dx_0^2}-K_A^2Y_2^A=-\frac{1}{\gamma}\left(\phi_2^A+\frac{c_2^A}{c_0^A}\right) \tag{6.103}$$

This equation must be solved, while satisfying the sidewall conditions

$$\frac{dY_2^A}{dx_0}=0 \quad \text{at } x_0=0 \tag{6.104}$$

and

$$\frac{dY_2^A}{dx_0}=0 \quad \text{at } x_0=W_0 \tag{6.105}$$

And in view of the fact that c_2^A and ϕ_2^A do not depend on x_0, the solution is

$$Y_2^A=\frac{1}{\gamma K_A^2}\left(\phi_2^A+\frac{c_2^A}{c_0^A}\right) \tag{6.106}$$

where c_2^A and ϕ_2^A remain to be determined.

Now turn to the cathode. The equilibrium condition at the cathode is

$$c^C=e^{V^C-\phi^C-\Delta\phi_{EQ}-\gamma 2H^C}$$

where $V^C=V_c^C-\frac{1}{2}\varepsilon^2$. This makes the cathode a little different from the anode since

$V_c^C-\frac{1}{2}\varepsilon^2$ will appear now in the exponential term prior to the ϕ expansion. So the

equilibrium equation can be written in the following form

$$c_0+\varepsilon\left(c_1+Y_1\frac{dc_0}{dy_0}\right)+\frac{1}{2}\varepsilon^2\left(c_2+2Y_1\frac{dc_1}{dy_0}+(Y_1)^2\frac{d^2c_0}{dy_0^2}+Y_2\frac{dc_0}{dy_0}\right)= \tag{6.107}$$
$$e^{V_c-\frac{1}{2}\varepsilon^2-\left[\phi_0+\varepsilon\left(\phi_1+Y_1\frac{d\phi_0}{dy_0}\right)+\frac{1}{2}\varepsilon^2\left(\phi_2+2Y_1\frac{d\phi_1}{dy_0}+(Y_1)^2\frac{d^2\phi_0}{dy_0^2}+Y_2\frac{d\phi_0}{dy_0}\right)\right]-\Delta\phi_{EQ}-\gamma\left[2H_0-\varepsilon\frac{d^2Y_1}{dx_0^2}-\frac{1}{2}\varepsilon^2\frac{d^2Y_2}{dx_0^2}\right]}$$

where the C superscripts standing for the cathode were eliminated. Now the way to handle this equation is no different than that used to deal with equation (6.99) except that Y_1^C is not zero here in addition to the appearance of $V_c^C-\frac{1}{2}\varepsilon^2$ in the exponential term.

Now observing that $c_1=\frac{dc_1}{dy_0}=\frac{d^2c_0}{dy_0^2}=0$ is valid on the left-hand side while on the right-hand side ϕ_1, $\frac{d\phi_1}{dy_0}$ and $\frac{d^2\phi_0}{dy_0^2}$ are all equal to zero, then equation (6.107) can be written as

$$c_0+\varepsilon\left(Y_1\frac{dc_0}{dy_0}\right)+\frac{1}{2}\varepsilon^2\left(c_2+Y_2\frac{dc_0}{dy_0}\right)=c_0e^{-\varepsilon\left(Y_1\frac{d\phi_0}{dy_0}-\gamma\frac{d^2Y_1}{dx_0^2}\right)-\frac{1}{2}\varepsilon^2\left(\phi_2+Y_2\frac{d\phi_0}{dy_0}+1-\gamma\frac{d^2Y_2}{dx_0^2}\right)} \tag{6.108}$$

Then following the same steps here, as in the anode, in writing the Taylor series expansion for the exponential term we can get

$$\frac{d^2Y_2^C}{dx_0^2}+k^2Y_2^C=\frac{1}{\gamma}\left(\phi_2^C+\frac{c_2^C}{c_0^C}+1\right)-\frac{1}{\gamma}\left(\frac{d\phi_0}{dy_0}Y_1^C-\gamma\frac{d^2Y_1^C}{dx_0^2}\right)^2 \tag{6.109}$$

Now substituting

$$Y_1^C=D_1\cos kx_0$$

into equation (6.109) we get

$$\frac{d^2Y_2^C}{dx_0^2}+k^2Y_2^C=\frac{1}{\gamma}\left(\phi_2^C+\frac{c_2^C}{c_0^C}+1\right)-\frac{1}{\gamma}D_1^2\cos^2kx_0\left(\frac{d\phi_0}{dy_0}+\gamma k^2\right)^2 \tag{6.110}$$

where Y_2^C must satisfy the two side wall conditions

$$\frac{dY_2^C}{dx_0} = 0 \quad \text{at } x_0 = 0 \tag{6.111}$$

and

$$\frac{dY_2^C}{dx_0} = 0 \quad \text{at } x_0 = W_0 \tag{6.112}$$

Like Y_2^A earlier, Y_2^C is also a function of c_2^A and ϕ_2^A but now, indirectly, as $c_2^C = -2\,U_2 + c_2^A$ and $\phi_2^C = -2\,Z\,U_2 + \phi_2^A$. This brings U_2 into the problem of determining Y_2^A and Y_2^C and so to this point we do not know c_2^A, ϕ_2^A, D_1 or U_2 but c_2^A and ϕ_2^A are not independent. To go on we turn to our integral conditions.

Now, as shown in Appendix F, constant volume at second order requires

$$\int_0^{W_0} Y_2^C dx_0 - \int_0^{W_0} Y_2^A dx_0 = 0 \tag{6.113}$$

To evaluate $\int_0^{W_0} Y_2^C dx_0$, integrate equation (6.110) and use $\frac{dY_2^C}{dx_0} = 0$ at the sidewalls to get

$$k^2 \int_0^{W_0} Y_2^C dx_0 = \frac{1}{\gamma}\left(\phi_2^C + \frac{c_2^C}{c_0^C} + 1\right) W_0 - \frac{1}{\gamma}\left(-\frac{dc_0/dy_0}{c_0^C}\right)^2 D_1^2 \int_0^{W_0} \cos^2 kx_0 dx_0 \tag{6.114}$$

where

$$\int_0^{W_0} \cos^2 kx_0 dx_0 = \frac{1}{2} W_0$$

whence

$$\int_0^{W_0} Y_2^C dx_0 = \frac{W_0}{\gamma k^2}\left(\phi_2^C + \frac{c_2^C}{c_0^C} + 1\right) - \frac{W_0}{2\gamma k^2}\left(-\frac{dc_0/dy_0}{c_0^C}\right)^2 D_1^2 \qquad (6.115)$$

Likewise $\int_0^{W_0} Y_2^A dx_0$ is given by

$$\int_0^{W_0} Y_2^A dx_0 = \frac{W_0}{\gamma K_A^2}\left(\phi_2^A + \frac{c_2^A}{c_0^A}\right) \qquad (6.116)$$

Then substituting equations (6.115) and (6.116) into equation (6.113) and using $c_2^C = -2\ U_2 + c_2^A$ and $\phi_2^C = -2\ Z\ U_2 + \phi_2^A$ we get

$$\left(\frac{1}{k^2 c_0^C} - \frac{1}{K_A^2 c_0^A}\right)c_2^A + \left(\frac{1}{k^2} - \frac{1}{K_A^2}\right)\phi_2^A = \frac{2\ U_2}{k^2 c_0^C} + \frac{2\ Z\ U_2}{k^2} - \frac{1}{k^2} + \frac{D_1^2}{2k^2}\left(-\frac{dc_0/dy_0}{c_0^C}\right)^2 \qquad (6.117)$$

which is an equation for c_2^A and ϕ_2^A in terms of U_2 and D_1^2.

Turning to the integral condition representing the constant average ionic concentration, which at second order is

$$\int_0^{W_0}\int_0^1 c_2 dy_0 dx_0 + \int_0^{W_0}\int_0^1 \frac{d}{dy_0}(c_0 y_2) dy_0 dx_0 + \int_0^{W_0}\int_0^1 \frac{d}{dy_0}\left(\frac{dc_0}{dy_0} y_1^2\right) dy_0 dx_0 = 0 \qquad (6.118)$$

Substituting for c_2 using equation (6.91) and carrying out the y_0 integrals in the second and third terms we get

$$\int_0^{W_0}\int_0^1 \left(-2U_2 y_0 + c_2^A\right) dy_0 dx_0 + \int_0^{W_0} c_0^C Y_2^C dx_0 - \int_0^{W_0} c_0^A Y_2^A dx_0 + \frac{dc_0}{dy_0}\left[\int_0^{W_0}\left(Y_1^C\right)^2 dx_0 - \int_0^{W_0}\left(Y_1^A\right)^2 dx_0\right] = 0 \qquad (6.119)$$

and then using $Y_1^A = 0$, $Y_1^C = D_1 \cos kx_0$ and $\int_0^{W_0} Y_2^C dx_0 = \int_0^{W_0} Y_2^A dx_0$, where

$Y_2^A = \frac{1}{\gamma K_A^2}\left(\phi_2^A + \frac{c_2^A}{c_0^A}\right)$, there obtains

$$\int_0^{W_0}\left(-U_2 + c_2^A\right)dx_0 + \left(c_0^C - c_0^A\right)\int_0^{W_0}\frac{1}{\gamma K_A^2}\left(\phi_2^A + \frac{c_2^A}{c_0^A}\right)dx_0 + \frac{dc_0}{dy_0}D_1^2\int_0^{W_0}\cos^2 kx_0 dx_0 = 0 \qquad (6.120)$$

which is simply

$$-U_2 + c_2^A + \frac{\left(c_0^C - c_0^A\right)}{\gamma K_A^2}\left(\phi_2^A + \frac{c_2^A}{c_0^A}\right) + \frac{1}{2}\frac{dc_0}{dy_0}D_1^2 = 0 \qquad (6.121)$$

which can be written in the form of equation (6.117) as

$$\left(1 + \frac{\left(c_0^C - c_0^A\right)}{\gamma K_A^2 c_0^A}\right)c_2^A + \frac{\left(c_0^C - c_0^A\right)}{\gamma K_A^2}\phi_2^A = U_2 - \frac{1}{2}\frac{dc_0}{dy_0}D_1^2 \qquad (6.122)$$

Now we have two linear equations in c_2^A and ϕ_2^A where D_1 and U_2 appear on the right hand sides. Equations (6.117) and (6.122) can be written in the form

$$\begin{pmatrix} \frac{1}{k^2 c_0^C} - \frac{1}{K_A^2 c_0^A} & \frac{1}{k^2} - \frac{1}{K_A^2} \\ 1 + \frac{c_0^C - c_0^A}{\gamma K_A^2 c_0^A} & \frac{c_0^C - c_0^A}{\gamma K_A^2} \end{pmatrix}\begin{pmatrix} c_2^A \\ \phi_2^A \end{pmatrix} = \begin{pmatrix} \frac{2U_2}{k^2 c_0^C} + \frac{2\,Z\,U_2}{k^2} - \frac{1}{k^2} + \frac{D_1^2}{2k^2}\left(-\frac{dc_0/dy_0}{c_0^C}\right)^2 \\ U_2 - \frac{1}{2}\frac{dc_0}{dy_0}D_1^2 \end{pmatrix}$$

or in short hand notation

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}\begin{pmatrix} c_2^A \\ \phi_2^A \end{pmatrix} = \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} \text{ or } A\begin{pmatrix} c_2^A \\ \phi_2^A \end{pmatrix} = \vec{b}$$

Now the determinant of the matrix A is zero and the proof for this is given in Appendix G. Because $\det A = 0$ and we must have a solution (i.e., c_2^A and ϕ_2^A must exist)

solvability must be satisfied and we have two unknowns in $\vec{b}$ (i.e., D_1 and U_2). Solvability then relates these two variables and their relation comes from

$$\left(-\frac{1}{k^2}\right)\left(\frac{c_0^C-c_0^A}{\gamma K_A^2}\right)+\frac{D_1^2}{2k^2}\left(-\frac{dc_0/dy_0}{c_0^C}\right)^2\left(\frac{c_0^C-c_0^A}{\gamma K_A^2}\right)+\left(\frac{2U_2}{k^2c_0^C}\right)\left(\frac{c_0^C-c_0^A}{\gamma K_A^2}\right)+$$
$$\left(\frac{2\,Z\,U_2}{k^2}\right)\left(\frac{c_0^C-c_0^A}{\gamma K_A^2}\right)-U_2\left(\frac{K_A^2-k^2}{K_A^2k^2}\right)+\frac{1}{2}\frac{dc_0}{dy_0}D_1^2\left(\frac{K_A^2-k^2}{K_A^2k^2}\right)=0 \qquad (6.123)$$

This is an important result. It tells us how the current responds as the potential difference moves through its critical value. Unfortunately, we do not find both D_1 and U_2 at the second order but we do find how D_1 and U_2 are related and D_1 appears only as D_1^2.

Let us separate this equation into two parts, the first contains D_1^2, and the other does not. First collecting the terms containing D_1^2 and using $K_A^2-k^2=\frac{1}{\gamma}\frac{dc_0}{dy_0}\left(\frac{c_0^A-c_0^C}{c_0^Ac_0^C}\right)$, we obtain

$$\frac{1}{2}\frac{1}{K_A^2k^2}\frac{dc_0}{dy_0}\left[\frac{c_0^C-c_0^A}{\gamma}\frac{dc_0}{dy_0}\left(\frac{1}{c_0^C}\right)^2+K_A^2-k^2\right]D_1^2 \qquad (6.124)$$

or

$$\frac{1}{2}\frac{(dc_0/dy_0)^2}{\gamma K_A^2k^2c_0^A\left(c_0^C\right)^2}\left[2c_0^Ac_0^C-\left(c_0^A\right)^2-\left(c_0^C\right)^2\right]D_1^2 \qquad (6.125)$$

that is similar to writing

$$-\frac{1}{2}\frac{(dc_0/dy_0)^2}{\gamma K_A^2k^2c_0^A\left(c_0^C\right)^2}\left(c_0^A-c_0^C\right)^2D_1^2 \qquad (6.126)$$

The factor multiplying D_1^2 is known from the base solution and it is always negative.

The part of equation (6.123) where D_1^2 is not present is

$$-\frac{\left(c_0^C - c_0^A\right)}{\gamma K_A^2 k^2} + \frac{2U_2\left(c_0^C - c_0^A\right)}{c_0^C \gamma K_A^2 k^2} + \frac{2Z\ U_2\left(c_0^C - c_0^A\right)}{\gamma K_A^2 k^2} - \frac{U_2\left(K_A^2 - k^2\right)}{K_A^2 k^2} \qquad (6.127)$$

and when $\frac{c_0^A - c_0^C}{\gamma K_A^2 k^2}$ is taken as a common factor it will be

$$\frac{c_0^A - c_0^C}{\gamma K_A^2 k^2}\left[1 - \left(\frac{2}{c_0^C} - 2Z\ - \frac{\left(dc_0/dy_0\right)}{c_0^A c_0^C}\right)U_2\right] \qquad (6.128)$$

where U_2 is our remaining unknown. To get a non-planar steady solution, we must have a positive value of D_1^2 (i.e., D_1 must be real) and this requires (6.128) to be positive. To help us see what is going on, let us go back to the base solution and see what U_2 would be if planar solutions persisted beyond the critical point.

6.4 Drawing Inferences from the U vs. $V^A - V^C$ Relationship

Now let us see how the base current responds to changes in the voltage drop (i.e., let us find out what we would expect to see if the plane solution persists). In the base problem, equation (6.46) can be written as

$$V^A - V^C = \ln\frac{1+U}{1-U} + 2ZU$$

According to this equation, as the voltage drop is increased, the base current will also increase and at the critical voltage drop, there is going to be a critical current or a critical velocity of the surface. Then once the critical voltage drop is passed by an amount

$\frac{1}{2}\varepsilon^2$ the current will go above the critical current by a small amount that we need to determine.

The way to run an experiment would be to increase the voltage drop across the cell and to measure the current to see if something interesting will happen once we advance the voltage above its critical value. Supposing the base solution persists, we can determine the corresponding value of U_2. The base formula for doing this is equation (6.46), viz.,

$$V^A - V^C = \ln\frac{1+U}{1-U} + 2\,Z\,U \tag{6.129}$$

At critical conditions we have

$$\left(V^A - V^C\right)_c = \ln\frac{1+U_c}{1-U_c} + 2\,Z\,U_c \tag{6.130}$$

and then a little beyond critical, when V^A is taken to be a constant, we write

$$-V^C = -V_c^C + \frac{1}{2}\varepsilon^2 \quad \text{or} \quad -V^C + V_c^C = \frac{1}{2}\varepsilon^2 \tag{6.131}$$

and

$$U = U_c + \frac{1}{2}\varepsilon^2\,U_2 \tag{6.132}$$

where U_2 is the response of the current to a small increment in the voltage drop.

Subtracting (6.130) from (6.129) we get

$$\ln\frac{1+U}{1+U_c} - \ln\frac{1-U}{1-U_c} + 2\,Z\,\left[U - U_c\right] = \frac{1}{2}\varepsilon^2 \tag{6.133}$$

whence substituting $U = U_{critical} + \frac{1}{2}\varepsilon^2 U_2$ and expanding the left-hand side gives us our result. First, the term

$$\ln\frac{1+U}{1+U_c}=\ln\left(\frac{1+U_c+\frac{1}{2}\varepsilon^2\ U_2}{1+U_c}\right) \tag{6.134}$$

can be written

$$\ln\frac{1+U}{1+U_c}=\ln\left(1+\frac{1}{2}\varepsilon^2\ \frac{U_2}{1+U_c}\right) \tag{6.135}$$

and the right hand side can be expanded using

$$\ln(1+x)=x-\frac{1}{2}x^2 \tag{6.136}$$

whence, to second order,

$$\ln\frac{1+U}{1+U_c}=\frac{1}{2}\varepsilon^2\ \frac{U_2}{1+U_c} \tag{6.137}$$

Likewise we get

$$\ln\frac{1-U}{1-U_c}=-\frac{1}{2}\varepsilon^2\ \frac{U_2}{1-U_c} \tag{6.138}$$

and substituting equations (6.132), (6.137) and (6.138) into equation (6.133) leads to

$$-V^C+V_c^C=\frac{1}{2}\varepsilon^2=\frac{1}{2}\varepsilon^2\left[\frac{U_2}{1+U_c}+\frac{U_2}{1-U_c}+2\ Z\ U_2\right] \tag{6.139}$$

whence

$$\frac{U_2}{1+U_c}+\frac{U_2}{1-U_c}+2\ Z\ U_2=1 \tag{6.140}$$

and

$$U_2=\frac{(1+U_c)(1-U_c)}{2\ Z(1+U_c)(1-U_c)+2} \tag{6.141}$$

which can be written in terms of base variables as

$$U_2 = \frac{c_0^A\, c_0^C}{2\left[1+Z\, c_0^A\, c_0^C\right]} \tag{6.142}$$

This is the value of U_2 assuming the base solution persists and we can write the nonlinear equation for U_2 in terms of D_1 in a better form by using this equation.

We would expect the velocity of a non-planar front to differ from the predicted plane speed. And so at second order we write $U_2 = U_{2,planar} + \delta$ and when $\delta = 0$ we ought to have $D_1^2 = 0$ for then the front is planar. By the calculations we have

$$U_{2,planar} = \frac{(1+U_c)(1-U_c)}{2\,Z(1+U_c)(1-U_c)+2} = \frac{c_0^A\, c_0^C}{2\left[1+Z\, c_0^A\, c_0^C\right]} \tag{6.143}$$

Let us turn to the problem of predicting U_2 given D_1^2.

6.5 Getting the Relation Between D_1 and U_2

Let us return to (6.128), viz.,

$$\frac{c_0^A - c_0^C}{\gamma K_A^2 k^2}\left[1 - \frac{2\,U_2}{c_0^C} - 2Z\,U_2 - \frac{U_2\,(dc_0/dy_0)}{c_0^A c_0^C}\right]$$

and substitute $U_2 = U_{2,planar} + \delta$, where $U_{2,planar}$ is given by equation (6.143), to get

$$\frac{\left(c_0^A - c_0^C\right)}{\gamma K_A^2 k^2 c_0^A c_0^C}\left[-2c_0^A - 2Zc_0^A c_0^C - \frac{dc_0}{dy_0}\right]\delta \tag{6.144}$$

which on using equations (6.39), (6.40) and (6.35) to write c_0^A, c_0^C and $\frac{dc_0}{dy_0}$ inside the bracket in terms of U_c becomes

$$\frac{2\left(c_0^A - c_0^C\right)}{\gamma K_A^2 k^2 c_0^A c_0^C}\left[Z\,U_c^2 - Z - 1\right]\delta \tag{6.145}$$

Now the factor $\frac{2\left(c_0^A - c_0^C\right)}{\gamma K_A^2 k^2 c_0^A c_0^C}$ is positive while the factor $\left[Z\ U_c^2 - Z - 1\right]$ is negative due to the fact that $U_{critical}$ is positive but less than one. Hence D_1^2 and U_2 are related as

$$D_1^2 = \frac{4c_0^C\left[Z\ U_c^2 - Z - 1\right]\delta}{\left(dc_0/dy_0\right)^2\left(c_0^A - c_0^C\right)} \tag{6.146}$$

where $\frac{4c_0^C\left[Z\ U_c^2 - Z - 1\right]}{\left(dc_0/dy_0\right)^2\left(c_0^A - c_0^C\right)}$ is negative. First, we see the plane front $D_1^2 = 0$ corresponding to $\delta = 0$. Second, we draw a conclusion about what ought to be seen in an experiment. The prediction is that no matter the size of D_1^2, δ must be negative. Hence as the critical point is passed on increasing the potential difference, the displaced front ought to move slower than a planar front would have been expected to move.

The factor $\frac{4c_0^C\left[Z\ U_c^2 - Z - 1\right]}{\left(dc_0/dy_0\right)^2\left(c_0^A - c_0^C\right)}$ that multiplies δ depends on the input variables. To visualize the effect of the different input variables, we will first write every term appears as a function of U_c. To do this, substitute for: $c_0^A = 1 + U_c$, $c_0^C = 1 - U_c$ and $\frac{dc_0}{dy_0} = -2U_c$ and $Z = 1$ to get the following equation instead of equation (6.146) viz.,

$$D_1^2 = \frac{\left(1 - U_c\right)\left(U_c^2 - 2\right)}{2U_c^3}\delta \tag{6.147}$$

Remember that this equation is a scaled equation and all the variables that appear here have superscripts star that was dropped for simplicity. Now U_c and δ are dimensionless variables, however the unscaled D_1 has a dimension of length since we know that $Y_1^C = D_1 \cos kx_0$. So the unscaled version of equation (6.147) is

$$D_1^2 = \frac{\left[1-(U_c/U_{\lim})\right]\left[(U_c/U_{\lim})^2-2\right]}{2(U_c/U_{\lim})^3} L_0^2\ \delta \tag{6.148}$$

The effect of the input variables is clear when we look at equation (6.148). Increasing $U/U_{\lim}$ or decreasing L_0 will decrease this factor. However, no effect of changing $\bar{c}$ can be seen according to this equation. This result is not a surprise since we already know that increasing $U/U_{\lim}$ and decreasing L_0 will always lead to the same consequences. Moreover, finding this equation to be independent of $\bar{c}$ is in the same stream to our result when we found that the critical point does not change as we change $\bar{c}$.

6.6 Predicting the Behavior of the Total Current After Passing the Critical Voltage

We know from our earlier work that talking about the velocity of the surfaces and the current density is no different. Now to see how the total current will respond when the critical voltage drop is passed, let us write the expression for the total current in its unscaled version as

$$I^A = \int_{S^A} dA\left[\vec{n}\cdot\vec{i}\right]^A \tag{6.149}$$

where I^A denotes the total current passing through the cell at the anode and in our two dimensional problem dA is ds multiplied by the depth of the cell. So per unit depth, I^A can be written

$$I^A = \int_0^{W_0} \sqrt{1+\left(Y_x^A\right)^2}\,dx\left[-z_1 F c_M\left(\vec{n}^A\cdot\vec{u}^A+\vec{n}^A\cdot\vec{U}\right)\right] \tag{6.150}$$

and knowing that

$$\vec{n}^A \cdot \vec{u}^A = u^A = \frac{Y_t^A}{\sqrt{1+\left(Y_x^A\right)^2}}$$

and

$$\vec{n}^A \cdot \vec{U} = \vec{n}^A \cdot U\vec{j} = \frac{U}{\sqrt{1+\left(Y_x^A\right)^2}}$$

equation (6.150) becomes

$$I^A = -z_1 F c_M \int_0^{W_0} dx_0 \left(Y_t^A + U\right) \tag{6.151}$$

Now since we are looking for a steady state solution, Y_t^A is zero and by expanding both I^A and U to second order we get

$$I_c^A + \varepsilon I_1^A + \frac{1}{2}\varepsilon^2 I_2^A = -z_1 F c_M \left(U_c + \frac{1}{2}\varepsilon^2 U_2\right) \int_0^{W_0} dx_0 \tag{6.152}$$

so the critical current is

$$I_c^A = -z_1 F c_M U_c W_0 \tag{6.153}$$

then $I_1^A = 0$, while the second order term will be

$$I_2^A = -z_1 F c_M U_2 W_0 \tag{6.154}$$

To write the last two equations according to the scaling introduced in this chapter let us define the scaled total current as $I^* = \frac{I}{z_1 F c_M D}$ and scale the right hand side following the scaling in this chapter to get

$$I_c^{A^*} = -U_c^* W_0^* \tag{6.155}$$

and

$$I_2^{A^*} = -U_2^* W_0^* \tag{6.156}$$

where $W_0^* = \frac{W_0}{L_0}$, $U^* = \frac{L_0}{D} U$. Now by dividing and multiplying the right hand side by $U_{\lim}^*$ and dropping the superscript star and redefine $\frac{U_c}{U_{\lim}} = U_c$ and $\frac{U_2}{U_{\lim}} = U_2$ these two equations will be in agreement with this chapter notation i.e.,

$$I_c^A = -U_{\lim} U_c W_0 \tag{6.157}$$

and

$$I_2^A = -U_{\lim} U_2 W_0 \tag{6.158}$$

Substituting $U_{2,planar} + \delta$ for U_2 in this equation will lead to finding the expression for I_2^A for the non-planar case i.e.,

$$I_2^A = -U_{\lim} W_0 \left(\frac{c_0^A \, c_0^C}{2\left[1 + Z \, c_0^A \, c_0^C\right]} + \frac{\left(dc_0/dy_0\right)^2 \left(c_0^A - c_0^C\right) D_1^2}{4 c_0^C \left[Z \, U_c^2 - Z - 1\right]} \right) \tag{6.159}$$

It is known that the second term on the right-hand side is negative which means that total current after the critical point will be reduced. This is not surprising since the velocity and the current are related one to one and since we found that the velocity is reduced then one will expect the same effect on the current.

Trigueros *et al.* (1994) noticed this drop in the current in their experiments but they did not comment on the reason behind it. They wrote: "When the cathode surface is fully covered by a regular deposit and a homogeneous structure is formed, current density increases until the transition to a finger pattern takes place. At this moment, current falls down and attains a minimum value to rise again when the finger structure is formed and grows steadily".

Now to check that replacing c with $\overline{c}$ in the migration term was not the reason for getting this drop in the velocity of the surface, the problem is worked again in Appendix H without applying the migration term approximation. It is shown in the appendix that a person would arrive at the same conclusion even without using this approximation which means that there is nothing wrong with applying it since it did not contradict the physics of the problem as we already know from chapter 5 calculations.

The result of the drop in the current seems unexpected since having wavy surfaces will lead to more surface area of the electrodes which will result in more total current. To address a physical argument why the decrease in the current might take place, remember that in this chapter the reaction was assumed to be in equilibrium, so the transport is really the controlling mechanism. But since we found that the total current will be reduced, this means that the transport must went slower.

Now a person might refer to the base solution to look for a crude argument to explain why the current will drop after passing the critical point. Let us pretend that we went to the third order and we found the value of D_1 so we know Y_1^C which is $D_1 \cos kx_0$. This means that some parts of the cathode will be closer to the anode than other parts, but the average distance between the electrodes will always be L_0 because the places that are closer to the anode are as much as the ones that are farther from it. So the mass transfer will be weaker at larger distances and it will be stronger at smaller ones. Now we can ask our selves: If we just go to the base solution and move L_0 a certain amount to the right then we move it the same amount to the left, is the change in U will be the same? In other words: Is U more sensitive to increasing or decreasing the distance between the electrodes?

To answer this question, let us write equation (3.85) viz.,

$$\frac{z_1 F}{RT}\left(V^A - V^C\right) = \left(1 - \frac{z_1}{z_2}\right) \ln\left(\frac{1 + \dfrac{U}{U_{\lim}}}{1 - \dfrac{U}{U_{\lim}}}\right)$$

Then remember that

$$U_{\lim} = \frac{2}{L_0} \frac{z_1 D_1 - z_2 D_2}{z_1 z_2 D_2} D \frac{\overline{c}}{c_M}$$

so if $\left(V^A - V^C\right)$ and $\overline{c}$ are held fixed in addition to the process variables, then for every L_0 we input we can calculate U, the velocity of the surface. If we found that increasing the distance between the electrodes affects U more than decreasing it, then we can argue that the places with larger distances are in control and this is the reason why the transport becomes weaker.

Now Figure 6-1 is drawn to show U vs. L_0 using the above two equations. It is clear from the figure that decreasing L_0 has a greater effect on U than increasing it by the same amount. Unfortunately this result does not support our argument that larger distances might be in control, but after all, this was just a crude argument that did not work and it seems that we cannot address any reason for the drop in the current at this point without going to higher orders.

In summary, what we have found from this chapter is that the velocity of the surface or the total current should decrease as we cross the critical voltage. Figure 6-2 shows that we will keep getting the total current expected from the base relation until we reach the critical point. Once we pass it, the total current will be lower from the predicted

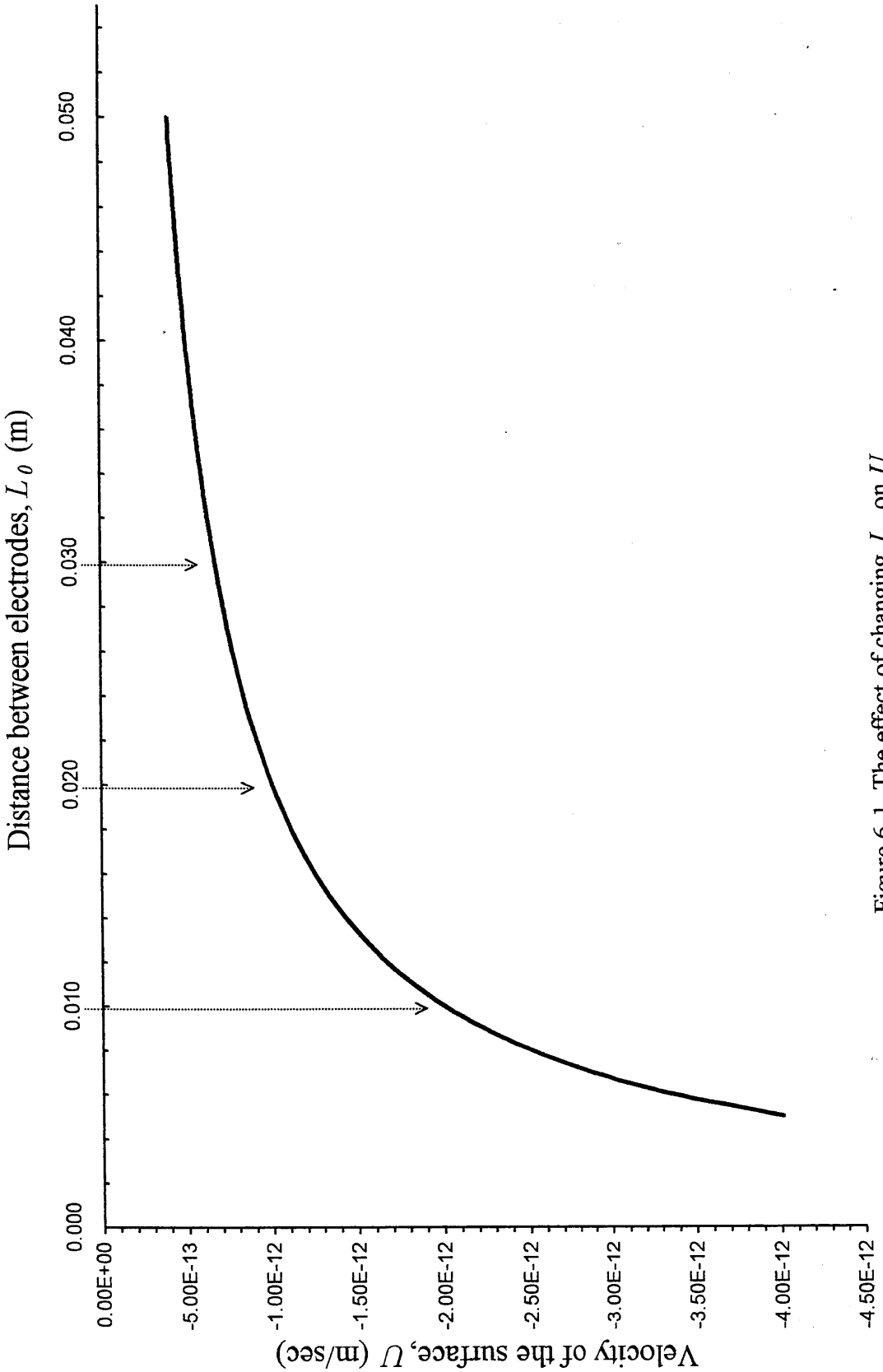


Figure 6-1. The effect of changing L_0 on U.

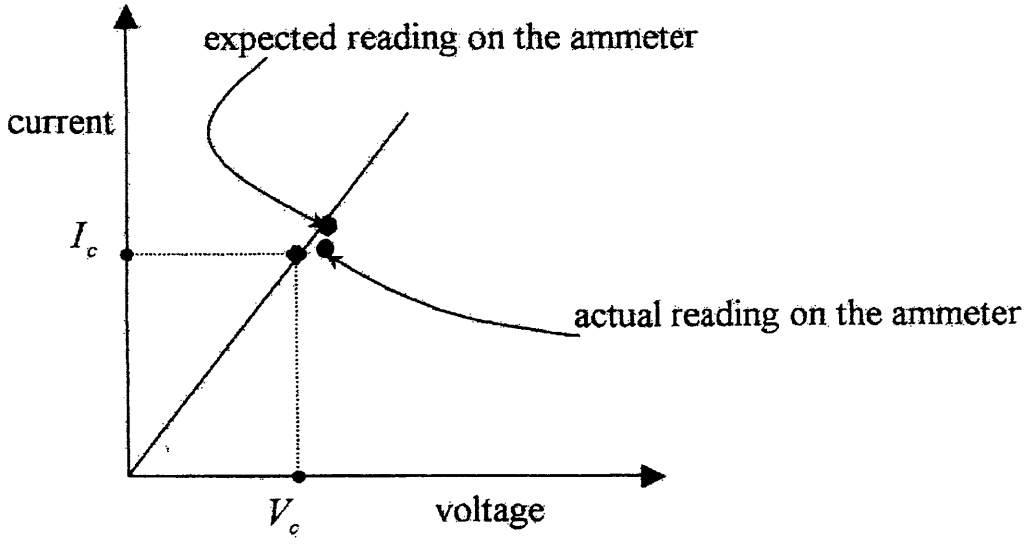


Figure 6-2. The expected current vs. voltage relation in an experiment.

value. One useful thing about this is that it might be hard to see the displacement, but it is much easier to see the current.

Now the reading on the ammeter will going to be less than what it is from the base solution, but we cannot tell by how much because we do not know D_1, the amplitude of the displacement. However, for any value of D_1 we will be able to do this and we hope that by going to higher orders we will learn the value of D_1.

Moreover, all along we have been viewing the problem as though as the potential difference is advanced through the critical so the instability sets in. Based on that, we have added $\frac{1}{2}\varepsilon^2$ to the critical voltage and that is the way Figure 6-2 is drawn. But the instability might occur before the critical in which case we would subtract $\frac{1}{2}\varepsilon^2$ from the critical value. We do not know which sign is right or what is the value of D_1^2 until we go to higher orders.

Without going to third order there is something important that remains and we have enough information to do it which is to decide what an experiment might look like which is our topic in chapter 7.

CHAPTER 7
THE DESIGN VARIABLES IN AN ELECTRODEPOSITION EXPERIMENT AND SOME CONCLUDING REMARKS ON THIS DISSERTATION

In this concluding chapter we shall provide the reader the information needed to design an electrodeposition experiment. To do this we shall use information gathered in the earlier chapters to obtain an intelligent choice of L_0, W_0 and $\overline{c}$, which are the natural input variables in designing an electrodeposition experiment, the output variables being the total current as well as the patterns that one sees upon the instability. The applied voltage is an input variable while the actual value of the applied voltage at which patterns just begin to appear can then be measured. To be definite let us continue to consider the copper-copper sulphate system.

Again we remind the reader that the main assumptions in our work are that:

1. the electrolytic solution is dilute.
2. local electrical neutrality throughout the solution holds.
3. no side reactions take place (i.e., the electrodeposition cell is operated far away from the limiting current so that no hydrogen evolution reaction takes place).
4. we always have a planar anode and a planar cathode with which to begin the experiment.

In addition, we shall assume that the chemical reactions at the electrodes are at equilibrium (the CRE approximation) and the approximation of replacing c with $\overline{c}$ in the migration term holds. We recall that one of the important results of the CRE approximation is that the value of $\frac{-z_1 F c_M U}{i_0}$ is small. Moreover, the fraction U/U_{lim}

must also be small so that unwanted side reactions such as hydrogen evolution at the electrodes will not occur.

Now in designing a cell, one might imagine that single crystal copper is to be used as it is important to start with a substrate that is flat and defect free and to choose $\overline{c}$, L_0 and W_0 such that the values of the critical voltage and the critical output current are in a measurable range. To this end we shall assume that measurements in voltages and currents of the orders of microvolts (μV) and picoamperes (pA) will be acceptable[1].

Now once the input variables are fixed, the critical value of $U/U_{\lim}$ can be calculated by using

$$\frac{\pi^2}{W_0^2}L_0 = -\frac{c_M RT}{\gamma}\left(\frac{-2\dfrac{U}{U_{\lim}}}{1-\dfrac{U}{U_{\lim}}} - 2\,Z\,\frac{U}{U_{\lim}}\right) \tag{7.1}$$

Then having gotten the critical value of $U/U_{\lim}$, we can calculate the critical voltage drop using equation (6.130), namely,

$$V^A - V^C = \frac{RT}{z_1 F}\left[\ln\frac{1+\dfrac{U}{U_{\lim}}}{1-\dfrac{U}{U_{\lim}}} + 2Z\frac{U}{U_{\lim}}\right] \tag{7.2}$$

and observing that

$$U_{\lim} = \frac{2}{L_0}\frac{z_1 D_1 - z_2 D_2}{z_1 z_2 D_2} D\frac{\overline{c}}{c_M}$$

[1] An example of a device that can measure voltages and currents in an acceptable range is the 2400 General-Purpose Source Meter from Keithley. This instrument allows application and measurement of voltage in a range extending from approximately $5\mu V$ to 200V DC and a current in a range from 10pA to 1 A.

we can obtain U, the velocity of the surface, from which the total current, I, can be found by writing

$$I = -z_1 F c_M U \, W_0^2$$

where W_0^2 denotes the area of a square-face electrode each of side equal to W_0. Table 7-1 gives the calculated critical voltages and output critical currents for a variety of input conditions of $\bar{c}$, L_0 and W_0.

Table 7-1. Calculated critical voltages and critical output currents at different input conditions.

$\bar{c}$ (kg-mole/m^3)	L_0 (mm)	W_0 (mm)	$V^A - V^C$ (μV)	I (pA)	$\frac{-z_1 F c_M U}{i_0}$	$\frac{U}{U_{\lim}}$
0.01	5	1	2.73	29.57	$9.3\text{x}10^{-6}$	$5.3\text{x}10^{-5}$
0.1	5	1	2.73	295.74	$3.0\text{x}10^{-5}$	$5.3\text{x}10^{-5}$
0.2	5	1	2.73	591.48	$4.2\text{x}10^{-5}$	$5.3\text{x}10^{-5}$
0.3	5	1	2.73	887.22	$5.1\text{x}10^{-5}$	$5.3\text{x}10^{-5}$
0.1	6	1	3.28	295.74	$3.0\text{x}10^{-5}$	$6.4\text{x}10^{-5}$
0.1	8	1	4.37	295.74	$3.0\text{x}10^{-5}$	$8.5\text{x}10^{-5}$
0.1	10	1	5.46	295.73	$3.0\text{x}10^{-5}$	$10\text{x}10^{-5}$
0.1	20	1	10.93	295.71	$3.0\text{x}10^{-5}$	$21\text{x}10^{-5}$
0.1	40	1	21.85	295.68	$3.0\text{x}10^{-5}$	$40\text{x}10^{-5}$
0.1	50	1	27.31	295.66	$3.0\text{x}10^{-5}$	$53\text{x}10^{-5}$
0.1	50	2	6.82	295.72	$7.4\text{x}10^{-6}$	$13\text{x}10^{-5}$
0.1	50	0.7	55.73	295.59	$6.0\text{x}10^{-5}$	$11\text{x}10^{-4}$
0.1	50	0.07	5283	279.74	$5.7\text{x}10^{-3}$	$10\text{x}10^{-2}$

In the above table recall that $\bar{c}$ is set low because we want an experiment that will respect the assumption of solution diluteness. So we shall select $\bar{c}$ to be 0.1 kg-mole/m^3. The calculated critical current for most of the conditions chosen is about 300 pA. Observe that we have deliberately chosen the input parameters $\bar{c}$, L_0 and W_0 so that the output parameters are in a measurable range that lies within the sensitivity of a commercial instrument.

Let us now examine the effect of changing L_0. It is clear that this variable will affect all of the output parameters as shown in the equations and in the above table. The current is the least sensitive to changing L_0 but it is obvious that as we increase the spacing between the electrodes, the actual values of U/U_{lim} and $V^A - V^C$ both increase. The reader might recall that in chapter 3 we discussed the effect of L_0 upon the critical value of U/U_{lim} and consequently upon $V^A - V^C$ where we explained this dependence in more detail. The increase in U/U_{lim} due to an increase in L_0 is apparent from equation (7.1) given above. From the numbers given in the table, a reasonable value for L_0 would be about 50 mm. This also will make the electrodes far enough from each other so that if they were not perfectly parallel (i.e., if one of them was slightly tilted) the large distance between them would minimize the effect of this imperfection. Moreover, choosing this value of L_0 will result in having a small U/U_{lim} so we do not ordinarily have to worry about the hydrogen evolution reaction and the approximation of making $c = \overline{c}$ in the migration term will be more meaningful. Note that increasing L_0 from 5 to 50 mm increases the critical voltage drop dramatically from about 3 μV to about 30 μV and it is obvious that there is more flexibility in choosing L_0 than in choosing $\overline{c}$ so a person might choose any value for L_0 between 40 and 50 mm.

The effect of W_0 on the output parameters is similar to that of L_0. However, it is clear that $V^A - V^C$ and U/U_{lim} are more sensitive to changes in W_0 than in L_0 which is not surprising as U/U_{lim} is proportional to L_0 while it is proportional to W_0^2 as shown

previously in equation (7.1). A good value for W_0 is about 1 mm and from this we can get a reasonable current (i.e., 295 pA) and a U/U_{lim} that is very small.

Finally for all the input variables chosen, the value of $\frac{-z_1 F c_M U}{i_0}$ turns out to be very small and this is good because it tells us that the CRE approximation is reasonably satisfied for almost any selected set of input conditions.

To summarize what we have said in the previous few pages, we have found a reasonable set of design variables to run an electrodeposition experiment. These are $\overline{c} = 0.1$ kg-mole/m^3, $L_0 = 50$ mm and $W_0 = 1$ mm. This will result in a critical current of about 300 pA and a critical voltage of around 28 μV. Figure 7-1 depicts a schematic of the electrodeposition cell. It is not unusual to have a cell with such dimensions as many researchers that study dendritic growth have performed experiments using smaller cells with dimensions in micrometers. An example of such work is given by Léger *et al.* (1997), Brissot *et al.* (1999) and Rosso *et al.* (2003).

We are now at the end of this dissertation and some concluding remarks are in order.

The main objective of this dissertation was to study morphological instability during the motion of phase boundaries. To this end, electrodeposition was used as an example where we learned that one must be very careful about understanding the rule of the control variables on the physics of the instability. We observed that the voltage drop is the true input while the current is an output because the total current is likely to change as the morphology changes and thus it is not easily controllable.

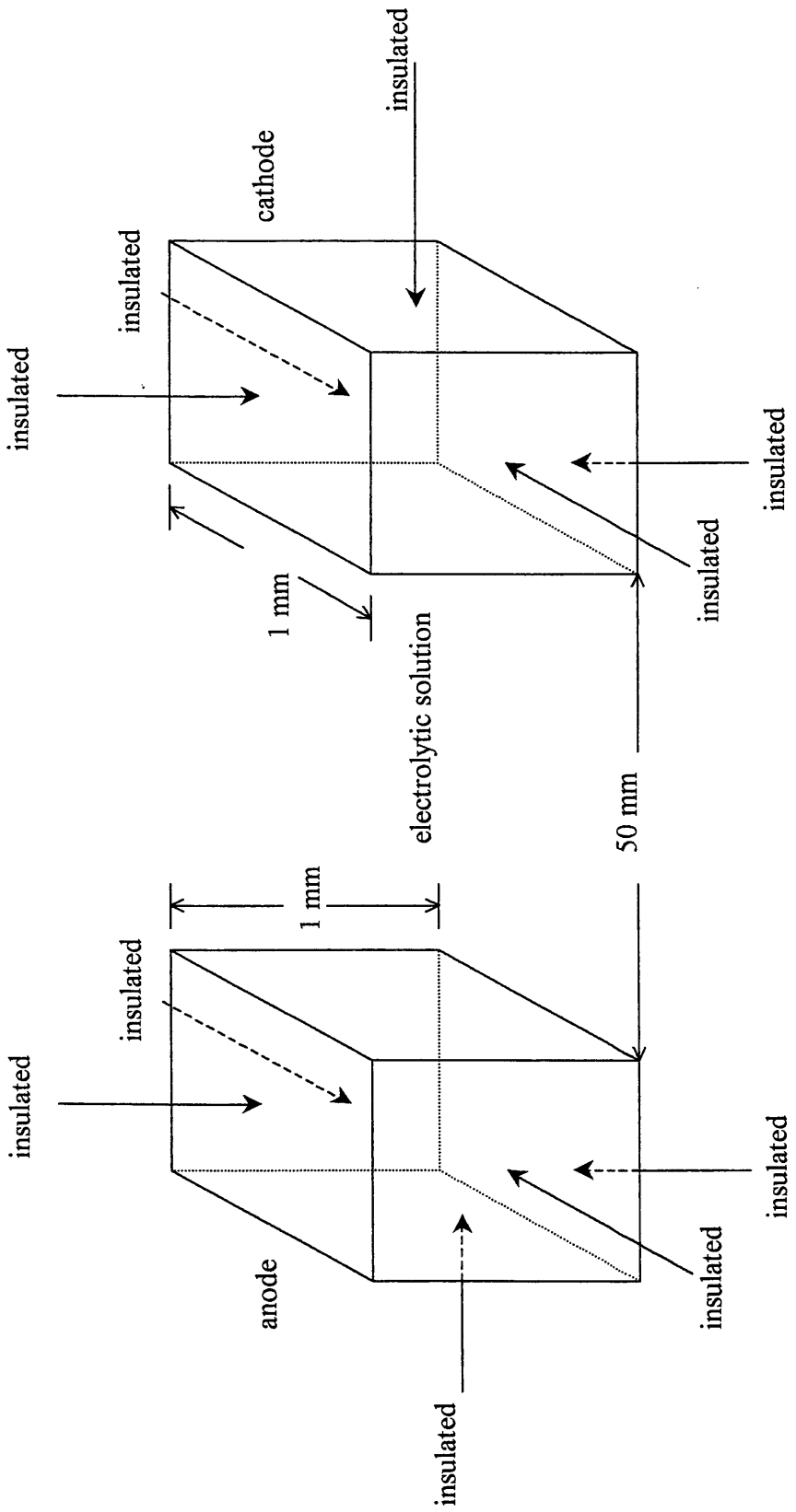


Figure 7-1. Schematic of electrodeposition cell.

One of the important conclusions in our work is that we have made three main approximations that seem to have little effect on the physics of the instability as well as the calculated critical conditions. One of these approximations is that the reaction at the electrodes is at equilibrium which implies that the reaction takes place very fast compared to the transport processes of diffusion and migration. Another important approximation was to assume that the concentration is the same as the average ionic concentration as far as the migration is concerned. Yet another approximation was that the growth constant in the domain is subservient to the growth constant coming from the movement of the boundary. These are all excellent approximations that reduce the algebra and the numerical calculations by an enormous amount so that we did not have to perform very complicated calculations and yet were able to get meaningful results.

The morphological instability implies an increase in the surface area and one might imagine that the total current ought to increase once the critical voltage input is surpassed. Surprisingly we learned that the output current falls disproportionably to the applied voltage after passing the critical point. This has been observed by other workers experimentally but no analytical proof has been advanced so far. As the model we used to arrive at this result was based on the idea that the reaction rate is fast compared to the transport, the only reason for the drop in the current must be that the transport processes become slower for reasons that we do not quite understand. While we were able to predict that the measured current will be lower than the base current at the second order calculations, we were not able to declare by how much the total current will drop. In order to know this information we have to obtain the constant D_1 which cannot be found from the weak nonlinear calculations at second order. Obtaining the amplitude of the

current and the non-planarity of the electrode surfaces must be the subject of future work. Our objective has been to understand the physics of the front instability and we have met this objective with the support of calculations.

Understanding electrodeposition is both useful and instructive. Yet there are other moving front instabilities such as those that occur in solidification, precipitation and viscous fingering. Each of these problems is different in the physics that drives it, yet much that we have learned from electrodeposition could be used fruitfully in their study.

APPENDIX A
ANNOTATED BIBLIOGRAPHY

In this work we referred repeatedly to a very interesting paper by Sundström and Bark (S&B) which is:

1. L-G Sundström and F. H. Bark, "On Morphological Instability During Electrodeposition with a Stagnant Binary Electrolyte," *Electrochim. Acta* **40,** 599 (1995).

S&B did not conduct experiments; they were interested in the origins of the morphological instability when certain approximations are applied. Among these approximations were the use of a dilute electrolytic solution and the neglecting of convection. S&B ultimate objective was to predict the wavelength of the patterns at the onset of instability and the rate of growth of disturbances.

S&B presented the model we are using; their important contribution is that they were talking about two electrodes where no body before them discussed working with two surfaces. Having two electrodes will lead to having a constant volume condition. None of the people suggested models with one surface can argue that they have got constant volume condition, so nobody working with one electrode can possibly make any sense out of this without introducing constant volume condition but that completely artificial. The constant volume condition did not make any difference for S&B but it made a lot of difference to us. This is because S&B only did the first order problem, and they only did it numerically for one set of parameters so there is no much use of it.

Here the reader will find the main research cited by S&B with a brief description about them:

The linear stability of a growing spherical particle immersed in a molten binary alloy and the investigation of the stability of a plane solidification front were first treated by Mullins and Sekerka in these two papers:

2. W. W. Mullins and R. F. Sekerka, "Morphological Stability of a Particle Growing by Diffusion or Heat Flow," *J. Appl. Phys.* **34**, 323 (1963).

3. W. W. Mullins and R. F. Sekerka, "Stability of a Planar Interface During Solidification of a Dilute Binary Alloy," *J. Appl. Phys.* **35**, 444 (1964).

Aogaki and co-workers used linear stability analysis to determine the critical size of a protrusion above which a planar surface becomes unstable in a diffusion-controlled, steady state galvnostatic electrodeposition. Their results were limited to cases where migration of the reacting species and kinetic polarization could be ignored. This work can be found in:

4. R. Aogaki, K. Kitazawa, Y. Kose and K. Fueki, "Theory of Powdered Crystal Formation in Electrocrystallization-Occurrence of Morphological Instability at the Electrode Surface," *Electrochim. Acta* **25**, 965 (1980).

5. R. Aogaki and T. Makino, "Theory of Powdered Crystal Formation in Electrochemistry-Morphological Instability in Galvnostatic Crystal Growth Under Diffusion Control," *Electrochim. Acta* **26**, 1509 (1981).

More work was done on the electrodeposition problem where researchers used the Nernst boundary layer assumption and introduced a diffusion layer thickness, which is assumed to be known. In this category are:

- Landau who included kinetic effects in his analysis and found that the initiation of surface roughening could be associated with a critical overpotential comprising concentration and kinetic terms in:

6. U. Landau, "Zinc Electrodeposition and Dendritic Growth from Zinc Halide Electrolytes," EPRI Report EM-2393. EPRI, Research Center, Palo Alto, CA (1982).

- Barkey and his group where they extended previous treatments by taking into account migrational transport in these two papers:

7. D. P. Barkey, R. H. Muller and C. W. Tobias, "Roughness Development in Metal Electrodeposition I. Experimental Results," *J. Electrochem. Soc.* **136**, 2199 (1989).

8. D. P. Barkey, R. H. Muller and C. W. Tobias, "Roughness Development in Metal Electrodeposition II. Stability Theory," *J. Electrochem. Soc.* **136**, 2207 (1989).

- Chen and Jorne who let the edge of the diffusion layer to follow the surface perturbations for large wavelengths in their paper:

9. C.-P. Chen and J. Jorne, "The Dynamics of Morphological Instability during Electrodeposition," *J. Electrochem. Soc.* **138**, 3305 (1991).

- Pritzker and Fahidy who coupled diffusion and migration more strongly than in the work of Barkey *et al.* and used the Butler-Volmer equation to describe the electrode kinetics in:

10. M. D. Pritzker and T. Z. Fahidy, "Morphological Stability of a Planar Metal Electrode during Potentiostatic Electrodeposition and Electrodissolution," *Electrochim. Acta* **37**, 103 (1992).

Pritzker and Fahidy (P&F) work is very close to S&B except they still have one electrode. Their work is the combination of the previous attempts to deal with this problem. So we will work through this paper and see how it is compared to our work.

P&F considered a system that involves the electrodeposition or electrodissolution of a metal from an aqueous solution according to the following reaction

$$M^{z_1^+} + z_1 e^- \rightleftharpoons M \qquad \text{(A.1)}$$

This reaction will continuously change the position of the electrode given by $S = y - Y(x, y, t)$ where y is the displacement of the electrode from the position of a

planar electrode. Within a distance δ from the surface (i.e., on the domain) transport of all species in the electrolyte occurs by diffusion and migration such that

$$\frac{\partial c_j}{\partial t} = D_j \nabla^2 c_j + \frac{z_j F}{RT} D_j \nabla \left(c_j \nabla \phi \right) \tag{A.2}$$

where c_j, D_j and z_j are the concentration, diffusion coefficient and valence of species j while ϕ is the solution potential. The second domain equation is the Laplace's equation given by

$$\nabla^2 \phi = 0 \tag{A.3}$$

The boundary conditions are given by the following equations. For each non-reacting species, the normal flux at the solid/liquid interface is zero i.e.,

$$\vec{n} \cdot \left[\nabla c_j + \frac{z_j F}{RT} c_j \nabla \phi \right] = 0 \text{ for } j = 2,3,4,... \tag{A.4}$$

where $\vec{n}$ is the outward unit normal vector at the surface. This equation is similar to equation (2.17) that we have in our model except that the right hand side in our case is not zero. The normal flux for reacting species is similar to what we have i.e., equation (2.16) under the assumption that the metal density is very large compared to the electrolyte density and it is given as follows

$$\vec{n} \cdot \left[D_1 \nabla c + \frac{z_1 F D_1}{RT} c \nabla \phi \right] = -\frac{i}{z_1 F} \tag{A.5}$$

The surface reaction is the cause of the movement of the boundary so that

$$\rho \left(\upsilon + \frac{dY}{dt} \right) = -\frac{i}{z_1 F} \tag{A.6}$$

where ρ is the density of the depositing or dissolving metal, υ is the steady-state velocity of the planar electrode. Now the current density and overpotential are related by a Butler-Volmer expression of the form

$$i = i_0 \left(\frac{c}{c_\infty} \right)^{\beta} \left[e^{\frac{\alpha_1 F}{RT}\eta_s} - e^{-\frac{\alpha_2 F}{RT}\eta_s} \right] \tag{A.7}$$

where the surface overpotential η_s is

$$\eta_s = V - \phi - U_\infty - \frac{RT}{z_1 F} \ln\left(\frac{c}{c_\infty} \right) + \frac{\gamma 2H}{\rho z_1 F} \tag{A.8}$$

where i_0 is the exchange current density, α_1 and α_2 are transfer coefficients, V, U_∞, γ and $2H$ are the applied potential, equilibrium potential for the reaction given by equation 1 based on bulk concentrations, the surface energy of the metal M and the curvature of the metal surface, respectively. The curvature and surface are related as follows:

$$2H = -\frac{\partial^2 Y}{\partial x^2} \tag{A.9}$$

$$i = i_0 \left\{ \left(\frac{c}{c_\infty} \right)^{\beta - \frac{\alpha_1}{z_1}} e^{\frac{\alpha_1 F}{RT}\left(V - \phi - U_\infty + \frac{\gamma 2H}{z_1 \rho F} \right)} - \left(\frac{c}{c_\infty} \right)^{\beta + \frac{\alpha_2}{z_1}} e^{-\frac{\alpha_2 F}{RT}\left(V - \phi - U_\infty + \frac{\gamma 2H}{z_1 \rho F} \right)} \right\} \tag{A.10}$$

In their paper, P&F assigned the following values of β, α_1 and α_2 for the copper/copper sulphate system: $\beta = 0.58$, $\alpha_1 = 1.09$ and $\alpha_2 = 0.36$ so their B-V equation can be written as

$$i = i_0 \left\{ \left(\frac{c}{c_\infty} \right)^{0.035} e^{\frac{\alpha_1 F}{RT}\left(V - \phi - U_\infty + \frac{\gamma 2H}{z_1 \rho F} \right)} - \left(\frac{c}{c_\infty} \right)^{0.76} e^{-\frac{\alpha_2 F}{RT}\left(V - \phi - U_\infty + \frac{\gamma 2H}{z_1 \rho F} \right)} \right\} \tag{A.11}$$

It is clear that P&F have not got the same powers for the ratio $\frac{c}{c_\infty}$ as in our version of the B-V equation where we had zero and one instead of 0.035 and 0.76 respectively. In addition, we do not know why it is like that since they did not mention from where they obtained the Butler-Volmer equation.

The electric field at the surface is given by

$$\vec{n}\cdot\nabla\phi = -\frac{i}{K_\infty} \text{ at the electrode surface} \tag{A.12}$$

where K_∞ is the bulk conductivity, whereas the field far from the surface is given by

$$\frac{d\phi}{dy} = -\frac{i}{K_\infty} \text{ at } y=\delta \tag{A.13}$$

These two boundary conditions given by equations (A.12) and (A.13) are also different than our boundary conditions given by equation (2.35) which is valid at both electrodes. In our model we predicted that K_∞ has to be different from one another at each electrode. A person can calculate $\vec{n}\cdot\nabla\phi$ from our model and then it can be easily seen that K_∞ depends on the concentration. But since the concentration at each electrode is different, K_∞ cannot be the same and moreover it must be perturbed as a result of its dependence on the concentration. The last boundary conditions which apply at the outer edge of the boundary layer are

$$c = c_\infty \text{ at } y=\delta \tag{A.14}$$

and

$$\phi = \phi_{\mathrm{Re}} \text{ at } y=\delta \tag{A.15}$$

At a very slow movement of the electrode surface, the pseudo-steady-state approximation for mass transport is valid and δ remains constant. This is similar to the approximation we used of dropping the growth constant from the domain. Equation (A.2) upon applying this approximation and using equation (A.3) will turn into

$$\nabla^2 c_j + \frac{z_j F}{RT} \nabla c_j \nabla \phi = 0 \tag{A.16}$$

P&F never said that they are using local electrical neutrality but some of their equations are not true unless local electrical neutrality is utilized. And it seems that the reason why they did not think they need this condition because they got enough equations. On the other hand, in our original model presented in chapter 2, we did not have the condition $\nabla^2 \phi = 0$ on the domain so we used the local electrical neutrality.

Now let us find the base solution for the planar surface (i.e., when $Y = 0$). After using equations (A.16), (A.5) and (A.14) and by assigning the subscript zero to represent the base solution to the c problem, one will find

$$c_0 = \frac{RTK_\infty}{z_1^2 F^2 D_1} + \left(c_\infty - \frac{RTK_\infty}{z_1^2 F^2 D_1} \right) e^{-\frac{z_1 F}{RT} \frac{i_s}{K_\infty} (\delta - y_0)} \tag{A.17}$$

where i_s denotes the steady state current density. Next, when solving the ϕ problem, we have $\nabla^2 \phi = 0$ with 3 boundary conditions luckily they are all satisfied but only if K_∞ is the same in equations (A.12) and (A.13) which we know cannot be true for electrical neutrality which they must be assuming. Now the base solution to the ϕ problem when using equation (A.3) subject to the boundary conditions (A.12), (A.13) and (A.15) is

$$\phi_0 = \frac{i_s}{K_\infty} (\delta - y_0) + \phi_{\mathrm{Re}} \tag{A.18}$$

It is clear that both c_0 and ϕ_0 are oriented only in the y-direction and c_0 is a nonlinear function of y while ϕ_0 is a linear function of y. This is different from what we found earlier in chapter 3 where the concentration profile had a linear dependence on y whereas ϕ_0 was the one with the nonlinear dependence.

To go on and study the stability of the base solution, one will write the following perturbation equations

$$Y = Y_0 + \varepsilon Y_1 \tag{A.19}$$

$$c = c_0 + \varepsilon\left(c_1 + Y_1 \frac{dc_0}{dy_0}\right) \tag{A.20}$$

$$\phi = \phi_0 + \varepsilon\left(\phi_1 + Y_1 \frac{d\phi_0}{dy_0}\right) \tag{A.21}$$

and

$$i = i_0 + \varepsilon\left(i_1 + Y_1 \frac{di}{dy_0}\right) \tag{A.22}$$

then to separate variables, we will use the following substitutions

$$Y_1 = \hat{Y}_1 e^{ikx_0} e^{\sigma t_0} \tag{A.23}$$

$$c_1 = \hat{c}_1 e^{ikx_0} e^{\sigma t_0} \tag{A.24}$$

$$\phi_1 = \hat{\phi}_1 e^{ikx_0} e^{\sigma t_0} \tag{A.25}$$

and

$$i_1 = \hat{i}_1 e^{ikx_0} e^{\sigma t_0} \tag{A.26}$$

Now we will concentrate on the neutral stability case with the target to obtain a relation between the critical wave number and the input variables that can be compared with the result of P&F. First, one can easily find that

$$i_1 = 0 \tag{A.27}$$

which is the result of perturbing equation (A.6). Then upon perturbing the ϕ equations we will get

$$\phi_1 = 0 \tag{A.28}$$

then when studying the c problem, the perturbed version of equation (A.16) will turn to be

$$\frac{d^2\hat{c}_1}{dy_0^2} - \frac{z_1 F}{RT}\frac{i_s}{K_\infty}\frac{d\hat{c}_1}{dy_0} - k^2\hat{c}_1 = 0 \tag{A.29}$$

which can be solved by using these boundary conditions

$$\frac{d\hat{c}_1}{dy_0} - \frac{z_1 F}{RT}\frac{i_s}{K_\infty}c_1 = 0 \quad \text{at} \quad y_0 = 0 \tag{A.30}$$

and

$$\hat{c}_1 = 0 \quad \text{at} \quad y_0 = \delta \tag{A.31}$$

which are the results of perturbing equations (A.5) and (A.14) respectively.

The solution to equation (A.29) is

$$\hat{c}_1 = A_1 e^{m_+ y_0} + B_1 e^{m_- y_0} \tag{A.32}$$

where

$$m_\pm = \frac{\frac{z_1 F}{RT}\frac{i_s}{K_\infty} \pm \sqrt{\left(\frac{z_1 F}{RT}\frac{i_s}{K_\infty}\right)^2 + 4k^2}}{2} \tag{A.33}$$

then the boundary conditions based on equation (A.32) are

$$A_1 e^{m_+\delta} + B_1 e^{m_-\delta} = 0 \tag{A.34}$$

and

$$m_+ A_1 + m_- B_1 - \frac{z_1 F}{RT}\frac{i_s}{K_\infty}\left(A_1 + B_1\right) = 0 \tag{A.35}$$

Now equations (A.34) and (A.35) are two, linear, homogeneous, algebraic equations in A_1 and B_1 which can be written as follows

$$\begin{pmatrix} e^{m_+\delta} & e^{m_-\delta} \\ m_+ - \frac{z_1 F}{RT}\frac{i_s}{K_\infty} & m_- - \frac{z_1 F}{RT}\frac{i_s}{K_\infty} \end{pmatrix}\begin{pmatrix} A_1 \\ B_1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{A.36}$$

and the determinant of the matrix containing the factors of A_1 and B_1 is

$$\det = e^{m_+\delta}\left(m_- - \frac{z_1 F}{RT}\frac{i_s}{K_\infty}\right) - e^{m_-\delta}\left(m_+ - \frac{z_1 F}{RT}\frac{i_s}{K_\infty}\right) \tag{A.37}$$

which can be written as

$$\det = m_- e^{m_+\delta} - m_+ e^{m_-\delta} - \frac{z_1 F}{RT}\frac{i_s}{K_\infty}\left(e^{m_+\delta} - e^{m_-\delta}\right) \tag{A.38}$$

By looking to equation (A.38) it is clear that $m_- e^{m_+\delta} - m_+ e^{m_-\delta}$ is negative while $\left(e^{m_+\delta} - e^{m_-\delta}\right)$ is positive. Based on that, one can conclude that if i_s is an input variable and $i_s > 0$ (anode) then the determinant will always be negative so $A_1 = B_1 = 0 = \hat{c}_1$. On the other hand, if $i_s < 0$ (cathode) then the determinant might be zero and $\hat{c}_1$ does not have to be equal to zero.

Now the applied voltage, V, is the input variable, so setting V will set i_s. Then when a person considers equation (A.38), the determinant is either zero or not and the only free parameter under control is the wave number, k^2, once all the input conditions

are set. So there is always one k^2 for which the determinant is equal to zero, for all other values of k^2, the determinant is not zero leading to $c_1 = 0$. In conclusion, for all cases, except one, the determinant will not be zero so a person will consider this case as the predominant situation and will set $c_1 = 0$ and go to the B-V equation to calculate the critical wave number.

P&F presented an equation for the critical wave number at high cathodic overpotentials. We will now use the B-V equation to try to obtain such a relation and see if we can get something close to their result. The perturbed B-V equation is

$$\begin{aligned} 0 = {} & \frac{\alpha_1 F}{RT}\left(\frac{c_0}{c_\infty}\right)^{\beta-\frac{\alpha_1}{z_1}} e^{\frac{\alpha_1 F}{RT}(V-\phi_0-U_\infty)}\left(-\hat{\phi}_1 - \hat{Y}_1\frac{d\phi_0}{dy_0} + \frac{\gamma}{z_1\rho F}k^2_{critical}\hat{Y}_1\right) \\ & + \left(\beta-\frac{\alpha_1}{z_1}\right)\left(\frac{c_0}{c_\infty}\right)^{\beta-\frac{\alpha_1}{z_1}-1} e^{\frac{\alpha_1 F}{RT}(V-\phi_0-U_\infty)}\frac{\left(\hat{c}_1 + \hat{Y}_1\frac{dc_0}{dy_0}\right)}{c_\infty} \\ & + \frac{\alpha_2 F}{RT}\left(\frac{c_0}{c_\infty}\right)^{\beta+\frac{\alpha_2}{z_1}} e^{-\frac{\alpha_2 F}{RT}(V-\phi_0-U_\infty)}\left(-\hat{\phi}_1 - \hat{Y}_1\frac{d\phi_0}{dy_0} + \frac{\gamma}{z_1\rho F}k^2_{critical}\hat{Y}_1\right) \\ & - \left(\beta+\frac{\alpha_2}{z_1}\right)\left(\frac{c_0}{c_\infty}\right)^{\beta+\frac{\alpha_2}{z_1}-1} e^{-\frac{\alpha_2 F}{RT}(V-\phi_0-U_\infty)}\frac{\left(\hat{c}_1 + \hat{Y}_1\frac{dc_0}{dy_0}\right)}{c_\infty} \end{aligned} \tag{A.39}$$

using our result that $c_1 = \phi_1 = 0$ and dropping the first two terms on the right hand side as a result of considering the case of high cathodic overpotentials one can get

$$0 = \frac{\alpha_2 F}{RT}\left(-\hat{Y}_1\frac{d\phi_0}{dy_0} + \frac{\gamma}{z_1\rho F}k^2_{critical}\hat{Y}_1\right) - \left(\beta+\frac{\alpha_2}{z_1}\right)\left(\frac{1}{c_0}\right)\left(\hat{Y}_1\frac{dc_0}{dy_0}\right) \tag{A.40}$$

then rearranging this equation will lead to the expression for the critical wave number

$$k^2_{critical} = \left(\beta+\frac{\alpha_2}{z_1}\right)\frac{1}{c_0}\frac{dc_0}{dy_0}\frac{RT}{\alpha_2}\frac{z_1\rho}{\gamma} - \frac{i_s}{K_\infty}\frac{z_1\rho F}{\gamma} \tag{A.41}$$

which is close to this expression given by P&F viz.,

$$k_{critical}^2 = \frac{\beta}{\alpha_2}\frac{\rho z_1 RT}{\gamma c_0}\frac{dc_0}{dy_0} - \frac{\rho RTi_s}{\gamma z_1 F D_1 c_0} \qquad (A.42)$$

Now some researchers performed experimental work in the area of dendritic growth which has some connection to our work. Trigueros *et al.* presented an experimental evidence on the drop of the current once the electrodes lose their planarity in their paper:

11. P. P. Trigueros, F. Sagués and J. Claret, "Influence of an inert electrolyte on the morphology of quasi-two-dimensional electrodeposits," *Phys. Rev. E* **49,** 4328 (1994).

In chapter 7 we proposed a design of an electrodeposition cell that has dimensions ranging between 1 mm and 50 mm. To show that this is not a strange thing when conducting experiments in this area, we want to point to the following work:

- Léger and coworkers used an electrochemical cell with these dimensions: 50 μm x 50 mm x 50 mm when they study the diffusive character of the mass transport in thin gap electrodeposition experiments. This can be found in:

12. C. Léger, J. Elezgaray and F. Argoul, "Experimental Demonstration of Diffusion-Limited Dynamics in Electrodeposition," *Phys. Rev. Lett.* **78,** 5010 (1997).

- Brissot and his group performed experiments to study dendritic electrodeposition of lithium under galvanostatic conditions. The thickness of the lithium electrodes they used were as small as 160 μm and the distance between the two electrodes is about 1 mm. This work is given in:

13. C. Brissot, M. Rosso, J.-N. Chazalviel and S. Lascaud, "Dendritic growth mechanisms in lithium/polymer cells," *J. Power Sources* **81-82,** 925 (1999).

- Rosso *et al.* reported experiments performed in electrodeposition cells with thickness ranging between 20-250 μm in:

14. M. Rosso, E Chassaing, V. Fleury and J.-N. Chazalviel, "Shape evolution of metals electrodeposited from binary electrolytes," *J. Electroanal. Chem.* **559,** 165 (2003).

APPENDIX B
DOMAIN PERTURBATIONS

In this appendix, we will explain the method of domain perturbations which is required for the stability analysis that was done in chapters 3-6. The material in this appendix is adapted from Johns and Narayanan, 2002. Now let u be the solution to a problem defined on a domain D where D is not specified and need to be determined as part of the solution. In addition, let the equations in our hands be sufficient in number on D and on its boundary to determine u. Now estimates of u and D can be found by solving a new problem defined on a known domain called the reference domain denoted D_0. What we want to do then is to adjust the problem on D to make up for using the reference domain instead of the current unknown domain. This will be achieved by determining both u and D in terms of the solutions defined on D_0.

Now to show how this is possible, we will work on a two dimensional problem where Cartesian coordinates will be used. Then we can choose a point O as the origin from which two perpendicular axes are originating namely Ox and Oy to define the points of D_0 which will be denoted by the coordinates x_0, y_0 and those of D by coordinates x, y. The main idea then is to imagine a number of domains D_ε emerging from the reference domain D_0 and to imagine that u must be found on each of these, one of them is the domain we want to find. So the points (x,y) of the domain D_ε are then determined in terms of the points (x_0,y_0) of the reference domain D_0 by the mapping

$$x = f(x_0, y_0, \varepsilon)$$

and

$$y = g(x_0, y_0, \varepsilon)$$

where according to these equations, each point of D_ε acquires an ancestor in D_0.

For all the work in this thesis it is adequate to let D_ε be unknown in only one part of its boundary and to let D_0 be specified and regular. After that let the domains D_ε grow out of the reference domain as part of the boundary of D_0, denoted $y_0 = Y_0(x_0)$, passes through a series of configurations $y = Y(x, \varepsilon)$ forming the matching parts of the boundaries of the domains D_ε. So it is satisfactory to write the mapping as

$$x = x_0$$

and

$$y = g(x_0, y_0, \varepsilon)$$

where this mapping will take the points $(x_0, y_0 = Y_0(x_0))$ of the boundary of D_0 into the matching points $(x, y = Y_0(x, \varepsilon))$ of the boundary of D_ε, namely

$$x = x_0$$

and

$$y = Y(x, \varepsilon) = Y(x_0, \varepsilon) = g(x_0, Y_0(x_0), \varepsilon)$$

This mapping is the foundation of performing the perturbation calculations when having a domain that is not known, as in our electrodeposition problem. Figure B-1 illustrates this mapping.

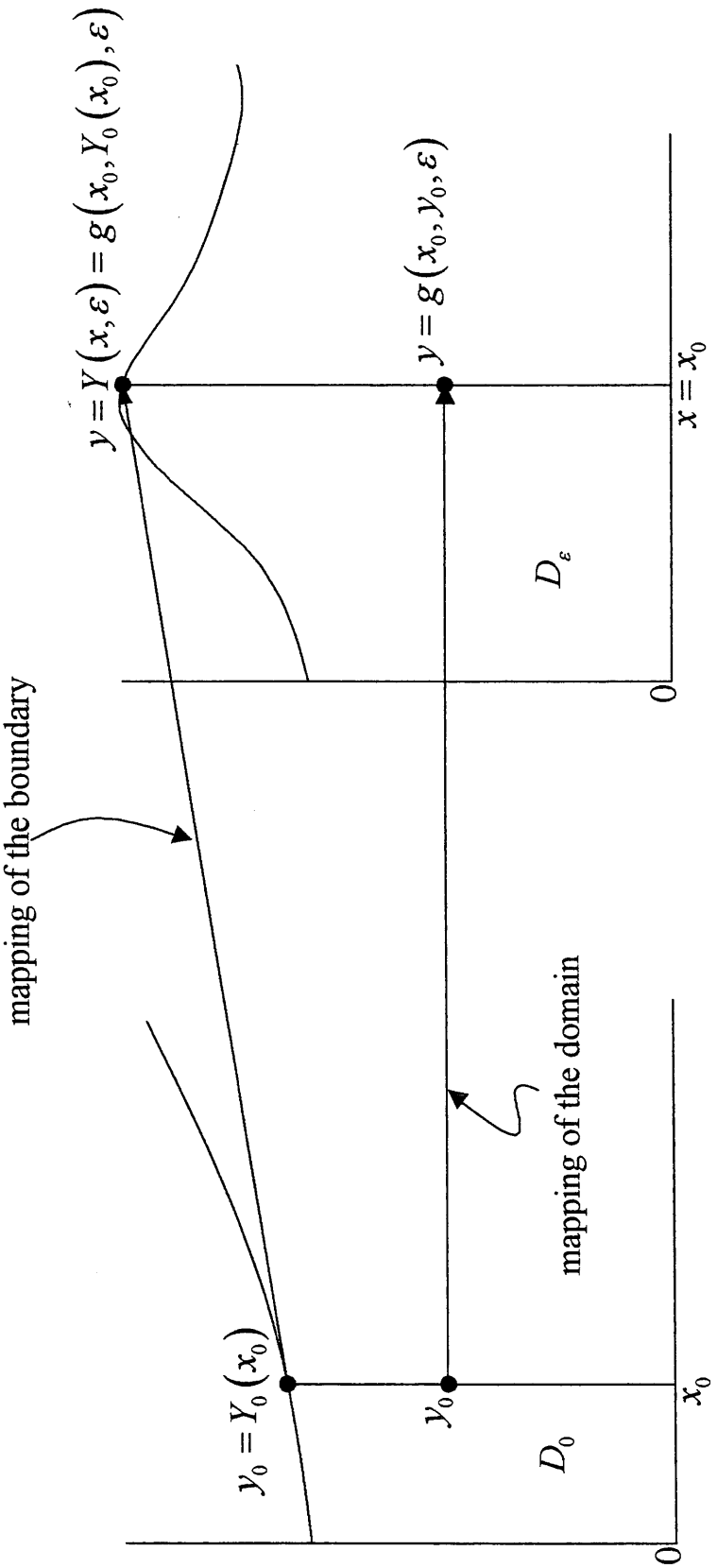


Figure B-1. The mapping of D_0 into D_ε.

Now let us expand the function g in power of ε as

$$g(x_0, y_0, \varepsilon) = g(x_0, y_0, \varepsilon = 0) + \varepsilon \frac{\partial g}{\partial \varepsilon}(x_0, y_0, \varepsilon = 0) + \frac{1}{2}\varepsilon^2 \frac{\partial^2 g}{\partial \varepsilon^2}(x_0, y_0, \varepsilon = 0) + \ldots$$

where $g(x_0, y_0, \varepsilon = 0) = y_0$ and where the derivatives of g, evaluated in the reference domain, are taken holding x_0 and y_0 fixed. Then, in terms of the notation

$$y_1(x_0, y_0) = \frac{\partial g}{\partial \varepsilon}(x_0, y_0, \varepsilon = 0) \tag{B.1}$$

$$y_2(x_0, y_0) = \frac{\partial^2 g}{\partial \varepsilon^2}(x_0, y_0, \varepsilon = 0) \tag{B.2}$$

etc

the mapping can be written as

$$x = x_0 \tag{B.3}$$

and

$$y = g(x_0, y_0, \varepsilon) = y_0 + \varepsilon y_1(x_0, y_0) + \frac{1}{2}\varepsilon^2 y_2(x_0, y_0) + \ldots \tag{B.4}$$

and this is the form in which it is used.

Now, the boundary of the reference domain must be carried into the boundary of the present domain by our mapping. Hence, the function $Y(x, \varepsilon)$, which describes the boundary of the current domain, inherits its expansion in powers of ε by putting $y_0 = Y_0(x_0)$ into the expansion of the domain mapping. Then, at the boundary, the mapping

$$x = x_0$$

and

$$y = Y(x,\varepsilon) = Y_0(x_0) + \varepsilon y_1(x_0, Y_0(x_0)) + \frac{1}{2}\varepsilon^2 y_2(x_0, Y_0(x_0)) + \ldots$$

which can be written as

$$x = x_0 \tag{B.5}$$

and

$$y = Y(x,\varepsilon) = Y_0(x_0) + \varepsilon Y_1(x_0) + \frac{1}{2}\varepsilon^2 Y_2(x_0) + \ldots \tag{B.6}$$

by introducing the notation

$$Y_1(x_0) = y_1(x_0, Y_0(x_0)) \tag{B.7}$$

$$Y_2(x_0) = y_2(x_0, Y_0(x_0)) \tag{B.8}$$

etc

It is $Y_1, Y_2, \ldots$ that must be found to specify the domain D_ε in terms of the reference domain D_0.

B.1 The Expansion of a Domain Variable and Its Derivatives Along the Mapping

Now, to determine the expansion of a domain variable and its derivatives along the mapping, note that there are two kinds of variables of interest to us: those defined on the domain, and hence on its boundary as well, and those defined only on the boundary of the domain. These latter variables ordinarily depend on the shape of the boundary and acquire their expansion by the expansion of the function determining this shape. The curvature of the surface, the normal and the normal velocity are examples of variables defined only on the boundary, but many variables of interest to us are defined on both the domain and the boundary which we will discuss next.

Let u denotes the solution to a family of problems on a family of domains, denoted D_ε. The domains D_ε grow out of a reference domain D_0. A point (x,y) of the domain D_ε is connected to its ancestor (x_0,y_0) of D_0 by equations (B.3) and (B.4). Let $u(x_0,y_0,\varepsilon=0)$ be denoted by $u_0(x_0,y_0)$ and the target is to determine u at the point (x,y) in D_ε in terms of u_0.

To achieve our target, we expand $u(x,y,\varepsilon)$ in powers of ε along the mapping and write this expansion

$$u(x,y,\varepsilon)=u(x=x_0,y=y_0,\varepsilon=0)+\varepsilon\frac{du}{d\varepsilon}(x=x_0,y=y_0,\varepsilon=0) \\ +\frac{1}{2}\varepsilon^2\frac{d^2u}{d\varepsilon^2}(x=x_0,y=y_0,\varepsilon=0)+\ldots \tag{B.9}$$

where $d/d\varepsilon$ denotes the derivative of a function depending on x,y and ε taken holding x_0 and y_0 fixed.

Then, with u_0 defined by

$$u_0(x_0,y_0)=u(x=x_0,y=y_0,\varepsilon=0)$$

let us find out $\frac{du}{d\varepsilon}$ and $\frac{d^2u}{d\varepsilon^2}$.

To obtain a formula for $\frac{du}{d\varepsilon}(x=x_0,y=y_0,\varepsilon=0)$, differentiate u along the mapping taking x and y to depend on ε, holding x_0 and y_0 fixed. By the chain rule, there results

$$\frac{du}{d\varepsilon}(x,y,\varepsilon)=\frac{\partial u}{\partial\varepsilon}(x,y,\varepsilon)+\frac{\partial u}{\partial y}(x,y,\varepsilon)\frac{\partial g}{\partial\varepsilon}(x_0,y_0,\varepsilon) \tag{B.10}$$

where $y = g(x_0, y_0, \varepsilon)$ and where the term $\frac{\partial u}{\partial x}(x, y, \varepsilon)\frac{\partial f}{\partial \varepsilon}(x_0, y_0, \varepsilon)$ does not appear due to the fact that equation (B.3), namely

$$x = f(x_0, y_0, \varepsilon) = x_0$$

is being used instead, where x_0 is being held fixed. Then, set ε to zero in equation (B.10) and use equation (B.1) to obtain

$$\frac{du}{d\varepsilon}(x = x_0, y = y_0, \varepsilon = 0) = \frac{\partial u}{\partial \varepsilon}(x_0, y_0, \varepsilon = 0) + y_1(x_0, y_0)\frac{\partial u}{\partial y}(x_0, y_0, \varepsilon = 0) \quad \text{(B.11)}$$

In equation (B.11), introduce u_1 via

$$u_1(x_0, y_0) = \frac{\partial u}{\partial \varepsilon}(x = x_0, y = y_0, \varepsilon = 0)$$

and observe that

$$\frac{\partial u}{\partial y}(x = x_0, y = y_0, \varepsilon = 0) = \frac{\partial u_0}{\partial y_0}(x_0, y_0)$$

to get

$$\frac{du}{d\varepsilon}(x = x_0, y = y_0, \varepsilon = 0) = u_1(x_0, y_0) + y_1(x_0, y_0)\frac{\partial u_0}{\partial y_0}(x_0, y_0) \quad \text{(B.12)}$$

where y_1 specifies the mapping to first order of ε and where u_1, like u_0, remains to be determined.

To work out the second derivative, differentiate equation (B.10) to obtain

$$\frac{d}{d\varepsilon}\left[\frac{du}{d\varepsilon}\right] = \frac{d}{d\varepsilon}\left[\frac{\partial u}{\partial \varepsilon} + \frac{\partial u}{\partial y}\frac{\partial g}{\partial \varepsilon}\right] = \frac{d}{d\varepsilon}\left[\frac{\partial u}{\partial \varepsilon}\right] + \frac{d}{d\varepsilon}\left[\frac{\partial u}{\partial y}\right]\frac{\partial g}{\partial \varepsilon} + \frac{\partial u}{\partial y}\frac{\partial^2 g}{\partial \varepsilon^2}$$

and substitute

$$\frac{d}{d\varepsilon}\left[\frac{\partial u}{\partial \varepsilon}\right] = \frac{\partial}{\partial \varepsilon}\left[\frac{\partial u}{\partial \varepsilon}\right] + \frac{\partial}{\partial y}\left[\frac{\partial u}{\partial \varepsilon}\right]\frac{\partial g}{\partial \varepsilon}$$

and

$$\frac{d}{d\varepsilon}\left[\frac{\partial u}{\partial y}\right]=\frac{\partial}{\partial \varepsilon}\left[\frac{\partial u}{\partial y}\right]+\frac{\partial}{\partial y}\left[\frac{\partial u}{\partial y}\right]\frac{\partial g}{\partial \varepsilon}$$

to obtain

$$\frac{d^2u}{d\varepsilon^2}=\frac{\partial^2 u}{\partial \varepsilon^2}+2\frac{\partial^2 u}{\partial y\partial \varepsilon}\frac{\partial g}{\partial \varepsilon}+\frac{\partial^2 u}{\partial y^2}\left[\frac{\partial g}{\partial \varepsilon}\right]^2+\frac{\partial u}{\partial y}\frac{\partial^2 g}{\partial \varepsilon^2} \tag{B.13}$$

Then, in equation (B.13), set $x=x_0$, $y=y_0$ and $\varepsilon=0$, introduce u_2 via

$$u_2(x_0,y_0)=\frac{\partial^2 u}{\partial \varepsilon^2}(x=x_0,y=y_0,\varepsilon=0)$$

observe that

$$\frac{\partial^2 u}{\partial y^2}(x=x_0,y=y_0,\varepsilon=0)=\frac{\partial^2 u_0}{\partial y_0^2}(x_0,y_0)$$

and use equations (B.1) and (B.2) to obtain

$$\begin{aligned}\frac{d^2u}{d\varepsilon^2}(x=x_0,y=y_0,\varepsilon=0)=u_2(x_0,y_0)+2y_1(x_0,y_0)\frac{\partial u_1}{\partial y_o}(x_0,y_0)\\ +y_1^2(x_0,y_0)\frac{\partial^2 u_0}{\partial y_0^2}(x_0,y_0)+y_2(x_0,y_0)\frac{\partial u_0}{\partial y_0}(x_0,y_0)\end{aligned} \tag{B.14}$$

where y_2 specifies the mapping to second order of ε and where u_2 remains to be determined.

Additional derivatives needed to write $u(x,y,\varepsilon)$ to any order in ε, but equations (B.12) and (B.14) are enough to write u to second order in ε as

$$u(x,y,\varepsilon)=u_0+\varepsilon\left[u_1+y_1\frac{\partial u_0}{\partial y_0}\right]+\frac{1}{2}\varepsilon^2\left[u_2+2y_1\frac{\partial u_1}{\partial y_0}+y_1^2\frac{\partial^2 u_0}{\partial y_0^2}+y_2\frac{\partial u_0}{\partial y_0}\right]+\ldots \tag{B.15}$$

where every variable on the right-hand side is evaluated at (x_0,y_0).

To determine u on the domain D_ε, then, it would seem as though $u_0, u_1, u_2, \ldots$ as well as $y_1, y_2, \ldots$ would need to be determined on the reference domain D_0. It turns out that while $u_0, u_1, u_2, \ldots$ can be determined, $y_1, y_2, \ldots$ cannot, and, although this presents a technical difficulty, it is helpful to be guided by the idea that what is required is a mapping-independent prediction of the values of u at the interior points of the domain D_ε.

Our aim, then, is to derive the equations that must be satisfied by the functions $u_0, u_1, u_2, \ldots$ on the reference domain D_0 from the equations satisfied by u on the present domain D_ε. Now, derivatives of u appear in most of the equations of interest; hence, in addition to the expansion of u, expansions of its derivatives e.g., expansions of $\partial u/\partial x$ and $\partial u/\partial y$, must be obtained. These can be used along with the expansion of u in determining the equations satisfied by $u_0, u_1, u_2, \ldots$ on the reference domain D_0.

Taking $\partial u/\partial y$ first, we must differentiate the right-hand side of equation (B.15) with respect to y, holding x and ε fixed, where the functions appearing there depend on x_0, y_0 and ε. To do this, equations (B.3) and (B.4) can be used to obtain x_0 and y_0 in terms of x, y and ε, and then the chain rule of differentiation can be used. In this use of the chain rule, functions of x_0, y_0 and ε are to be differentiated with respect to y, holding x and ε fixed; earlier, to obtain equations (B.12) and (B.14), functions of x, y and ε were differentiated with respect to ε, holding x_0 and y_0 fixed.

The chain rule, then, requires functions of x_0 and y_0 to be differentiated according to

$$\frac{\partial}{\partial y}[\ ]=\frac{\partial}{\partial x_0}[\ ]\frac{\partial x_0}{\partial y}+\frac{\partial}{\partial y_0}[\ ]\frac{\partial y_0}{\partial y}$$

but $\partial x_0/\partial y$ is zero, due to the fact that $x=f(x_0,y_0,\varepsilon)=x_0$, and by this, the chain rule reduces to

$$\frac{\partial}{\partial y}[\ ]=\frac{\partial}{\partial y_0}[\ ]\frac{\partial y_0}{\partial y}$$

Hence, we must differentiate the right-hand side of equation (B.15) with respect to y_0, holding x_0 and ε fixed, and then multiply this by $\partial y_0/\partial y$ which comes from equation (B.4), holding x and ε fixed. Doing this leads to

$$\begin{aligned}\frac{\partial u}{\partial y}=&\left[\frac{\partial u_0}{\partial y_0}\frac{\partial y_0}{\partial y}\right]+\varepsilon\left[\frac{\partial u_1}{\partial y_0}\frac{\partial y_0}{\partial y}+y_1\frac{\partial^2 u_0}{\partial y_0^2}\frac{\partial y_0}{\partial y}+\frac{\partial y_1}{\partial y}\frac{\partial u_0}{\partial y_0}\right]\\&+\frac{1}{2}\varepsilon^2\left[\frac{\partial u_2}{\partial y_0}\frac{\partial y_0}{\partial y}+2y_1\frac{\partial^2 u_1}{\partial y_0^2}\frac{\partial y_0}{\partial y}+2\frac{\partial y_1}{\partial y}\frac{\partial u_1}{\partial y_0}+y_1^2\frac{\partial^3 u_0}{\partial y_0^3}\frac{\partial y_0}{\partial y}\right.\\&\left.+2y_1\frac{\partial y_1}{\partial y}\frac{\partial^2 u_0}{\partial y_0^2}+y_2\frac{\partial^2 u_0}{\partial y_0^2}\frac{\partial y_0}{\partial y}+\frac{\partial y_2}{\partial y}\frac{\partial u_0}{\partial y_0}\right]+\ldots\end{aligned}\qquad\text{(B.16)}$$

where the chain rule has been used to differentiate $u_0,\partial u_0/\partial y_0,\partial^2 u_0/\partial y_0^2,u_1,\partial u_1/\partial y_0$ and u_2, but it has not been used to differentiate y_1 and y_2. These derivatives have been indicated as $\partial y_1/\partial y$ and $\partial y_2/\partial y$ for reasons to appear presently.

Now, equations (B.3) and (B.4) can be used to determine $\partial y_0/\partial y$ as

$$\frac{\partial y_0}{\partial y}=1-\varepsilon\frac{\partial y_1}{\partial y}-\frac{1}{2}\varepsilon^2\frac{\partial y_2}{\partial y}-\ldots$$

and this reduces equation (B.16), the expansion of $\partial u/\partial y$, to its final form, that is

$$\frac{\partial u}{\partial y}(x,y,\varepsilon)=\frac{\partial u_0}{\partial y_0}+\varepsilon\left[\frac{\partial u_1}{\partial y_0}+y_1\frac{\partial^2 u_0}{\partial y_0^2}\right] +\frac{1}{2}\varepsilon^2\left[\frac{\partial u_2}{\partial y_0}+2y_1\frac{\partial^2 u_1}{\partial y_0^2}+y_1^2\frac{\partial^3 u_0}{\partial y_0^3}+y_2\frac{\partial^2 u_0}{\partial y_0^2}\right]+\ldots \tag{B.17}$$

The main thing to observe in this formula is that all the terms in equation (B.16) in which derivatives of $y_1, y_2, \ldots$ appear e.g., $\frac{\partial y_1}{\partial y}\frac{\partial u_0}{\partial y_0}$, are lost in taking the last step, with the result that the expansion of $\partial u/\partial y$ looks just like the expansion of u, as might have been anticipated, namely

$$u=u_0+\varepsilon\left[u_1+y_1\frac{\partial u_0}{\partial y_0}\right]+\frac{1}{2}\varepsilon^2\left[u_2+2y_1\frac{\partial u_1}{\partial y_0}+y_1^2\frac{\partial^2 u_0}{\partial y_0^2}+y_2\frac{\partial u_0}{\partial y_0}\right]+\ldots$$

and

$$\frac{\partial u}{\partial y}=\frac{\partial u_0}{\partial y_0}+\varepsilon\left[\frac{\partial u_1}{\partial y_0}+y_1\frac{\partial^2 u_0}{\partial y_0^2}\right]+\frac{1}{2}\varepsilon^2\left[\frac{\partial u_2}{\partial y_0}+2y_1\frac{\partial^2 u_1}{\partial y_0^2}+y_1^2\frac{\partial^3 u_0}{\partial y_0^3}+y_2\frac{\partial^2 u_0}{\partial y_0^2}\right]+\ldots$$

and this would lead us to expect the expansion of $\frac{\partial^2 u}{\partial y^2}$ to be

$$\frac{\partial^2 u}{\partial y^2}=\frac{\partial^2 u_0}{\partial y_0^2}+\varepsilon\left[\frac{\partial^2 u_1}{\partial y_0^2}+y_1\frac{\partial^3 u_0}{\partial y_0^3}\right] +\frac{1}{2}\varepsilon^2\left[\frac{\partial^2 u_2}{\partial y_0^2}+2y_1\frac{\partial^3 u_1}{\partial y_0^3}+y_1^2\frac{\partial^4 u_0}{\partial y_0^4}+y_2\frac{\partial^3 u_0}{\partial y_0^3}\right]+\ldots \tag{B.18}$$

which, indeed, is correct. In all these formulas, the variables on the left-hand side are evaluated at x, y and ε whereas all the variables on the right-hand side are evaluated at x_0 and y_0.

Turning to $\partial u/\partial x$, we must differentiate the right-hand side of equation (B.15) with respect to x, holding y and ε fixed. Now, x is equal to x_0, but y is being held fixed;

hence, y_0 cannot be fixed. The result is that $\partial/\partial x$, where y is held fixed, operating on the right-hand side cannot be replaced by $\partial/\partial x_0$, where y_0 is being held fixed, even though $x = x_0$. The mapping must be used to determine y_0 as a function of x at a fixed values of y and ε. Again, all of the variables on the right-hand side of the expansion of $u(x, y, \varepsilon)$, outside of ε itself, which is being held fixed, depend only on x_0 and y_0. In view of this, our calculation of $\partial u/\partial x$ again requires the use of the chain rule, and in this case it has the form

$$\frac{\partial}{\partial x}[\ ] = \frac{\partial}{\partial x_0}[\ ]\frac{\partial x_0}{\partial x} + \frac{\partial}{\partial y_0}[\ ]\frac{\partial y_0}{\partial x}$$

Once more using equations (B.3) and (B.4) to express x_0 and y_0 in terms of x and y, there now obtain

$$\frac{\partial x_0}{\partial x} = 1$$

and

$$0 = \frac{\partial y_0}{\partial x} + \varepsilon\frac{\partial y_1}{\partial x} + \frac{1}{2}\varepsilon^2\frac{\partial y_2}{\partial x} + \ldots$$

whence the chain rule takes the form

$$\frac{\partial}{\partial x}[\ ] = \frac{\partial}{\partial x_0}[\ ] + \frac{\partial}{\partial y_0}[\ ]\frac{\partial y_0}{\partial x}$$

where

$$\frac{\partial y_o}{\partial x} = -\varepsilon\frac{\partial y_1}{\partial x} - \frac{1}{2}\varepsilon^2\frac{\partial y_2}{\partial x} - \ldots \qquad \text{(B.19)}$$

Working out $\partial/\partial x$ applied to the right-hand side of equation (B.15) then leads to

$$\frac{\partial u}{\partial x}=\left[\frac{\partial u_0}{\partial x_0}+\frac{\partial u_0}{\partial y_0}\frac{\partial y_0}{\partial x}\right]+\varepsilon\left[\left[\frac{\partial u_1}{\partial x_0}+\frac{\partial u_1}{\partial y_0}\frac{\partial y_0}{\partial x}\right]+y_1\left[\frac{\partial^2 u_0}{\partial x_0\partial y_0}+\frac{\partial^2 u_0}{\partial y_0^2}\frac{\partial y_0}{\partial x}\right]+\frac{\partial u_0}{\partial y_0}\frac{\partial y_1}{\partial x}\right]$$
$$+\frac{1}{2}\varepsilon^2\left[\left[\frac{\partial u_2}{\partial x_0}+\frac{\partial u_2}{\partial y_0}\frac{\partial y_0}{\partial x}\right]+2y_1\left[\frac{\partial^2 u_1}{\partial x_0\partial y_0}+\frac{\partial^2 u_1}{\partial y_0^2}\frac{\partial y_0}{\partial x}\right]+2\frac{\partial u_1}{\partial y_0}\frac{\partial y_1}{\partial x}\right.$$
$$\left.+y_1^2\left[\frac{\partial^3 u_0}{\partial x_0\partial y_0^2}+\frac{\partial^3 u_0}{\partial y_0^3}\frac{\partial y_0}{\partial x}\right]+2y_1\frac{\partial^2 u_0}{\partial y_0^2}\frac{\partial y_1}{\partial x}+y_2\left[\frac{\partial^2 u_0}{\partial x_0\partial y_0}+\frac{\partial^2 u_0}{\partial y_0^2}\frac{\partial y_0}{\partial x}\right]+\frac{\partial u_0}{\partial y_0}\frac{\partial y_2}{\partial x}\right]+\ldots$$

where the chain rule has been used to differentiate $u_0, \partial u_0/\partial y_0, \partial^2 u_0/\partial y_0^2, u_1, \partial u_1/\partial y_0$ and u_2, but it has not been used to differentiate y_1 and y_2. Again, these derivatives are simply denoted $\partial y_1/\partial x$ and $\partial y_2/\partial x$.

The final formula for $\partial u/\partial x$ obtains on eliminating $\partial y_0/\partial x$ by the use of equation (B.19) and it is

$$\frac{\partial u}{\partial x}=\frac{\partial u_0}{\partial x_0}+\varepsilon\left[\frac{\partial u_1}{\partial x_0}+y_1\frac{\partial^2 u_0}{\partial x_0\partial y_0}\right]$$
$$+\frac{1}{2}\varepsilon^2\left[\frac{\partial u_2}{\partial x_0}+2y_1\frac{\partial^2 u_1}{\partial x_0\partial y_0}+y_1^2\frac{\partial^3 u_o}{\partial x_0\partial y_0^2}+y_2\frac{\partial^2 u_0}{\partial x_0\partial y_0}\right]+\ldots \qquad \text{(B.20)}$$

Again, the derivatives of $y_1, y_2, \ldots$ are lost in the last step and the formula for $\partial u/\partial x$, similar to the formula for $\partial u/\partial y$, takes the form of the formula for u itself. This, of course, makes it possible to guess other formulas *e.g.*, the formula for $\partial^2 u/\partial x^2$. It is worthwhile observing that each time $\partial y_0/\partial x$ is eliminated, by substituting $-\varepsilon\frac{\partial y_1}{\partial x}-\frac{1}{2}\varepsilon^2\frac{\partial y_2}{\partial x}-\ldots$ in its place, terms to all higher order in ε are introduced. It is by this that the derivatives of $y_1, y_2, \ldots$ cancel out; for example, just as $\frac{\partial u_0}{\partial y_0}\frac{\partial y_0}{\partial x}$ cancels

$\varepsilon \frac{\partial u_0}{\partial y_0}\frac{\partial y_1}{\partial x}$ and $\frac{1}{2}\varepsilon^2 \frac{\partial u_0}{\partial y_0}\frac{\partial y_2}{\partial x}$ in the forgoing calculations, so too it will cancel

$\frac{1}{6}\varepsilon^3 \frac{\partial u_0}{\partial y_0}\frac{\partial y_3}{\partial x}$ at the third order.

Equations (B.15), (B.17), (B.18) and (B.20) are the final result that we were looking for. In the next section an example is presented to help the reader understand how to apply what he learned here.

B.2 An Example on How to Use the Expansions of u and Its Derivatives

The most direct way to obtain the equations satisfied by u_0, u_1, u_2, etc. on the reference domain is to substitute the expansions of u and its derivatives into the equations that must be satisfied on the present domain. Then as the right-hand sides of these expansions depend only on x_0, y_0 and ε, on setting the coefficients of each power of ε to zero, a set of equations in u_0, u_1, u_2, etc. appear.

The next example will illustrate the method and it will mainly show that the mapping does not survive in the equations satisfied by u_0, u_1, u_2, etc.

Let u satisfy

$$u\frac{\partial u}{\partial y} + \varepsilon u + \varepsilon^2 + 1 = 0$$

on the current domain. Then substituting the expansions of $u(x, y, \varepsilon)$ and $\frac{\partial u}{\partial y}(x, y, \varepsilon)$ into this, there obtains

$$\left[u_0+\varepsilon\left(u_1+y_1\frac{\partial u_0}{\partial y_0}\right)+\frac{1}{2}\varepsilon^2\left(u_2+2y_1\frac{\partial u_1}{\partial y_0}+y_1^2\frac{\partial^2 u_0}{\partial y_0^2}+y_2\frac{\partial u_0}{\partial y_0}\right)+\cdots\right]$$
$$\times\left[\frac{\partial u_0}{\partial y_0}+\varepsilon\left(\frac{\partial u_1}{\partial y_0}+y_1\frac{\partial^2 u_0}{\partial y_0^2}\right)+\frac{1}{2}\varepsilon^2\left(\frac{\partial u_2}{\partial y_0}+2y_1\frac{\partial^2 u_1}{\partial y_0^2}+y_1^2\frac{\partial^3 u_0}{\partial y_0^3}+y_2\frac{\partial^2 u_0}{\partial y_0^2}\right)+\cdots\right]$$
$$+\varepsilon\left[u_0+\varepsilon\left(u_1+y_1\frac{\partial u_0}{\partial y_0}\right)+\cdots\right]+\varepsilon^2+1=0$$

which leads, on requiring the coefficient of each power of ε to vanish, to

$$u_0\frac{\partial u_0}{\partial y_0}+1=0 \tag{B.21}$$

$$u_0\left(\frac{\partial u_1}{\partial y_0}+y_1\frac{\partial^2 u_0}{\partial y_0^2}\right)+\left(u_1+y_1\frac{\partial u_0}{\partial y_0}\right)\frac{\partial u_0}{\partial y_0}+u_0=0$$

$$\frac{1}{2}u_0\left(\frac{\partial u_2}{\partial y_0}+2y_1\frac{\partial^2 u_1}{\partial y_0^2}+y_1^2\frac{\partial^3 u_0}{\partial y_0^3}+y_2\frac{\partial^2 u_0}{\partial y_0^2}\right)+\frac{1}{2}\left(u_2+2y_1\frac{\partial u_1}{\partial y_0}+y_1^2\frac{\partial^2 u_0}{\partial y_0^2}+y_2\frac{\partial u_0}{\partial y_0}\right)\frac{\partial u_0}{\partial y_0}$$
$$+\left(u_1+y_1\frac{\partial u_0}{\partial y_0}\right)\left(\frac{\partial u_1}{\partial y_0}+y_1\frac{\partial^2 u_0}{\partial y_0^2}\right)+\left(u_1+y_1\frac{\partial u_0}{\partial y_0}\right)+1=0$$

Now by using $\frac{\partial}{\partial y_0}\left(u_0\frac{\partial u_0}{\partial y_0}+1\right)=0$, the first equation, equation (B.21) eliminates $y_1\left(u_0\frac{\partial^2 u_0}{\partial y_0^2}+\frac{\partial u_0}{\partial y_0}\frac{\partial u_0}{\partial y_0}\right)$ in the second, reducing it to

$$u_0\frac{\partial u_1}{\partial y_0}+u_1\frac{\partial u_0}{\partial y_0}+u_0=0 \tag{B.22}$$

while the third equation can be written

$$\frac{1}{2}u_0\frac{\partial u_2}{\partial y_0}+\frac{1}{2}u_2\frac{\partial u_0}{\partial y_0}+u_1\frac{\partial u_1}{\partial y_0}+u_1+1+y_1\left(u_0\frac{\partial^2 u_1}{\partial y_0^2}+\frac{\partial u_1}{\partial y_0}\frac{\partial u_0}{\partial y_0}+\frac{\partial u_0}{\partial y_0}\frac{\partial u_1}{\partial y_0}+u_1\frac{\partial^2 u_0}{\partial y_0^2}+\frac{\partial u_0}{\partial y_0}\right)$$
$$+\frac{1}{2}y_1^2\left(u_0\frac{\partial^3 u_0}{\partial y_0^3}+\frac{\partial^2 u_0}{\partial y_0^2}\frac{\partial u_0}{\partial y_0}+2\frac{\partial u_0}{\partial y_0}\frac{\partial^2 u_0}{\partial y_0^2}\right)+\frac{1}{2}y_2\left(u_0\frac{\partial^2 u_0}{\partial y_0^2}+\frac{\partial u_0}{\partial y_0}\frac{\partial u_0}{\partial y_0}\right)=0$$

In this, the terms multiplying y_1 add to zero, as do the terms multiplying y_1^2 and those multiplying y_2. The sum of the terms multiplying y_1 vanishes on the use of

$$\frac{\partial}{\partial y_0}\left(u_0\frac{\partial u_1}{\partial y_0}+\frac{\partial u_0}{\partial y_0}u_1+u_0\right)=0$$

while the sums of terms multiplying y_1^2 and y_2 vanish on the use of

$$\frac{\partial^2}{\partial y_0^2}\left(u_0\frac{\partial u_0}{\partial y_0}+1\right)=0=\frac{\partial}{\partial y_0}\left(u_0\frac{\partial u_0}{\partial y_0}+1\right)$$

whence the third equation reduces to

$$\frac{1}{2}u_0\frac{\partial u_2}{\partial y_0}+\frac{1}{2}\frac{\partial u_0}{\partial y_0}u_2+u_1\frac{\partial u_1}{\partial y_0}+u_1+1=0 \qquad \text{(B.23)}$$

Again a sequence of equations on the reference domain is obtained, equations (B.21), (B.22) and (B.23), and, again they are free of the mapping. The mapping is lost in writing the equations on the reference domain. The earlier equations in the sequence eliminate the mapping in the later equations. The result, then, is an equation for u_0 at order zero. It is just the original equation for u written on the reference domain. Then comes an equation for u_1 in terms of u_0, succeeded by an equation for u_2 in terms of u_0 and u_1, etc.

A useful thing to conclude our discussion about domain perturbations is to explain a rule by which the correct equations on the reference domain can be obtained without the need to remove the mapping at each step by using equations found in earlier steps.

B.3 The Rule

The rule states that: To get the equations satisfied by u_0, u_1, u_2, etc. on the reference domain, replace u on the present domain by

$$u_0+\varepsilon u_1+\frac{1}{2}\varepsilon^2 u_2+\cdots$$

and then replace $\frac{\partial}{\partial y}$ by $\frac{\partial}{\partial y_0}$, $\frac{\partial}{\partial x}$ by $\frac{\partial}{\partial x_0}$, etc.

To check, let u satisfy the following equation on the current domain

$$u\frac{\partial u}{\partial y}+\varepsilon u+\varepsilon^2+1=0$$

Then, making the substitution we get

$$\left(u_0+\varepsilon u_1+\frac{1}{2}\varepsilon^2 u_2+\cdots\right)\left(\frac{\partial u_0}{\partial y_0}+\varepsilon\frac{\partial u_1}{\partial y_0}+\frac{1}{2}\varepsilon^2\frac{\partial u_2}{\partial y_0}+\cdots\right)$$
$$+\left(u_0+\varepsilon u_1+\frac{1}{2}\varepsilon^2 u_2+\cdots\right)+\varepsilon^2+1=0$$

and setting the coefficient of each power of ε to zero leads to

$$u_0\frac{\partial u_0}{\partial y_0}+1=0$$

$$u_0\frac{\partial u_1}{\partial y_0}+u_1\frac{\partial u_0}{\partial y_0}+u_0=0$$

$$\frac{1}{2}u_0\frac{\partial u_2}{\partial y_0}+\frac{1}{2}u_2\frac{\partial u_0}{\partial y_0}+u_1\frac{\partial u_1}{\partial y_0}+u_1+1=0$$

etc.

These are equations (B.21), (B.22) and (B.23) obtained earlier, but with a lot less work.

APPENDIX C
A SIMPLER PROBLEM TO SUPPORT THE (CRE) RESULTS

Consider a reaction surface that is being fed from a large well-mixed reservoir through a film of a certain thickness l. The reservoir is mainly filled with substance A and with a concentration C_{A0} that does not change. The substance A diffuses across the film to reach the reaction surface where the concentration is C_{Al} and where the reaction $A \rightleftarrows B$ is taking place to produce the substance B. Figure C-1 depicts the configuration of this problem and shows the concentration profile of the two substances.

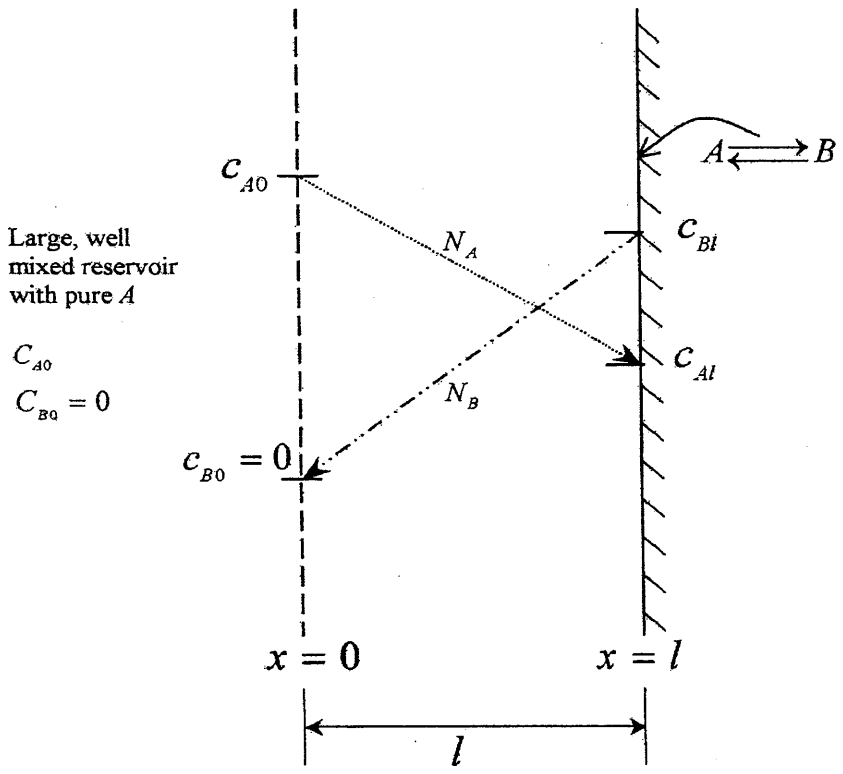


Figure C-1. Configuration of the simpler problem where the reaction $A \rightleftarrows B$ takes place on the right, fed by a reservoir of pure A through a film of thickness l.

At $x = 0$ (i.e., at the left boundary of the film) the concentrations of substances A and B are C_{A0} and $C_{B0} = 0$ respectively since there is no B in the reservoir. On the other hand, the concentrations are C_{Al} and C_{Bl} at the reaction surface where $x = l$. So A comes over from the film, makes B then B diffuses out and it is mixed in this large reservoir where its concentration is zero. The reaction $A \rightleftarrows B$ is just taking place on the reaction surface at $x = l$ and there are no reactions happening in the film.

In our model, the reaction surface is the electrode where the reaction takes place and for certain reaction speed we want to know as we make the thickness of the film larger and larger, sooner or later the diffusion will become so slow that the reaction will come to equilibrium. So what we really want to know is how big is l so that the diffusion is so slow and the reaction is so fast that C_{Al} and C_{Bl} at the reaction surface are related by equilibrium.

Let us now formulate the model for the simpler problem explained above. The reaction rate for the reaction $A \underset{\bar{k}}{\overset{\bar{k}}{\rightleftarrows}} B$ that takes place on the reaction surface is

$$r_A = \bar{k}C_{Bl} - \bar{k}C_{Al}$$

At steady state, the diffusion equations for species A and B in the film can be written as

$$D_A \frac{d^2C_A}{dx^2} = 0 \qquad \text{(C.1)}$$

and

$$D_B \frac{d^2C_B}{dx^2} = 0 \qquad \text{(C.2)}$$

where the boundary conditions, as shown in Figure C-1 are

$$C_A = C_{A0} \text{ at } x = 0 \text{ and } C_A = C_{Al} \text{ at } x = l$$

and

$$C_B = C_{B0} = 0 \text{ at } x = 0 \text{ and } C_B = C_{Bl} \text{ at } x = l$$

Now the solution to equations (C.1) and (C.2) subject to these boundary conditions are

$$C_A = C_{A0} + [C_{Al} - C_{A0}]\frac{x}{l} \tag{C.3}$$

and

$$C_B = (C_{Bl})\frac{x}{l} \tag{C.4}$$

In addition, the molar diffusion rate for species A (i.e., the rate of destruction of A) is

$$N_A = -D_A[C_{Al} - C_{A0}]\frac{1}{l} \tag{C.5}$$

and the molar diffusion rate for species B or the rate of formation of B is

$$N_B = -D_B C_{Bl}\frac{1}{l} \tag{C.6}$$

The above two rates are equal; moreover, they are equal to $\bar{k}C_{Bl} - \bar{k}C_{Al}$. As a result, we can write

$$D_B C_{Bl}\frac{1}{l} = \bar{k}C_{Bl} - \bar{k}C_{Al} \tag{C.7}$$

and by rearranging the above equation, one can easily get

$$\frac{C_{Al}}{C_{Bl}} = \frac{\bar{k} - \frac{D_B}{l}}{\bar{k}} \tag{C.8}$$

It is obvious that in the above equation as the distance between the two surfaces, l increases, the ratio $\frac{C_{Al}}{C_{Bl}}$ will approach $\frac{\vec{k}}{\bar{k}}$ (i.e., $C_{Al} = \frac{\vec{k}}{\bar{k}} C_{Bl}$) which is the equilibrium criteria. That is increasing the distances between the two surfaces will shift the system more towards the equilibrium and this is similar to what we found in our results.

Furthermore, this simpler problem predicts the correct dependence on the concentration C_{A0}. It is obvious from equation (C.5) that decreasing C_{A0} will make the transport rate weaker shifting the system more towards equilibrium. So if we consider l and C_{A0} as our input variables to this simpler problem, then increasing l and decreasing C_{A0} will both shift the system to equilibrium. This conclusion is in total agreement with the results obtained from the CRE model.

APPENDIX D
HEAT FLUX THROUGH A ROD

This simpler problem is given here to present the main idea that if two processes occur in series, then the slower one takes control of the overall rate. Now consider Figure D-1 which depicts a rod of uniform cross-sectional area attached to a well-stirred tank at one end, and exposed to the surroundings at the other, where the temperature is held constant.

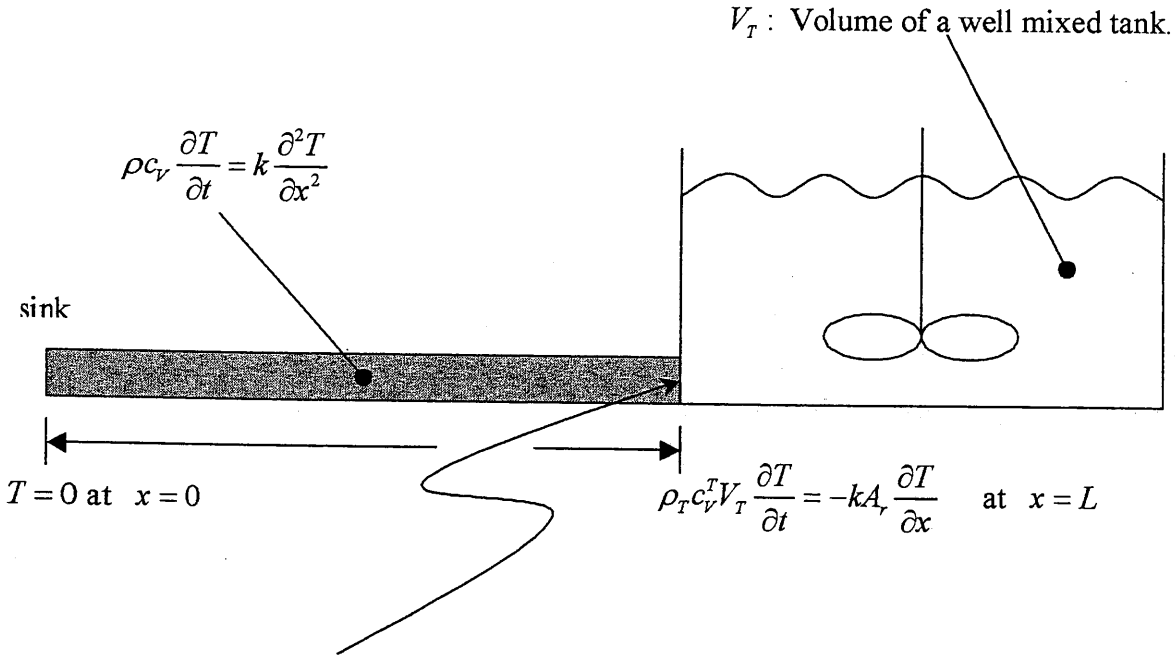


Figure D-1. Configuration of the heat flux through a rod problem.

In this problem two growth constants will appear, one that is related to how fast things happen in the reservoir and the other will be concerned with how fast things happen in the rod. Now there is only one σ that will be found for the whole problem

when it is solved. This σ will represent how things are changing with time in both the rod and the reservoir.

Now if we can think of these two rates to be in series making up the total rate, it is fair to say that if one σ is very slow and the other one is very fast then the overall rate will reflect almost entirely the slow one. So the main issue will be to figure out when we can approximate the σ for the whole problem by dropping the σ in the rod (i.e., the σ coming from the domain) and keeping the one in the reservoir, in other words the σ coming out of the boundary.

To begin dealing with this problem, let the temperature throughout the tank be T_H at $t = 0$ where $T_H > 0$. This is also the temperature of the end of the rod attached to the tank. The other end temperature of the rod is maintained at zero for all time. When $t > 0$, the tank will start losing heat by conduction and T_H will decrease, although it will always be uniform in the well-stirred tank. As heat passes through the rod its temperature will change and this will affect the rate of heat loss.

Now, in the domain (i.e., through the rod) the heat conduction equation is

$$\rho c_V \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} \qquad \text{at} \qquad 0 < x < L \tag{D.1}$$

where ρ is the density of the rod material, c_V is the heat capacity of the rod and k is the thermal conductivity of the rod all of which are taken to be constant. The first boundary condition is

$$T = 0 \qquad \text{at } x = 0 \tag{D.2}$$

that is the temperature is held at zero for all time at the left end of the rod. The other boundary condition is obtained from an energy balance at $x = L$ (i.e., where the rod is connected to the tank). The equation at this boundary is

$$\rho_T c_v^T V_T \frac{\partial T}{\partial t} = -kA_r \frac{\partial T}{\partial x} \qquad \text{at } x = L \tag{D.3}$$

where ρ_T is the density of the material in the tank, c_v^T is the heat capacity of the material in the tank and V_T is the volume occupied by the material in the tank. The temperature T at $x = L$ is taken to be T^T whence T^T is eliminated from the problem.

Now at this stage we are ready to introduce σ to the problem by expecting a solution for T in the following form

$$T = \hat{T}(x)e^{-\sigma t}$$

In a sensible view of the problem and according to the above equation, σ is introduced as a decay constant and our job is to estimate its value. Dealing with the domain equation first, let us substitute for T in equation (D.1) and differentiate and rearrange it to get

$$\frac{d^2\hat{T}}{dx^2} = -\frac{\rho c_V}{k}\sigma\hat{T}(x) \tag{D.4}$$

Now, by scaling x as $x^* = \frac{x}{L}$ and substituting this expression into equation (D.4) we get

$$\frac{d^2\hat{T}}{dx^{*2}} = -\frac{\rho c_V L^2}{k}\sigma\hat{T}(x^*) \tag{D.5}$$

It is clear from this domain equation that the right hand side that contains σ can be ignored if ρ, c_V and L of the rod are small or if k is large. That is to say, for example, that σ coming from the domain can be neglected if the rod is too short or the thermal

conductivity of the rod is large so the change in the temperature in the rod will die out very fast. For simplicity, let us call the term $-\frac{\rho c_V}{k}L^2$, $-A^2$ and write equation (D.5) as

$$\frac{d^2\hat{T}}{dx^{*2}} + \sigma A^2 \hat{T}\left(x^*\right) = 0 \tag{D.6}$$

Equation (D.6) is the domain equation obtained after separation of variables and scaling the problem to reduce the number of parameters. The solution of equation (D.6) is

$$\hat{T} = c_1 \cos\left(A\sqrt{\sigma}x^*\right) + c_2 \sin\left(A\sqrt{\sigma}x^*\right) \tag{D.7}$$

Now using the first boundary condition in it's scaled form (i.e., $\hat{T} = 0$ at $x^* = 0$) we can conclude that $c_1 = 0$ and equation (D.7) will be reduced to

$$\hat{T} = c_2 \sin\left(A\sqrt{\sigma}x^*\right) \tag{D.8}$$

Turning to the second boundary condition and defining $T = \hat{T}(x)e^{-\sigma t}$ to separate variables and using $x^* = \frac{x}{L}$ to scale the length as we did before, we get the following equation

$$\frac{d\hat{T}}{dx^*} = \frac{\rho_T c_v^T L V_T}{A_r k}\sigma \hat{T}\left(x^*\right) \quad \text{at} \quad x^* = 1 \tag{D.9}$$

where the effect of the different parameters of the tank and the rod on σ at the boundary appear. For example, it is clear from this equation that if the volume of the tank or its heat capacity is large then any change in the temperature at the boundary will take a long time to die out. Now by defining $B^2 = \frac{\rho_T c_v^T L V_T}{A_r k}$, equation (D.9) will become

$$\frac{d\hat{T}}{dx^*} = B^2 \sigma \hat{T}\left(x^*\right) \quad \text{at} \quad x^* = 1 \tag{D.10}$$

Equation (D.8) can be used with equation (D.10) to get an expression for σ as a function of the input parameters namely, A^2 and B^2. So by substituting equation (D.8) into equation (D.10) we get

$$\tan\left(A\sqrt{\sigma}\right)-\frac{A}{B^2}\frac{1}{\sqrt{\sigma}}=0 \tag{D.11}$$

Equation (D.11) can be used to calculate σ if the variables A and B are given.

Let us now turn to see what happens if σ in the domain is neglected (i.e., if σ is set to zero in the domain equation). Then equation (D.6) will reduce to

$$\frac{d^2\hat{T}}{dx^{*2}}=0 \tag{D.12}$$

whose solution is

$$\hat{T}=c_1x^*+c_2 \tag{D.13}$$

Applying the boundary condition $\hat{T}=0$ at $x^*=0$ will give $c_2=0$ and equation (D.13) will reduce to

$$\hat{T}=c_1x^* \tag{D.14}$$

Now, by applying the second boundary condition i.e., equation (D.10), we get the following equation for σ as a function of B

$$\sigma=\frac{1}{B^2} \tag{D.15}$$

Equations (D.11) and (D.15) are the two equations we want to focus on. Although, σ can be easily calculated from either expression for any values of A and B, notice how dropping the growth constant from the domain equation simplifies the final expression and enables us to get an explicit equation for σ. So what is left to do is to

input different values of A and B and calculate σ using the two equations and compare the results. Table D-1 shows this comparison.

Table D-1. The effect of dropping the decay constant from the domain equation for the rod problem.

A	B	σ from $\tan\left(A\sqrt{\sigma}\right)-\frac{A}{B^2}\frac{1}{\sqrt{\sigma}}=0$ (Keeping σ in the domain)	σ from $\sigma=\frac{1}{B^2}$ (Dropping σ from the domain)
0.0001	1	0.999	1
0.001	1	0.999	1
0.01	1	0.999	1
0.1	1	0.998	1
1	1	0.86	1
10	1	0.467	1
100	1	0.487	1
1000	1	0.501	1
10000	1	0.499	1

In Table D-1 above, B is fixed to one for simplicity and A is the variable that we kept changing. The table shows that for small values of A compared to B, dropping σ from the domain has nearly no effect on the precision of the results obtained. This conclusion is still valid even if B is just one order of magnitude larger than A. And it is clear from the table that when the order of magnitude of A and B is the same or that of A surpasses the order of magnitude of B, then the approximation of dropping σ from the domain produces inaccurate results.

It is important to remind the reader here what is meant by A and B. The parameter A^2 was defined as $A^2=\frac{\rho c_V}{k}L^2$ which is totally determined by the variables of the rod and which can increase by choosing a material with large density or heat capacity etc. On the other hand, the parameter B^2 which is defined by $B^2=\frac{\rho_T c_v^T L V_T}{A_r k}$ is affected by both

the variables related to the rod and those corresponding to the tank. Also it can be adjusted by changing the variables appear in it, for example it can become larger for larger volume or heat capacity of the tank etc. So these parameters are fully under our control.

So what we learned from this model problem is that the order of magnitude of the factor that is multiplied by each σ in the equations will determine if dropping σ in the domain is a good approximation or not. That is to say, if A, which is the factor multiplied by σ in equation (D.6) corresponding to the domain, was small compared to B, that is multiplied to the other σ appearing in equation (D.10), then σ in the domain can be dropped with no harm.

So what we expect is this: scaling the equations properly and evaluating the order of magnitude for every factor multiplying a σ will determine when dropping σ from one part a problem and retaining it in another will be a good move.

APPENDIX E
THE EXPANSION OF THE CURVATURE TO SECOND ORDER

The expressions for the curvature of the surface at both the anode and the cathode were given in chapter 2. Then the expansion of the curvature to first order was enough for the linear perturbation analysis used in chapters 3 to 5. But when we extend our calculations to the weakly non linear regime, we were in need for the expression of the curvature to the second order.

The expression for the curvature at the anode as was given back in chapter 2 is

$$2H^A = \frac{\dfrac{d^2Y^A}{dx^2}}{\left(1+\left(\dfrac{dY^A}{dx}\right)^2\right)^{\frac{3}{2}}} \tag{E.1}$$

where Y can be expanded to second order in ε such that

$$Y = Y_0 + \varepsilon Y_1 + \frac{1}{2}\varepsilon^2 Y_2 \tag{E.2}$$

and the first derivative of Y with respect to x is simply

$$\frac{dY}{dx} = \frac{dY_0}{dx_0} + \varepsilon\frac{dY_1}{dx_0} + \frac{1}{2}\varepsilon^2\frac{dY_2}{dx_0} \tag{E.3}$$

and noticing that Y_0 is not a function of x_0 so that $\dfrac{dY_0}{dx_0} = 0$ and the second derivative $\dfrac{d^2Y}{dx^2}$ will turn to

$$\frac{d^2Y}{dx^2} = \varepsilon\frac{d^2Y_1}{dx_0^2} + \frac{1}{2}\varepsilon^2\frac{d^2Y_2}{dx_0^2} \tag{E.4}$$

Now to go on looking for the second order expansion for the curvature let us say that $x = \left(\frac{dY}{dx}\right)^2$ and then recall that the Taylor series expansion for $(1+x)^{-\frac{3}{2}}$ is given by

$$(1+x)^{-\frac{3}{2}} = 1 - \frac{3}{2}x + \frac{15}{8}x^2 + \ldots$$

so the expression for x should be obtained from equation (E.3) by squaring the right hand side and writing it to just the second order of ε will be

$$x = \left(\frac{dY}{dx}\right)^2 = \varepsilon^2 \left(\frac{dY_1}{dx_0}\right)^2 \tag{E.5}$$

The next step will be to substitute for the expressions in equation (E.1). So we can write

$$\frac{\frac{d^2Y}{dx^2}}{\left(1+\left(\frac{dY}{dx}\right)^2\right)^{\frac{3}{2}}} = \left(\varepsilon \frac{d^2Y_1}{dx_0^2} + \frac{1}{2}\varepsilon^2 \frac{d^2Y_2}{dx_0^2}\right)\left(1 - \frac{3}{2}\varepsilon^2 \left(\frac{dY_1}{dx_0}\right)^2\right) \tag{E.6}$$

and this will lead to the following equation of the curvature at the anode when expanded to second order of ε

$$2H^A = \varepsilon \frac{d^2Y_1}{dx_0^2} + \frac{1}{2}\varepsilon^2 \frac{d^2Y_2}{dx_0^2} \tag{E.7}$$

On the other hand the curvature at the cathode as given earlier is

$$2H^C = \frac{-\frac{d^2Y^C}{dx^2}}{\left(1+\left(\frac{dY^C}{dx}\right)^2\right)^{\frac{3}{2}}} \tag{E.8}$$

so $2H^C$ is just different from $2H^A$ by the negative sign that multiplies $\frac{d^2Y}{dx^2}$. As a result the expansion for $2H^C$ will be similar to that of $2H^A$ except it will have the opposite sign and since our work in this chapter will not require more than going to second order non linear calculations, the expressions for $2H^A$ and $2H^C$ are

$$2H^A = \varepsilon \frac{d^2Y_1^A}{dx_0^2} + \frac{1}{2}\varepsilon^2 \frac{d^2Y_2^A}{dx_0^2} \tag{E.9}$$

and

$$2H^C = -\varepsilon \frac{d^2Y_1^C}{dx_0^2} - \frac{1}{2}\varepsilon^2 \frac{d^2Y_2^C}{dx_0^2} \tag{E.10}$$

APPENDIX F
THE EXPANSION OF THE INTEGRAL CONDITIONS TO SECOND ORDER

The scaled integral conditions that represent the constant volume and the constant average ionic concentration are

$$\int_0^{W_0}\int_{Y^A}^{Y^C} dydx = \text{constant} \tag{F.1}$$

and

$$\int_0^{W_0}\int_{Y^A}^{Y^C} c\ dydx = \text{constant} \tag{F.2}$$

respectively.

Now these two equations are written on the present domain, which is unknown, and in order to use them we have to expand them in powers of ε as integrals over the reference domain, the domain on which we are solving our equations. This can be done by expressing the integral over the present domain in x and y as an integral over the reference domain in x_0 and y_0.

Taking equation (F.1) we write

$$\int_0^{W_0}\int_{Y^A}^{Y^C} dydx = \int_0^{W_0}\int_0^1 \frac{\partial(x,y)}{\partial(x_0,y_0)}\, dy_0 dx_0 = \text{constant} \tag{F.3}$$

where

$$\frac{\partial(x,y)}{\partial(x_0,y_0)}=\begin{vmatrix}\dfrac{\partial x}{\partial x_0} & \dfrac{\partial y}{\partial x_0}\\ \dfrac{\partial x}{\partial y_0} & \dfrac{\partial y}{\partial y_0}\end{vmatrix}=\frac{\partial x}{\partial x_0}\frac{\partial y}{\partial y_0}-\frac{\partial y}{\partial x_0}\frac{\partial x}{\partial y_0}$$

and noticing that the mapping is given by

$$x = x_0 \tag{F.4}$$

and

$$y = y_0 + \varepsilon y_1 + \frac{1}{2}\varepsilon^2 y_2 + \cdots \tag{F.5}$$

so $\dfrac{\partial(x,y)}{\partial(x_0,y_0)}$ is given by

$$\frac{\partial(x,y)}{\partial(x_0,y_0)} = 1 + \varepsilon\frac{\partial y_1}{\partial y_0} + \frac{1}{2}\varepsilon^2\frac{\partial y_2}{\partial y_0} \tag{F.6}$$

and hence to first order we have

$$\int_0^{W_0}\int_{Y^A}^{Y^C} dy dx = \int_0^{W_0}\int_0^1 \left(1+\varepsilon\frac{\partial y_1}{\partial y_0}\right) dy_0 dx_0 = \int_0^{W_0}\int_0^1 dy_0 dx_0 + \varepsilon\int_0^{W_0}\int_0^1 \frac{dy_1}{dy_0} dy_0 dx_0 = \text{constant} \tag{F.7}$$

hence the correction, viz., $\varepsilon\displaystyle\int_0^{W_0}\int_0^1 \frac{dy_1}{dy_0} dy_0 dx_0$, to the volume of the base state, namely,

$\displaystyle\int_0^{W_0}\int_0^1 dy_0 dx_0$, must vanish and we have

$$\int_0^{W_0}\int_0^1 \frac{dy_1}{dy_0} dy_0 dx_0 = \int_0^{W_0}\left(Y_1^C - Y_1^A\right) dx_0 = 0 \tag{F.8}$$

or,

$$\int_0^{W_0} Y_1^C dx_0 - \int_0^{W_0} Y_1^A dx_0 = 0 \qquad \text{(F.9)}$$

The equation, which requires that the average concentration of the ions in the solution remain constant, can be written on the reference domain as

$$\text{constant} = \int_0^{W_0}\int_{Y^A}^{Y^C} c\, dydx = \int_0^{W_0}\int_0^1 \left(c_0 + \varepsilon\left(c_1 + y_1\frac{dc_0}{dy_0}\right)\right)\left(1+\varepsilon\frac{dy_1}{dy_0}\right) dy_0 dx_0 \qquad \text{(F.10)}$$

Again we recover the base equation, $\int_0^{W_0}\int_0^1 c_0\, dy_0 dx_0 = \text{constant}$, plus a correction which must be zero, viz.,

$$\varepsilon\int_0^{W_0}\int_0^1 \left(c_1 + c_0\frac{dy_1}{dy_0} + y_1\frac{dc_0}{dy_0}\right) dy_0 dx_0 = \varepsilon\left[\int_0^{W_0}\int_0^1 c_1 dy_0 dx_0 + \int_0^{W_0}\int_0^1 \frac{d}{dy_0}(c_0 y_1)\, dy_0 dx_0\right] = 0 \qquad \text{(F.11)}$$

Our second equation is then

$$\int_0^{W_0} c_1 dx_0 + \int_0^{W_0} c_0^C Y_1^C dx_0 - \int_0^{W_0} c_0^A Y_1^A dx_0 = 0 \qquad \text{(F.12)}$$

Now constant volume requires

$$\int_0^{W_0}\int_{Y^A}^{Y^C} dydx = \int_0^{W_0}\int_0^1 \frac{\partial(x,y)}{\partial(x_0,y_0)} dy_0 dx_0 = \int_0^{W_0}\int_0^1 dy_0 dx_0 + \varepsilon\int_0^{W_0}\int_0^1 \frac{dy_1}{dy_0} dy_0 dx_0 + \frac{1}{2}\varepsilon^2\int_0^{W_0}\int_0^1 \frac{dy_2}{dy_0} dy_0 dx_0 = \text{constant}$$

(F.13)

and hence at second order we must have

$$\int_0^{W_0} Y_2^C dx_0 - \int_0^{W_0} Y_2^A dx_0 = 0 \qquad \text{(F.14)}$$

To get another equation turn to the condition $\int_0^{W_0}\int_0^1 c\, dydx = \text{constant}$ which

expresses the fact that the average ion concentration remain constant. It can be written

$$\int_0^{W_0}\int_{Y^A}^{Y^C} c dydx = \int_0^{W_0}\int_0^1 c\frac{\partial(x,y)}{\partial(x_0,y_0)}\, dy_0 dx_0 = \text{constant}$$

where

$$c = c_0 + \varepsilon\left(c_1 + y_1\frac{\partial c_0}{\partial y_0}\right) + \frac{1}{2}\varepsilon^2\left(c_2 + 2y_1\frac{\partial c_1}{\partial y_0} + y_1^2\frac{\partial^2 c_0}{\partial y_0^2} + y_2\frac{\partial c_0}{\partial y_0}\right)$$

and

$$\frac{\partial(x,y)}{\partial(x_0,y_0)} = 1 + \varepsilon\frac{\partial y_1}{\partial y_0} + \frac{1}{2}\varepsilon^2\frac{\partial y_2}{\partial y_0}$$

whence at second order we have

$$\int_0^{W_0}\int_0^1\left[\frac{1}{2}\left(c_2 + 2y_1\frac{\partial c_1}{\partial y_0} + y_1^2\frac{\partial^2 c_0}{\partial y_0^2} + y_2\frac{\partial c_0}{\partial y_0}\right) + \left(c_1 + y_1\frac{\partial c_0}{\partial y_0}\right)\frac{\partial y_1}{\partial y_0} + \frac{1}{2}c_0\frac{\partial y_2}{\partial y_0}\right] dy_0 dx_0 = 0$$

which can be written

$$\frac{1}{2}\int_0^{W_0}\int_0^1\left[c_2 + \frac{d}{dy_0}(c_0 y_2) + \frac{d}{dy_0}(c_1 y_1) + \frac{d}{dy_0}\left(\frac{dc_0}{dy_0}y_1^2\right)\right] dy_0 dx_0 = 0 \qquad \text{(F.15)}$$

which upon using $c_1 = 0$ we have

$$\int_0^{W_0}\int_0^1 c_2 dy_0 dx_0 + \int_0^{W_0}\int_0^1 \frac{d}{dy_0}(c_0 y_2) dy_0 dx_0 + \int_0^{W_0}\int_0^1 \frac{d}{dy_0}\left(\frac{dc_0}{dy_0}y_1^2\right) dy_0 dx_0 = 0 \qquad \text{(F.16)}$$

APPENDIX G
CALCULATING THE DETERMINANT FROM THE NONLINEAR PROBLEM

The matrix that contains the factors multiplying c_2^A and ϕ_2^A which was obtained from the nonlinear second order calculation is

$$\begin{bmatrix} \dfrac{1}{k^2 c_0^C} - \dfrac{1}{K_A^2 c_0^A} & \dfrac{1}{k^2} - \dfrac{1}{K_A^2} \\ 1 + \dfrac{c_0^C - c_0^A}{\gamma K_A^2 c_0^A} & \dfrac{c_0^C - c_0^A}{\gamma K_A^2} \end{bmatrix}$$

which determinant is given by

$$\det = \frac{\left(K_A^2 c_0^A - k^2 c_0^C\right)\left(c_0^C - c_0^A\right)}{\gamma c_0^A c_0^C K_A^4 k^2} - \frac{\left(K_A^2 - k^2\right)\left(c_0^C - c_0^A + \gamma K_A^2 c_0^A\right)}{\gamma c_0^A K_A^4 k^2}$$

then taking $\gamma K_A^2 k^2 c_0^A c_0^C$ as a common denominator and performing the multiplication of the different terms we get

$$\det = \frac{1}{\gamma K_A^2 k^2 c_0^A c_0^C}\left(2c_0^A c_0^C - \left(c_0^A\right)^2 - \left(c_0^C\right)^2 + c_0^A c_0^C\left(\gamma k^2 - \gamma K_A^2\right)\right)$$

Now the expressions for K_A^2 and k^2 as given previously are

$$K_A^2 = -\frac{1}{\gamma}\left(\frac{dc_0/dy_0}{c_0^A} + \frac{d\phi_0}{dy_0}\right) \text{ or } -\gamma K_A^2 = \frac{dc_0/dy_0}{c_0^A} + \frac{d\phi_0}{dy_0}$$

and

$$k^2 = -\frac{1}{\gamma}\left(\frac{dc_0/dy_0}{c_0^C} + \frac{d\phi_0}{dy_0}\right) \text{ or } \gamma k^2 = -\frac{dc_0/dy_0}{c_0^C} - \frac{d\phi_0}{dy_0}$$

and when we substituted for K_A^2 and k^2 in the numerator of the expression for the determinant we get

$$\det = \frac{-\left(c_0^A\right)^2 - \left(c_0^C\right)^2 + 2c_0^A c_0^C - \frac{dc_0}{dy_0} c_0^A + \frac{dc_0}{dy_0} c_0^C}{\gamma c_0^A c_0^C K_A^2 k^2}$$

then when the numerator is put in terms of U_c by using our knowledge that $\frac{dc_0}{dy_0} = -2U_c$, $c_0^A = 1 + U_c$ and $c_0^C = 1 - U_c$ all from the base solution, one will get

$$\det = \frac{-1 - 2U_c - U_c^2 - 1 + 2U_c - U_c^2 + 2 - 2U_c^2 + 2U_c + 2U_c^2 - 2U_c + 2U_c^2}{\gamma c_0^A c_0^C K_A^2 k^2}$$

which can be shown to be equal to zero upon collecting similar terms together as

$$\det = \frac{4U_c^2 - 4U_c^2 + 4U_c - 4U_c + 2 - 2}{\gamma c_0^A c_0^C K_A^2 k^2} = 0$$

APPENDIX H
WEAKLY NONLINEAR CALCULATIONS WITHOUT THE APPLICATION OF THE MIGRATION TERM APPROXIMATION

In this appendix it will be shown how a person will reach the same conclusion obtained in chapter 6 even if c was not equal to $\overline{c}$ in the migration term. Since the derivation was explained in detail in chapter 6, our job here will be to present the main equations and to show where these equations are different from those in chapter 6.

H.1 The Nonlinear Equations

The domain equations that hold through the electrolytic solution are

$$\frac{\partial c}{\partial t} = D\nabla^2 c \tag{H.1}$$

and

$$P\nabla^2 c + \frac{z_1 F}{RT}\nabla\cdot\left(c\nabla\phi\right) = 0 \tag{H.2}$$

At the boundaries, the following equations must be satisfied

$$D\,\vec{n}\cdot\nabla c = \frac{-z_1 z_2 D_2}{z_1 D_1 - z_2 D_2} c_M\left[\vec{n}\cdot\vec{u} + \vec{n}\cdot\vec{U}\right] \quad \text{(at both electrodes)} \tag{H.3}$$

$$P\,\vec{n}\cdot\nabla c + \frac{z_1 F}{RT} c\,\vec{n}\cdot\nabla\phi = \frac{z_1^2 c_M}{z_1 D_1 - z_2 D_2}\left[\vec{n}\cdot\vec{u} + \vec{n}\cdot\vec{U}\right] \quad \text{(at both electrodes)} \tag{H.4}$$

$$\frac{c^A}{\overline{c}} = e^{\frac{z_1 F}{RT}\left[\Delta\phi^A - \Delta\phi_{EQ} - \frac{\gamma}{z_1 F c_M}2H^A\right]} \quad \text{(at the anode)} \tag{H.5}$$

and

$$\frac{c^C}{\overline{c}} = e^{\frac{z_1 F}{RT}\left[\Delta\phi^C - \Delta\phi_{EQ} - \frac{\gamma}{z_1 F c_M}2H^C\right]} \quad \text{(at the cathode)} \tag{H.6}$$

where equations (H.2) and (H.4) are different from the corresponding equations given in chapter 6. The next step will be to scale the nonlinear equations.

H.2 The Scaled Nonlinear Equations

Following the same scaling procedure in chapter 6 and after dropping the superscript stars corresponding to scaled variables we obtain

$$\frac{\partial c}{\partial t} = \nabla^2 c \tag{H.7}$$

and

$$P\ \nabla^2 c + \nabla \cdot (c \nabla \phi) = 0 \tag{H.8}$$

on the domain, while at the boundaries, the equations are

$$\vec{n} \cdot \nabla c = \frac{-2}{U_{\text{lim}}} \left[\vec{n} \cdot \vec{u} + \vec{n} \cdot \vec{U} \right] \quad (\text{at both electrodes}) \tag{H.9}$$

$$c\ \vec{n} \cdot \nabla \phi = \frac{-2Z}{U_{\text{lim}}} \left[\vec{n} \cdot \vec{u} + \vec{n} \cdot \vec{U} \right] \quad (\text{at both electrodes}) \tag{H.10}$$

$$c^A = e^{\Delta\phi^A - \Delta\phi_{EQ} - \gamma 2 H^A} \quad (\text{at the anode}) \tag{H.11}$$

and

$$c^C = e^{\Delta\phi^C - \Delta\phi_{EQ} - \gamma 2 H^C} \quad (\text{at the cathode}) \tag{H.12}$$

Equations (H.8) and (H.10) are the two equations that differ from their corresponding equations in chapter 6 namely. Now we are ready to find the base solution, which we will be doing next.

H.3 The Base Solution

Here we are seeking a one dimensional steady state solution for the nonlinear equations presented above. A subscript zero will be introduced from here on to denote the base solution and the fraction U/U_{lim} will be simply denoted by U.

The solution to the concentration profile will be the same as that in chapter 6, so one can write

$$\frac{dc_0}{dy_0} = -2U_0 \text{ at } y_0 = 0 \text{ and at } y_0 = 1 \tag{H.13}$$

and

$$c_0 = (-2y_0 + 1)U_0 + 1 \tag{H.14}$$

so at the anode where $y_0 = 0$, the concentration is

$$c_0^A = 1 + U_0 \tag{H.15}$$

while at $y_0 = 1$ (i.e., at the cathode) we have

$$c_0^C = 1 - U_0 \tag{H.16}$$

Now when solving for the electrical potential, equation (H.8) will turn into

$$\frac{d}{dy_0}\left[c_0 \frac{d\phi_0}{dy_0}\right] = 0 \tag{H.17}$$

while equation (H.10) at the boundaries will be

$$\frac{d\phi_0}{dy_0} = \frac{-2ZU_0}{c_0} \tag{H.18}$$

and solving this equation along with equation (H.13) we obtain

$$\phi_0 = Z \ln c_0 + \text{constant} \tag{H.19}$$

then realizing that $\phi_0 = \phi_0^A$ at $y_0 = 0$ and $\phi_0 = \phi_0^C$ at $y_0 = 1$, equation (H.19) will be

$$\phi_0^C - \phi_0^A = Z \ln \frac{c_0^C}{c_0^A} \tag{H.20}$$

Finally using equations (H.11) and (H.12) along with equation (H.20), the following equation is obtained to relate the voltage drop to the velocity of the surface

$$V^A - V^C = (1+Z)\ln\left(\frac{1+U_0}{1-U_0}\right) \tag{H.21}$$

Looking to the base solution, it is obvious that according to this model the electrical potential is not constant as it was in chapter 6 while the base relation between the voltage drop and the velocity of the surface is simpler than it was in chapter 6. The following step is to work the first order problem to see what we can learn from it.

H.4 The First Order Problem

In this section, our main purpose will be to check if the first order calculations will lead to similar results as those in chapter 6. First, the c problem will not change from that in chapter 6 and the following equations can be written

$$\nabla_0^2 c_1 = 0 \tag{H.22}$$

and

$$\frac{dc_1}{dy_0} = 0 \text{ at } y_0 = 0 \text{ and at } y_0 = 1 \tag{H.23}$$

while when dealing with the electrical potential problem, perturbing equation (H.8) will result in getting

$$\nabla_0 (c_0 \nabla_0 \phi_1) + \nabla_0 (c_1 \nabla_0 \phi_0) = 0 \tag{H.24}$$

and the perturbed version of equation (H.10) is

$$c_0 \frac{d\phi_1}{dy_0} + c_1 \frac{d\phi_0}{dy_0} = 0 \tag{H.25}$$

Then perturbing the chemical reaction equilibrium equations will yield

$$\frac{d^2Y_1^A}{dx_0^2}+\frac{1}{\gamma}\left(\frac{dc_0/dy_0}{c_0^A}+\frac{d\phi_0^A}{dy_0}\right)Y_1^A=-\frac{1}{\gamma}\left(\phi_1+\frac{c_1}{c_0^A}\right) \text{ at the anode} \qquad \text{(H.26)}$$

and

$$\frac{d^2Y_1^C}{dx_0^2}-\frac{1}{\gamma}\left(\frac{dc_0/dy_0}{c_0^C}+\frac{d\phi_0^C}{dy_0}\right)Y_1^C=-\frac{1}{\gamma}\left(\phi_1+\frac{c_1}{c_0^C}\right) \text{ at the cathode} \qquad \text{(H.27)}$$

which are different from those in chapter 6 in one way which is that the term $\frac{d\phi_0}{dy_0}$ is not a constant and it is different at each equation. The last two equations in the first order problem are the two integral relations which resulted from the constant volume and the constant average concentration conditions viz.,

$$\int_0^{W_0} Y_1^C dx_0-\int_0^{W_0} Y_1^A dx_0=0 \qquad \text{(H.28)}$$

and

$$\int_0^{W_0} c_1 dx_0+\int_0^{W_0} c_0^C Y_1^C dx_0+\int_0^{W_0} c_0^A Y_1^A dx_0=0 \qquad \text{(H.29)}$$

These are no different than those given in chapter 6. From here on, one can follow the same steps in chapter 6 to conclude that

$$c_1=\phi_1=Y_1^A=0 \qquad \text{(H.30)}$$

and

$$Y_1^C=D_1\cos kx_0 \qquad \text{(H.31)}$$

where $k^2=-\frac{1}{\gamma}\left(\frac{d\phi_0^C}{dy_0}+\frac{dc_0/dy_0}{c_0^C}\right)$.

This completes the first order calculations with no major differences from the calculations in chapter 6. We will now go on to investigate weakly nonlinear calculations.

H.5 The Second Order Problem

Here we will investigate what will happen to the velocity of the surface as we increase the voltage beyond the critical point. Based on that, one will write

$$V^C = V_c^C - \frac{1}{2}\varepsilon^2 \tag{H.32}$$

and

$$U = U_c + \frac{1}{2}\varepsilon^2\, U_2 \tag{H.33}$$

Starting with the c problem, we will write the equations as they appear in chapter 6 since they are not affected by the migration term approximation viz.,

$$\nabla_0^2 c_2 = 0 \tag{H.34}$$

and

$$\frac{\partial c_2}{\partial y_0} = -2U_2 \text{ at } y_0 = 0 \text{ and } y_0 = 1 \tag{H.35}$$

while the solution is

$$c_2 = -2\, U_2\, y_0 + \text{constant} \tag{H.36}$$

and at the anode we have

$$c_2^A = c_2(y_0 = 0) = \text{constant} \tag{H.37}$$

then at the cathode one can write

$$c_2^C = c_2(y_0 = 1) = -2\, U_2 + c_2^A \tag{H.38}$$

Now dealing with the electrical potential equations is different from that in chapter 6. First, equation (H.8) on the domain when expanded to second order will be

$$\nabla_0 c_0 \nabla_0 \phi_2 + \nabla_0 c_2 \nabla_0 \phi_0 + c_0 \nabla_0^2 \phi_2 + c_2 \nabla_0^2 \phi_0 = 0 \tag{H.39}$$

which can be written as

$$\nabla_0 \left(c_0 \nabla_0 \phi_2 + c_2 \nabla_0 \phi_0 \right) = 0 \tag{H.40}$$

Moreover, the second order expansion to equation (H.10), which is valid at the boundaries, will lead to

$$c_0 \frac{d\phi_2}{dy_0} + c_2 \frac{d\phi_0}{dy_0} = -2\ Z\ U_2 \tag{H.41}$$

so this equation shows that ϕ_2 is a function of only y_0 and not x_0. Based on that, equation (H.40) can be written in this form

$$c_0 \frac{d\phi_2}{dy_0} + c_2 \frac{d\phi_0}{dy_0} = \text{constant} \tag{H.42}$$

This means that the following equation is valid everywhere viz.,

$$c_0 \frac{d\phi_2}{dy_0} + c_2 \frac{d\phi_0}{dy_0} = -2\ Z\ U_2 \tag{H.43}$$

Now to get the expression for ϕ_2, let us divide equation (H.43) by c_0 and then substitute for c_2, $\frac{d\phi_0}{dy_0}$ and c_0 from equations (H.36), (H.18) and (H.14) respectively, to get

$$\frac{d\phi_2}{dy_0} = \frac{-2\ Z\ U_2}{-2U_c y_0 + c_0^A} - \frac{4ZU_c U_2\ y_0}{\left(-2U_c y_0 + c_0^A\right)^2} + \frac{2ZU_c c_2^A}{\left(-2U_c y_0 + c_0^A\right)^2} \tag{H.44}$$

and the solution to this equation is simply

$$\phi_2 = \frac{Z\ c_2^A}{c_0} - \frac{Z\ c_0^A\ U_2}{U_c\ c_0} + \text{constant} \tag{H.45}$$

then at the anode, a person can write

$$\phi_2^A = \frac{Z\, c_2^A}{c_0^A} - \frac{Z\, U_2}{U_c} + \text{constant} \tag{H.46}$$

while at the cathode, it is true that

$$\phi_2^C = \phi_2^A + \frac{2\, Z\, U_c c_2^A}{c_0^A c_0^C} - \frac{2\, Z\, U_2}{c_0^C} \tag{H.47}$$

which is different than the expression for ϕ_2^C in chapter 6. Turning to the CRE equations at the electrodes, when expanded to second order, one will get at the anode

$$\frac{d^2 Y_2^A}{dx_0^2} - K_A^2 Y_2^A = -\frac{1}{\gamma}\left(\phi_2^A + \frac{c_2^A}{c_0^A}\right) \tag{H.48}$$

where $K_A^2 = -\frac{1}{\gamma}\left(\frac{d\phi_0^A}{dy_0} + \frac{dc_0/dy_0}{c_0^A}\right)$ which is exactly what we had earlier in chapter 6. On the other hand, the CRE equation at the cathode to second order is

$$\frac{d^2 Y_2^C}{dx_0^2} + k^2 Y_2^C = \frac{1}{\gamma}\left(\phi_2^C + \frac{c_2^C}{c_o^C} + 1\right) - \frac{1}{\gamma} D_1^2 \cos^2 kx_0 \left(\frac{d\phi_0^C}{dy_0} + \gamma k^2\right) + \frac{1}{\gamma}\frac{d^2\phi_0^C}{dy_0^2} D_1^2 \cos^2 kx_0 \tag{H.49}$$

with the only difference between this equation and its companion in chapter 6 is the presence of the term $\frac{1}{\gamma}\frac{d^2\phi_0^C}{dy_0^2} D_1^2 \cos^2 kx_0$ on the right hand side which was zero previously since $\frac{d^2\phi_0^C}{dy_0^2}$ was equal to zero.

Now the integral conditions to second order are the same as those in chapter 6 namely,

$$\int_0^{W_0} Y_2^C dx_0 - \int_0^{W_0} Y_2^A dx_0 = 0 \tag{H.50}$$

and

$$\int_0^{W_0}\int_0^1 c_2 dy_0 dx_0 + \int_0^{W_0} c_0^C Y_2^C dx_0 - \int_0^{W_0} c_0^A Y_2^A dx_0 + \frac{dc_0}{dy_0}\left[\int_0^{W_0}\left(Y_1^C\right)^2 dx_0 - \int_0^{W_0}\left(Y_1^A\right)^2 dx_0 = 0\right] \quad \text{(H.51)}$$

then upon the substitution for the variables that appear in equation (H.50) by their expressions, we get

$$\left(\frac{1}{\gamma k^2 c_0^C} - \frac{1}{\gamma K_A^2 c_0^A} + \frac{2ZU}{\gamma k^2 c_0^C c_0^A}\right) c_2^A + \left(\frac{1}{\gamma k^2} - \frac{1}{\gamma K_A^2}\right)\phi_2^A = \frac{2U_2}{\gamma k^2 c_0^C} + \frac{2ZU_2}{\gamma k^2 c_0^C} - \frac{1}{\gamma k^2} + \frac{D_1^2}{2\gamma k^2}\left[\left(\frac{dc_0/dy_0}{c_0^C}\right)^2 - \frac{d^2\phi_0^C}{dy_0^2}\right] \quad \text{(H.52)}$$

then doing the same thing for equation (H.51) will turn it into

$$\left(1 + \frac{\left(c_0^C - c_0^A\right)}{\gamma K_A^2 c_0^A}\right) c_2^A + \frac{\left(c_0^C - c_0^A\right)}{\gamma K_A^2}\phi_2^A = U_2 - \frac{1}{2}\frac{dc_0}{dy_0} D_1^2 \quad \text{(H.53)}$$

Equations (H.52) and (H.53) are two linear equations in c_2^A and ϕ_2^A where U_2 and D_1^2 appear on the right hand side. So we can write them in the form

$$\begin{pmatrix} \frac{1}{\gamma k^2 c_0^C} - \frac{1}{\gamma K_A^2 c_0^A} + \frac{2ZU_c}{\gamma k^2 c_0^C c_0^A} & \frac{1}{\gamma k^2} - \frac{1}{\gamma K_A^2} \\ 1 + \frac{\left(c_0^C - c_0^A\right)}{\gamma K_A^2 c_0^A} & \frac{\left(c_0^C - c_0^A\right)}{\gamma K_A^2} \end{pmatrix} \begin{pmatrix} c_2^A \\ \phi_2^A \end{pmatrix} = \begin{pmatrix} \frac{2U_2}{\gamma k^2 c_0^C} + \frac{2ZU_2}{\gamma k^2 c_0^C} - \frac{1}{\gamma k^2} + \frac{D_1^2}{2\gamma k^2}\left[\left(\frac{dc_0/dy_0}{c_0^C}\right)^2 - \frac{d^2\phi_0^C}{dy_0^2}\right] \\ U_2 - \frac{1}{2}\frac{dc_0}{dy_0} D_1^2 \end{pmatrix} \quad \text{(H.54)}$$

then substituting $\frac{dc_0}{dy_0} = -2U_c$, $\frac{d\phi_0^A}{dy} = \frac{-2ZU_c}{c_0^A}$ and $\frac{d\phi_0^C}{dy} = \frac{-2ZU_c}{c_0^C}$ in

$\gamma K_A^2 = -\left(\frac{d\phi_0^A}{dy_0} + \frac{dc_0/dy_0}{c_0^A}\right)$ and $\gamma k^2 = -\left(\frac{d\phi_0^C}{dy_0} + \frac{dc_0/dy_0}{c_0^C}\right)$ we get $\gamma K_A^2 = \frac{2ZU_c + 2U_c}{c_0^A}$ and

$\gamma k^2 = \dfrac{2ZU_c + 2U_c}{c_0^C}$ which with usage of $c_0^A = 1+U_c$ and $c_0^C = 1-U_c$ will simplify (H.54)

into

$$\begin{pmatrix} Z & -(1+U_c) \\ \dfrac{2ZU_c}{1+U_c} & -2U_c \end{pmatrix}\begin{pmatrix} c_2^A \\ \phi_2^A \end{pmatrix} = \begin{pmatrix} (1+Z)U_2 + U_c(1+Z)D_1^2 \\ -(1-U_c) + 2(1+Z)U_2 + \dfrac{2(1+Z)U_c^2}{1-U_c}D_1^2 \end{pmatrix} \quad \text{(H.55)}$$

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}\begin{pmatrix} c_2^A \\ \phi_2^A \end{pmatrix} = \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} \text{ or } \vec{A}\begin{pmatrix} c_2^A \\ \phi_2^A \end{pmatrix} = \vec{b} \quad \text{(H.56)}$$

Now the determinant of the matrix A is simply

$$\det = -2ZU_c + \frac{2ZU(1+U_c)}{1+U_c} = 0 \quad \text{(H.57)}$$

so because $\det A = 0$ and we must have a solution (i.e., c_2^A and ϕ_2^A must exist) so solvability must be satisfied and we have two unknowns in $\vec{b}$ (i.e., D_1 and U_2). Solvability then relates these two variables and their relation comes from

$$-(1+Z)2U_cU_2 - 2U_c^2(1+Z)D_1^2 + (1+U_c)\left[(U_c-1) + 2(1+Z)U_2 + \frac{2(1+Z)}{1-U_c}U_c^2D_1^2\right] = 0 \quad \text{(H.58)}$$

which can be rearranged to

$$\left[-2U_c^2(1+Z) + \frac{2(1+Z)(1+U_c)}{1-U_c}U_c^2\right]D_1^2 = \left[(1+Z)2U_c - 2(1+Z)(1+U_c)\right]U_2 + (1+U_c)(U_c-1) \quad \text{(H.59)}$$

Now the factor that multiplies D_1^2 is always positive while the right hand side is simply $-2(1+Z)U_2 + (1+U_c)(1-U_c)$. Then substituting for $U_2 = U_{2,planar} + \delta$ and observing that

$$U_{2,planar} = \frac{1-U_c^2}{2(1+Z)} \tag{H.60}$$

will simplify the right hand side into $-2(1+Z)\delta$ which is always negative. This means, as in chapter 6, that in order to get non-planar solution then we must have had $U_2 = U_{2,planar} - \delta$ (i.e., the velocity of the surface must be less than the predicted value from the base).

LIST OF REFERENCES

Aogaki, R., Kitazawa, K., Kose, Y., and Fueki, K., *Electrochim. Acta* **25,** 965 (1980).

Aogaki, R., and Makino, T., *Electrochim. Acta* **26,** 1509 (1981).

Barkey, D. P., Muller, R. H., and Tobias, C. W., *J. Electrochem. Soc.* **136,** 2199 (1989a).

Barkey, D. P., Muller, R. H., and Tobias, C. W., *J. Electrochem. Soc.* **136,** 2207 (1989b).

Bockris, J. O'M., Reddy, A.K.N., and Gamboa-Aldeco, M., Modern Electrochemistry 2A: Fundamentals of Electrodics, Chap. 7, Kluwer Academic/ Plenum Publishers 2nd ed., New York (2000).

Brissot, C., Rosso, M., Chazalviel, J.-N., and Lascaud, S., *J. Power Sources* **81-82,** 925 (1999).

Chen, C.-P., and Jorne, J., *J. Electrochem. Soc.* **138,** 3305 (1991).

Johns, L.E. and Narayanan, R., Interfacial Instability, Springer-Verlag, New York (2002).

Krishnan, R., Johns, L.E., and Narayanan, R., *Electrochim. Acta* **48,** 1-6 (2002).

Landau, U., EPRI Report EM-2393. EPRI, Research Center, Palo Alto, CA (1982).

Léger, C., Elezgaray, J., and Argoul, F., *Phys. Rev. Lett.* **78,** 5010 (1997).

López-Salvans, M.-Q., Trigueros, P.P., Vallmitjana, S., Claret, J., and Sagués, F., *Phys. Rev. Lett.* **76,** 4062 (1996).

Mickley, H. S., Sherwood, T. K., and Reed, C. E., Applied Mathematics in Chemical Engineering, Chap. 5, p 174, McGraw-Hill 2nd ed., New York (1957).

Mullins, W. W., and Sekerka, R. F., *J. Appl. Phys.* **34,** 323 (1963).

Mullins, W. W., and Sekerka, R. F., *J. Appl. Phys.* **35,** 444 (1964).

Newman, J. S., Electrochemical Systems, Chap. 1, p 10, Prentice-Hall 2nd ed., New Jersey (1991).

Oldham, K. B., and Myland, J. C., Fundamentals of Electrochemical Science, Chap. 2, pp 31-32, Academic Press, San Diego (1994).

Prentice, G., Electrochemical Engineering Principles, Chap. 5, p 94, Prentice-Hall, New Jersey (1991).

Pritzker, M. D., and Fahidy, T. Z., *Electrochim. Acta* **37,** 103 (1992).

Rosso, M., Chassaing, E., Fleury, V., and Chazalviel, J.-N., *J. Electroanal. Chem.* **559,** 165 (2003).

Sundström, L-G., and Bark, F. H., *Electrochim. Acta* **40,** 599 (1995).

Trigueros, P. P., Sagués, F., and Claret, J., *Phys. Rev. E* **49,** 4328 (1994).

Watson, G. N., Theory of Bessel Functions, Chap. 3, p 80, Cambridge University Press 2nd ed., Cambridge, United Kingdom (1944).

BIOGRAPHICAL SKETCH

Qais BuAli was born on February 26, 1973, in Muharaq, Bahrain. In 1997, he graduated with a Bachelor of Engineering degree in chemical engineering from King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia. From January 1997 to September 1998 he was with the Chemical Engineering Department at the University of Bahrain, where he worked as a graduate assistant. In October 1998 he joined the Chemical Engineering Department at the University of Manchester Institute of Science and Technology, United Kingdom, as a graduate student. In December 1999, he graduated with a Master of Science in environmental technology. Between December 1999 and August 2000, he returned to work at the Chemical Engineering Department at the University of Bahrain, where he worked as a graduate assistant. In pursuit of a high quality education, he came to the University of Florida in August 2000 and joined the Department of Chemical Engineering with Professors Louis E. Johns and Ranga Narayanan as his advisors. He worked on patterns occurring during the motion of phase boundaries during an electrodeposition process.