APPLICATION OF THE GENERAL TRANSPORT THEORY TO NONISOTHERMAL GALVANIC CELLS

By

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ABSTRACT

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The goal of the research described here is the solution of the set of partial differential equations from nonequilibrium thermodynamics, hydrodynamics, and electrostatics which describes ion transport through a variety of energy conversion devices. The solution is obtained both numerically and analytically under a variety of boundary conditions. This permits simulation of many different electrode/electrolyte/electrode systems. The electrolyte spans the solution space and is assumed to be a continuous phase, incompressible, free of chemical reactions, and subject only to conservative external forces. The solutions to the differential equations are in the forms of both numerical finite difference simulations and approximate analytical expressions.

The importance of electrolytic properties in determining the cell efficiency is evaluated. Inclusion of temperature as a dependent variable allows examination of the feasibility of using temperature gradients to enhance economic performance. Contact with experiment is made through the numerical calculation of the ohmic voltage drop across the electrolyte. Extrapolation of the curve of ohmic drop versus

current yields a value for the bulk conductivity in good agreement with the value previously obtained from a.c. measurements.

To gain information concerning overpotentials, a.c. circuit theory is employed. Certain circuit components, (resistors, capacitors), combine to form circuits whose behavior mimics that of real systems. Measurements of cell impedances taken over a wide range of frequencies are analyzed in the complex plane. The analysis leads to estimates of the effect of overpotentials upon cell efficiency.

Mass transport transient behavior is examined and a simple formula is derived for calculating the time required for establishment of the steady state.

To Marilyn, Brucie, Sara, and Erica

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TABLE OF CONTENTS

Chapter	Page
LIST OF TABLES	ix
LIST OF FIGURES	x
CHAPTER 1 - MACROSCOPIC ANALYSIS OF ENERGY CONVERSION DEVICES	1
A. Introduction	1
B. Objectives	2
C. Plan of the Dissertation	3
CHAPTER 2 - ION TRANSPORT EQUATIONS	6
A. Introduction	6
B. Nonequilibrium Thermodynamic Equations	6
C. Continuity Equations	11
D. Electrostatic Equations	11
E. Combined System of Equations	13
F. Solving the Equations	15
CHAPTER 3 - BOUNDARY CONDITIONS	18
A. Introduction	18

Chapter Page

B. Physical Interpretation of the Boundary Conditions. 21

C. Applications of the Boundary Conditions 27

CHAPTER 4 - STEADY STATE TRANSPORT IN OPEN SYSTEMS 34

A. Introduction 34

B. Description of the System. 34

C. Steady State Equations. 37

D. Solution to the Isothermal Problem. 39

E. Determination of Efficiency 47

F. Results and Discussion. 49

1. Introduction. 49

2. The Mixed Conductor System 50

3. Calculation of Efficiency 53

CHAPTER 5 - STEADY STATE NONISOTHERMAL TRANSPORT IN OPEN SYSTEMS. 61

A. Introduction 61

B. Temperature Distribution 62

C. Solution to the Nonisothermal Problem. 66

Chapter Page

D. Efficiency. 68

E. Results and Discussion. 73

CHAPTER 6 - NUMERICAL APPROACH. 79

A. Introduction 79

B. Finite Difference Formulation 82

C. Numerical Results 85

CHAPTER 7 - THE TIME DEPENDENT PROBLEM 100

A. Introduction 100

B. Formulation of the Problem 101

C. Solution of the Soret Problem 106

CHAPTER 8 - FUTURE WORK 115

APPENDIX A - TRANSPORT COEFFICIENTS 118

APPENDIX B - FIRST ORDER SOLUTION FOR THE STEADY STATE ISOTHERMAL PROBLEM 121

APPENDIX C - DIMENSIONLESS VARIABLES USED FOR COMPUTER SIMULATION 129

APPENDIX D - JOULE HEATING 131

APPENDIX E - TRANSPORT EQUATIONS IN FINITE DIFFERENCE FORM 133

Chapter Page

APPENDIX F - LISTING OF PROGRAM "IONFLO" 137

REFERENCES 180

LIST OF TABLES

Table		Page
4-1	LEAST SQUARES VALUES OF THE EMPIRICAL CONSTANTS GIVEN IN THE EQUATIONS $(\phi_V - \phi_{IV}) = a + b\rho$, $\eta = c + d\rho$, AND $R = e + f\rho$ FOR VARIOUS VALUES OF THE CURRENT.	56
5-1	LEAST SQUARES VALUES OF THE EMPIRICAL CONSTANTS GIVEN IN $\eta = a + b[Q^*\Delta T/T]$ FOR VARIOUS VALUES OF THE CURRENT.	78
6-1	COMPARISON OF $\Delta\phi_o$ OBTAINED FROM INTEGRATION OF EQ. (4-30) AND THE COMPUTER SIMULATION RESULTS FOR THE DOPED SOLID ELECTROLYTE $CeO_2 + CaO$	86
6-2	COMPARISON OF THE VALUES OF R_1 AND R_2 MEASURED AT HIGH TEMPERATURES FOR THE DOPED SOLID ELECTROLYTE $CeO_2 + CaO$	99
6-3	COMPARISON OF POWER DENSITIES WITH AND WITHOUT OVERPOTENTIALS	99

LIST OF FIGURES

Figure		Page
3-1	INTERFACIAL REGION AT A PHASE BOUNDARY	20
3-2	DEPENDENCE OF THE KINETIC RATE CONSTANTS ON α_i.	24
3-3	CIRCUIT REPRESENTATIONS OF SOLID SOLID INTERFACES. (a) PARTIALLY BLOCKING ELECTRODE, (b) IDEALLY POLARIZED ELECTRODE, (c) IDEALLY DEPOLARIZED ELECTRODE.	29
3-4	SUBDIVISION OF THE ELECTROLYTE INTO THREE PSEUDOPHASES WITH PSEUDOPHASE BOUNDARIES SHOWN AT $X = \pm L/2$.	31
4-1	NONISOTHERMAL GALVANIC CELL.	36
4-2	DEPENDENCE OF EFFICIENCY ON CURRENT DENSITY. (a) OHM'S LAW BEHAVIOR, (b) BEHAVIOR PREDICTED BY EQ. (4-57)	58
4-3	DEPENDENCE OF R ON CURRENT DENSITY	60
5-1	DEPENDENCE OF THE EFFICIENCY ON CURRENT DENSITY. (a) $Q^*\Delta T < 0$, (b) $Q^*\Delta T = 0$, (c) $Q^*\Delta T > 0$	76
6-1	NONUNIFORM SPACE AND TIME GRID	81
6-2	DEPENDENCE OF THE OHMIC VOLTAGE DROP ON CURRENT DENSITY.	89
6-3	EQUIVALENT CIRCUITS AND THEIR CORRESPONDING ADMITTANCE PLOTS. THE CONDUCTANCE (G) IS PLOTTED VERSUS THE SUSCEPTIBILITY (B)	92
6-4	WARBURG IMPEDANCE PLOT	95

Figure Page

6-5 DEPENDENCE OF THE EFFICIENCY ON THE CURRENT DENSITY. (+) NEGLECTING OVERPOTENTIALS, (o) INCLUDING OVERPOTENTIALS 98

CHAPTER 1

MACROSCOPIC ANALYSIS OF ENERGY CONVERSION DEVICES

A. Introduction

A fuel cell is a device for converting chemical energy (fuel) to electrical energy without the use of moving mechanical parts. Extensive studies on a wide variety of fuel cells using different electrodes, electrolytes, and geometries have been carried out (Etsell and Flengas [1970] and Foley [1969]). There are generally three sources of power loss associated with the steady state operation of such devices, and they are the central foci of research in the field of energy conversion today. These three sources of power loss are classified as activation, mass transfer, and ohmic overpotentials. Of these the first two arise as a consequence of the kinetic limitations of the electrolyte/electrode interface involved. The ohmic overpotential is a result of ionic transport across the bulk or electrolyte phase. A theoretical treatment of these phenomena is possible using the nonequilibrium thermodynamic formalism. We are interested in the performance characteristics of the fuel cell in the steady state where the production of entropy has reached a minimum (Onsager [1931]).

The combined nonequilibrium, hydrodynamic, and electrostatic set of equations can be used for many purposes. Rice [1982] uses these

equations to describe the steady state isothermal transport of ions through a membrane. Tasaka, Morita, and Nagasawa [1965] have investigated membrane potentials in nonisothermal systems. Several authors have studied the transport of vacancies, electrons, and holes in solid state electrolytes using the macroscopic formalism (Howard and Lidiard [1963], Ohachi and Taniguchi [1977], Cheung, Steele, and Dudley [1979], Dudley, Cheung, and Steele [1980], and Weppner and Huggins [1977]). This dissertation deals with the theoretical study of transport phenomena in the steady state operation of fuel cells, and how independent variables such as temperature, current, and external load can be adjusted to optimize performance.

B. Objectives

The principal objective of this work is to relate in a general way the steady state cell performance to electrolytic properties and externally adjustable parameters such as load voltage and temperature. This relationship is derived from the macroscopic equations of nonequilibrium thermodynamics, hydrodynamics, and electrostatics which govern the transport of matter, and is independent of the events occuring at the electrode electrolyte interface. This phase of the investigation thus deals only with ways of minimizing the ohmic overpotential losses suffered by any operating cell. Inclusion of a temperature gradient in the formulation of the problem is undertaken in order to assess the feasibility of using the nonisothermal properties of an electrolyte for the purpose of increasing power output. The assumption of electroneutrality or the neglect of regions of space

charge in many of the treatments cited above seems rather unrealistic in light of the fact that one expects a buildup of charge in the region of electrolyte near the charged surfaces of the electrodes. Provisions are therefore made for its inclusion in the formulation of the boundary conditions of the problem, and the importance of non-electroneutrality in electrolytic behavior is evaluated.

The evaluation of nonohmic overpotential losses is undertaken with the aid of equivalent circuit analogies and simple a.c. circuit theory. The goal here is to assess the relative importance of these sources of power loss. Power losses due to concentration and activation overpotentials are dependent upon the kinetic parameters of the electrode/electrolyte interface and are related to kinetic rate constants derivable from the macroscopic transport equations (Horne, Leckey, and Perram [1981]).

C. Plan of the Dissertation

In Chapter 2 we begin with a review of the fundamental equations of nonequilibrium thermodynamics, hydrodynamics, and electrostatics used to formulate the macroscopic transport equations. The last part of Chapter 2 deals with the separation of the starting equations into a part due to bulk behavior and a part due to nonelectroneutrality, and the specialization of these equations to the steady state. Chapter 3 is devoted to a discussion of the boundary conditions and in particular their application to open systems in which the irreversible transfer of charge is taking place. In Chapters 4 and 5 analytical solutions to the

steady state equations are derived for the transport of ions in galvanic cells under a variety of boundary conditions. These solutions highlight the separation of the bulk behavior of the system from behavior due to non-electroneutrality. Also the role of the nonisothermal properties of the electrolyte in enhancing cell performance is discussed (Borey and Horne [1982]). The importance of higher order terms in the analytical solutions is considered and the performance of the cell as a function of current is examined.

Chapter 6 begins with a brief discussion of the numerical formulation of the transport equations (Leckey [1981]) and their modification and adaptation to include nonisothermal terms. A comparison of numerical results with analytical results is made in an attempt to verify the accuracy of the latter, and to make contact with experiment. Simple a.c. circuit theory in conjunction with equivalent circuit representations is invoked to extract information about interfacial parameters such as contact resistances. This information is then used to estimate the relative importance of nonohmic overpotentials.

In Chapter 7 we briefly examine the time dependent problem. The accuracy of the solution is verified by comparison to the steady state solution, and the transient behavior of the system is examined. The transient behavior of the system is taken to be the behavior over the period from the closing of the circuit to the establishment of the steady state. A simple formula is derived from which the time required to complete this transient phase can be estimated. This transient

behavior in many applications may be of great importance since operating periods may be of comparable or shorter length than this time range, making steady state operation the exception rather than the rule (Jasinski [1967]).

CHAPTER 2

ION TRANSPORT EQUATIONS

A. Introduction

The macroscopic equations used to describe ion transport come from the fields of hydrodynamics, electrostatics, and nonequilibrium thermodynamics. Details of the assumptions which lead to the phenomenological equations of nonequilibrium thermodynamics are available from many sources (deGroot and Mazur [1962], Haase [1969], and Horne [1966]). The systems dealt with in this dissertation are one-dimensional, binary electrolyte-solvent mixtures in which pressure effects are negligible.

B. Nonequilibrium Thermodynamic Equations

In a charged system there are three independent velocities (solvent, cation, and anion) and therefore two independent diffusion fluxes and four diffusion coefficients. With the cation and anion chosen as the independent species (1 and 2 respectively) the Hittorf diffusion fluxes defined by

$$J_i = c_i(v_i - v_0), \quad i=1,2, \tag{2-1}$$

where v_i is the velocity of species i and v_0 is the solvent velocity, are, according to Onsager [1931], linear combinations of the gradients in electrochemical potential $\tilde{\mu}_i$ and temperature T,

$$-J_i = \sum l_{ij}\left[\partial\tilde{\mu}_j/\partial x\right]_T + l_{iq}\left[\partial \ln T/\partial x\right]. \tag{2-2}$$

Here x represents the space coordinate and the l_{ij} are the Onsager coefficients. The Onsager equation for the flux of heat J_q is

$$-J_q = \sum l_{qi}\left[\partial\tilde{\mu}_i/\partial x\right]_T + l_{qq}\left[\partial \ln T/\partial x\right]. \tag{2-3}$$

The matrix of Onsager coefficients is symmetric,

$$l_{ij} = l_{ji}, \quad i,j = 1,2, \tag{2-4}$$

$$l_{iq} = l_{qi}, \quad i = 1,2. \tag{2-5}$$

The electrochemical potential of ion i is given by

$$\tilde{\mu}_i = \mu_i^{\infty} + (RT)\ln\left[y_i c_i\right] + z_i F\phi, \tag{2-6}$$

where y_i is the molar activity coefficient, z_i is the charge number of ion i, F is Faradays constant, and ϕ is the electrostatic potential. Dudley and Steele [1980] and Horne [1981] write the gradient of $\tilde{\mu}_i$ in terms of the independent c_i and ϕ as

$$\partial\tilde{\mu}_i/\partial x = \sum \mu_{ik}(\partial c_k/\partial x) + z_i F(\partial\phi/\partial x) - S_i(\partial T/\partial x) \tag{2-7}$$

where S_i is the partial molar entropy of ion i with

$$\left[\partial\tilde{\mu}_i/\partial x\right]_T = \left[\partial\tilde{\mu}_i/\partial x\right] + S_i\left[\partial T/\partial x\right], \tag{2-8}$$

$$\mu_{ij} = \left[\partial\tilde{\mu}_i/\partial c_j\right] = (RT/c_j)\left[\delta_{ij} + (\partial \ln y_i/\partial \ln c_j)\right], \tag{2-9}$$

where δ_{ij} is the Kronecker delta. With the substitution of Eq. (2-7) into Eq. (2-2), the diffusion fluxes become for each ion

$$-J_i = \sum D_{ij}\left[\partial c_j/\partial x\right] + (\lambda t_i/Fz_i)\left[\partial\phi/\partial x\right] + l_{iq}\left[\partial \ln T/\partial x\right], \tag{2-10}$$

with

$$D_{ij} = \sum l_{ik}\mu_{kj}, \quad t_i = [z_iF^2/\lambda)] \sum z_k l_{ik},$$

$$\lambda = F^2\sum\sum z_iz_jl_{ij}, \quad \sum t_i = 1. \tag{2-11}$$

The requirement of reciprocity imposes upon the diffusion coefficients the relation

$$D_{12}\mu_{11} - D_{11}\mu_{12} = D_{21}\mu_{22} - D_{22}\mu_{21}. \tag{2-12}$$

Eq. (2-9) reduces to the Nernst-Planck equation under the necessary and sufficient conditions that (Horne [1981])

i) $v_0 = 0$,

ii) $l_{ij} = l_{ii}\delta_{ij}, \qquad i,j = 1,2$

iii) $\ln(y_i) = 0, \qquad i = 1,2.$ (2-13)

The Nernst-Planck equations are valid only for ideal solutions, in which moreover there is no diffusional coupling.

The condition of local charge neutrality implies that the current of one species must everywhere be counterbalanced by that of the oppositely charged species. This coupled motion can be described by only <u>two</u> independent velocities (electrolyte and solvent), and accordingly only <u>one</u> independent diffusion flux. For nonisothermal diffusion we have as well only one independent thermal diffusion coefficient. Haase [1969] defines the diffusion fluxes under these conditions as

$$-J = D\left[(\partial c/\partial x) - \sigma c(\partial T/\partial x)\right] \qquad (2\text{-}14)$$

where c is the concentration of the neutral electrolyte, σ is the Soret coefficient, and D is the diffusion coefficient (also known as the "ambipolar" or "chemical" or "mutual" diffusion coefficient). The diffusion coefficient defined by Eq. (2-14) can be related to the D_{ij} of Eq. (2-9) by

$$D = 2(D_{11}D_{22}-D_{12}D_{21})/(D_{11} + D_{22} - (z_1/z_2)D_{12} - (z_2/z_1)D_{21}) \qquad (2\text{-}15)$$

Dudley and Steele [1980] evaluate this diffusion coefficient in terms of

what they call a thermodynamic factor. Wagner [1975] derives an expression for this same diffusion coefficient for the case of a metal excess δ diffusing in compounds of stoichiometric composition $A_{1+\delta}X_v$ in terms of the Onsager coefficients and chemical potential gradients. Horne [1981] directly relates the diffusion coefficients of Eq. (2-9) to the mutual diffusion coefficient D for a symmetrical electrolyte.

For a nonisothermal system the Soret coefficient σ in Eq. (2-14) can be related to the individual ionic heats of transport by

$$\sigma = -Q^*/Tc(\partial\mu/\partial c) \tag{2-16}$$

where Q^* is the heat of transport of the electrolyte given by $Q^* = v_1Q_1^* + v_2Q_2^*$ and v_1 and v_2 are the stoichiometric coefficients of species 1 and 2 respectively. The individual ionic heats of transport are defined by

$$l_{iq} = \sum l_{ij}Q_j^*. \tag{2-17}$$

With Eq. (2-17) the heat flux can be rewritten in terms of the heats of transport as

$$-J_q = -\sum J_i^H Q_i^* + K_\infty(\partial T/\partial x) \tag{2-18}$$

where

$$K_\infty = l_{qq}/T - \sum (l_{qi}Q_i^*)/T. \tag{2-19}$$

C. Continuity Equations

In addition to the flux equations of nonequilibrium thermodynamics given above, the system will also obey the relevant conservation of mass equations given by

$$(\partial c_i/\partial t) = -(\partial J_i/\partial x) + \sum \sum v_{ir} b_r \tag{2-20}$$

where t is time, v_{ir} is the stoichiometric coefficient of species i in chemical reaction r, and b_r is the rate of chemical reaction r. An additional transport equation comes from the conservation of energy which for a nonisothermal system is written as Haase [1969]

$$\rho \bar{C}_p(\partial T/\partial t) = -(\partial J_q/\partial x) - I(\partial \phi/\partial x)$$

$$- \sum \sum v_{ir} b_r H_i - \sum J_i(\partial H_i/\partial x) \tag{2-21}$$

where ρ is the system density, $\bar{C}_p$ is the specific heat, I is the total current, and H_i is the partial molar enthalpy of component i. An excellent approximation to this equation for problems in which there are neither reactions nor current flow (Horne and Anderson [1968]) is

$$\rho \bar{C}_p(\partial T/\partial t) = (\partial/\partial x)\left[K_{\infty}(\partial T/\partial x)\right]. \tag{2-22}$$

D. Electrostatic Equations

A fundamental law of electromagnetism (Bleaney [1957]) which relates the electrostatic potential to the concentrations of charged species in the system is Poisson's equation and is given by

$$\varepsilon(\partial E/\partial x) = F \sum c_i z_i, \tag{2-23}$$

where ε, the permittivity of the medium, is considered constant, and the electric field E is defined by

$$E = -(\partial \phi/\partial x). \tag{2-24}$$

Taking the time derivative of the left hand side of Poisson's equation, and substituting Eq. (2-20) for the right hand side, we find

$$\varepsilon(\partial/\partial t)(\partial E/\partial x) = -F\sum z_i(\partial J_i/\partial x), \tag{2-25}$$

where we have also used

$$\sum v_{ir} b_r z_i = 0. \tag{2-26}$$

If the electric field and charge density as well as their space and time derivatives are continuous functions, then it is permissible to interchange the order of differentiation in Eq. (2-25), giving

$$(\partial/\partial x)\left[F\sum z_i J_i + \varepsilon(\partial E/\partial t)\right] = 0. \tag{2-27}$$

Ampere's law requires that

$$\partial I/\partial x = 0, \tag{2-28}$$

and therefore it would be incorrect to define the total current as being equal to the summation term in Eq. (2-27), which accounts only for the motion of the electric charges, because this would conflict with the continuity equations whose validity is confirmed by all experiments. Maxwell [1865] was the first to reconcile this difficulty and correctly defined the current as

$$I = F \sum z_i J_i + \varepsilon(\partial E/\partial t), \tag{2-29}$$

where the second term, the Maxwell displacement current, arises because of the time dependence of the electric field.

E. Combined System of Equations

The displacement current equation, Eq. (2-29), along with the conservation of mass and energy equations coupled with the nonequilibrium thermodynamic equations provide the basis for a complete macroscopic description of the system in terms of material properties and the dependent variables c_1, c_2, and E. The full set of equations is obtained by substitution of Eq. (2-10) into Eqs. (2-20) and (2-29):

$$(\partial c_i/\partial t) = (\partial/\partial x)\Big[\sum D_{ij}(\partial c_j/\partial x) + l_{iq}(\partial \ln T/\partial x)$$

$$- (\lambda t_i/Fz_i)E \Big] + \sum v_{ir}b_r, \qquad i=1,2, \tag{2-30}$$

$$\varepsilon(\partial E/\partial T) = I + F \sum\sum z_i D_{ij}(\partial c_j/\partial x) + F \sum z_i l_{iq}(\partial \ln T/\partial x)$$

$$- \lambda E, \qquad i,j=1,2 \tag{2-31}$$

where the solvent reference velocity has been neglected.

Leckey and Horne [1981] distinguished electrically neutral behavior such as ambipolar or mutual diffusion from behavior due to non-electroneutrality and introduced the sum S, and difference or charge density Δ composition variables,

$$S = (1/2)\Big[(c_2/z_1) - (c_1/z_2)\Big], \tag{2-32}$$

$$\Delta = (1/2)\Big[(c_2/z_1) + (c_1/z_2)\Big]. \tag{2-33}$$

The transport equations become

$$\partial S/\partial t = (\partial/\partial x)\Big[Y_{SS}(\partial S/\partial x) + Y_{S\Delta}(\partial \Delta/\partial x) + Y_{Sq}(\partial T/\partial x)$$

$$- (\varepsilon Y_{SE}/2z_1z_2F)E \Big] + (1/2z_1z_2) \sum (v_{2r}z_2 - v_{1r}z_1)b_r, \tag{2-34}$$

$$\partial \Delta/\partial t = \partial/\partial x\Big[Y_{\Delta S}(\partial S/\partial x) + Y_{\Delta\Delta}(\partial \Delta/\partial x) + Y_{\Delta q}(\partial T/\partial x)$$

$$- (\varepsilon Y_{\Delta E}/2z_1z_2F)E \Big], \tag{2-35}$$

$$\varepsilon(\partial E/\partial t) = I - (1/2z_1z_2F)\Big[\, Y_{\Delta S}(\partial S/\partial x) + Y_{\Delta\Delta}(\partial\Delta/\partial x)$$

$$+ Y_{\Delta q}(\partial T/\partial x) - (\varepsilon Y_{\Delta E}/2z_1z_2F)E \,\Big], \qquad (2\text{-}36)$$

where the Y_{ij} $(i,j = S,\Delta,E,q)$ are defined in Appendix A. These transformed equations highlight the very different physical behaviors associated with diffusion of neutral matter on the one hand, and diffusion of charged matter on the other.

Eqs. (2-34) through (2-36) along with the conservation of energy given by Eq. (2-21) form the complete set of partial differential equations whose solution we seek. The solution will depend upon the system's material parameters and the boundary conditions placed upon it.

F. Solving the Equations

The nonlinearity of Eq. (2-21) and Eqs. (2-34) through (2-36) makes it highly unlikely that one can obtain analytical solutions to them in closed form. The Y_{ij} are in general concentration and temperature dependent and so is the conductivity. For systems in which there are reactions some sort of model dependent behavior for the reaction rate must be postulated. Additionally much information is required in order to define the material parameters necessary for expressing a solution. For solid state systems such information is scarce.

In addition to attempting analytical solutions to the transport

equations, it is necessary to obtain numerical or computer solutions as well in lieu of analytical solutions. Cohen and Cooley [1965] were the first to simulate ion transport on a large scale. Several others (Kahn and Maycock [1966], Feldberg [1970], Sandifer and Buck [1975]) have numerically solved the simplified set of transport equations (Nernst-Planck equations) under a variety of conditions. Brumlevé and Buck [1978] have developed the most general program of this type. The program used in the research which led to this dissertation was developed by Leckey [1981], and extends the generality of the Brumlevé and Buck program by using the full set of transport equations (Eqs. (2-34) to (2-36)) valid at any concentration, for isothermal systems of uni-univalent electrolytes. Here, the transformation of the full set of transport equations to finite difference form is extended to include both electrolytes of any valence and nonisothermal systems. The use of the full set of equations allows one the option of incorporating cross effects and activity coefficient effects, both of which are ignored in the Nernst-Planck formulation.

A listing of the complete set of dimensionless variables chosen for this system is included in Appendix C. A listing of the program "IONFLO" is shown in Appendix F. A more complete discussion of the details surrounding the transformation of the transport equations to finite difference form can be found in Chapter 6.

The principal value in carrying out numerical solutions to problems like this one is that one can (1) model the behavior of various material parameters based on available data, and (2) test models by comparison

with experiment. Numerical solutions also provide a check on the accuracy of analytical solutions, they allow verification of the assumptions involved in obtaining them, and they provide clues to improved analytical solutions.

CHAPTER 3

BOUNDARY CONDITIONS

A. Introduction

For the one dimensional system described in Chapter 2 there are two boundaries. At each boundary it is necessary to make a statement about the concentrations of the ions, and for nonisothermal systems it is necessary to make a statement about the temperature as well.

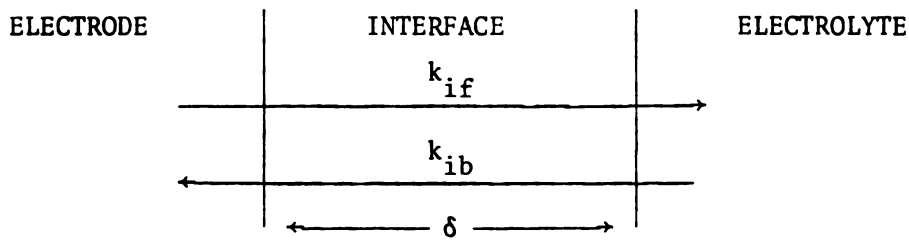
In order to make contact with experimental results boundary conditions must be devised which enable one to simulate as closely as possible actual experimental conditions. For applications considered here, battery-type devices, boundary conditions of the type

$$J_i = k_{if}c_{i1} - k_{ib}c_{i0} \tag{3-1}$$

previously used by Brumlevé and Buck [1978] are employed. The flux of an ion i at an interface is described by a forward and reverse rate constant k_{if} and k_{ib} and ion concentrations in each phase c_{i1} and c_{i0}. The direction of flux and interfacial concentrations are shown in Figure (3-1).

The assumptions required for the validity of boundary conditions of

Figure (3-1). Interfacial region at a phase boundary.



$$J_i = k_{if}C_{il} - k_{ib}C_{io}$$

Figure (3-1)

this type have been discussed previously by Horne, Leckey, and Perram [1983]. For closed systems application of the above boundary conditions is a simple matter, in that all interfacial rate constants are set equal to zero, and no matter traverses the boundaries of the system. For open systems where electrode reactions may be occurring it becomes necessary to assign to these constants "reasonable" values that reflect the behavior of the particular electrode system. This requires additional experimental data in the form of measurements of the a.c. and d.c. properties of the electrode-electrolyte system of interest. Braunshtein, Tannhauser, and Riess [1981] have measured these properties for platinum electrode-doped metal oxide systems.

In the event that the electrode system behaves in a completely reversible manner, $J_i = 0$ and the rate constants in Eq. (3-1) approach infinity while $c_{i0} \rightarrow c_{i1}$ (Leckey [1981]). The application of these boundary conditions becomes more difficult for real systems ($k's \neq 0,\infty$) and requires that we look at the physical interpretation of the terms in Eq. (3-1).

B. Physical Interpretation of the Boundary Conditions

The three assumptions which lead to the kinetic flux expressions given by Eq. (3-1) (Horne, Leckey, and Perram [1981]) are:

i. The cross terms within the interfacial region are negligible.
ii. The quantity $\mu_i^o + z_i F\phi$ is a linear function of x through the interface.
iii. The flux J_i and diffusion coefficient D_i are constants through the interface.

These assumptions result in the following expressions for the rate

constants,

$$k_{if} = (D_i/\delta) \left[\alpha_i \exp(-\alpha_i)/(1-\exp(-\alpha_i)) \right], \tag{3-2}$$

$$k_{ib} = (D_i/\delta) \left[\alpha_i/(1-\exp(-\alpha_i)) \right], \tag{3-3}$$

where

$$\alpha_i = \Delta[\mu_i^o + z_i F\phi]/RT, \tag{3-4}$$

and δ is the interfacial thickness. The standard state chemical potential is included here because it is a property of the phase in question and in general we are speaking of the exchange of matter between two different phases. For phase boundaries at which $|z_i F\Delta\phi| >> |\Delta\mu_i^o|$, a large positive value of α_i corresponds to the situation in which a positive ion is moving to a region of more positive electrostatic potential, or a negative ion is moving to a region of more negative electrostatic potential. In either event the magnitude of the rate constant for movement in this direction (k_{if}) is expected to be small while the rate constant for movement in the reverse direction (k_{ib}) should be large (see Figure (3-2)). Conversely, when α_i is a large negative number exactly the opposite should be the case, namely movement of positive ions to a region of more negative potential, or negative ions to a region of more positive potential. In either case we expect that k_{if} becomes large, while k_{ib} becomes small (see Figure (3-2)). In cases where $|\Delta\mu_i^o| >> |z_i F\Delta\phi|$, Eqs. (3-2) and (3-3) predict movement of ions to the phase in which their standard state chemical

Figure (3-2). Dependence of the kinetic rate constants on α_i.

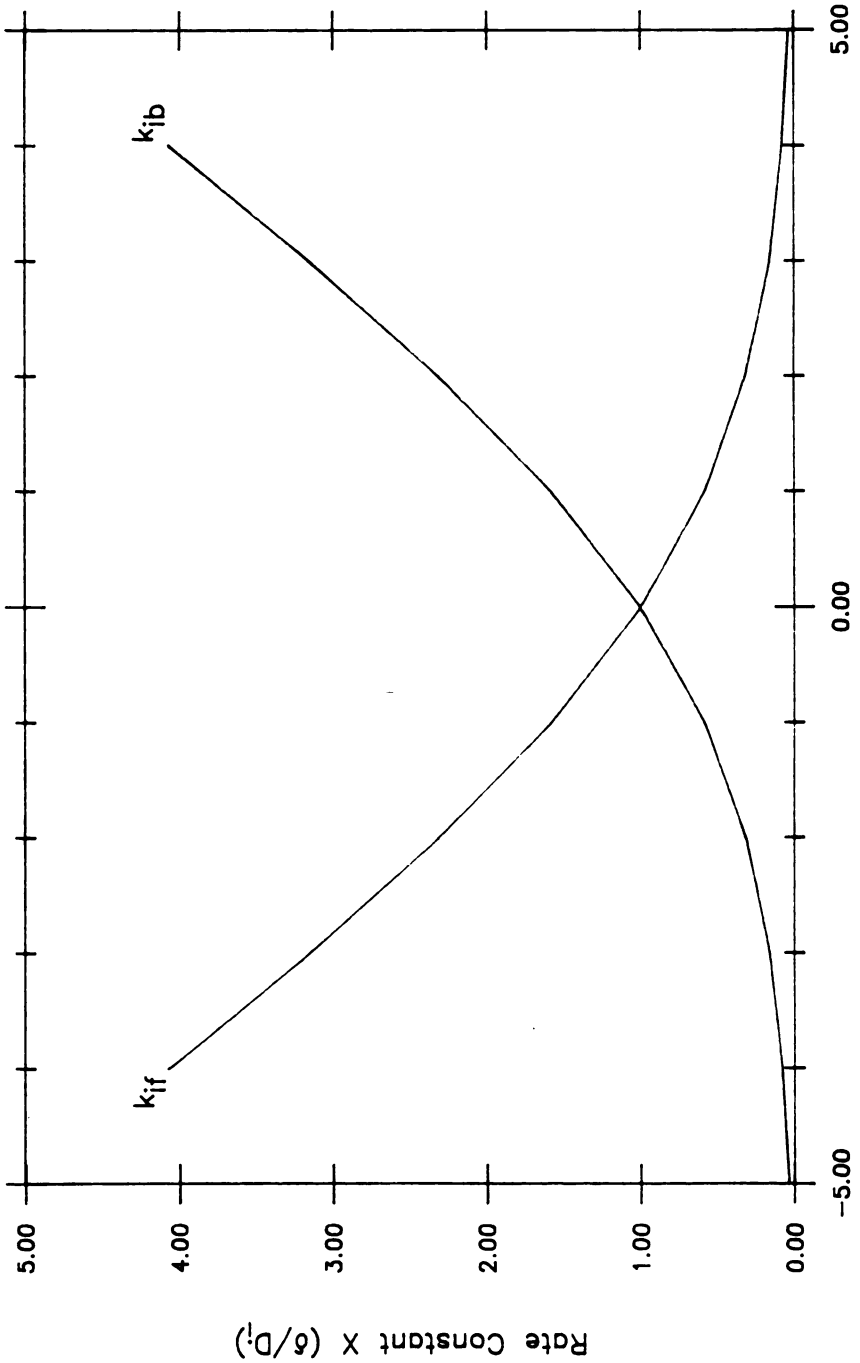

Rate Constant x (δ/Dᵢ)
5.00
4.00
3.00
2.00
1.00
0.00
−5.00
0.00
5.00
k_{if}
k_{ib}
$(\Delta\mu_i^o + z_iF\Delta\Phi)/RT$

Figure (3-2)

potential is lower, $(\Delta\mu_i^o) \rightarrow -\infty$ implies $\alpha_i \rightarrow -\infty$ and $k_{if} \rightarrow \infty$. Perram [1980] approximates the value of $\Delta\mu_i^o$ from the Born equation

$$\Delta\mu_i^o = [(z_iF)^2/2a_i] \left[(1/\varepsilon_r) - (1/\varepsilon_l)\right] \qquad (3\text{-}5)$$

where a_i is the radius of ion i, and ε_r and ε_l are the permittivities of the right and left hand phases respectively. In accordance with the argument presented above, when $\varepsilon_l < \varepsilon_r$, $\Delta\mu_i^o < 0$, and transfer of material to the phase with the higher dielectric constant is favored.

The application of the kinetic boundary conditions given by Eq. (3-1) should simulate as closely as possible the experimental conditions. Under certain conditions it is possible to make quantitative statements concerning the values these constants should assume. For instance when an electrode is blocking to a particular ion, that ion cannot penetrate the interface from either direction, and one can assign values of zero to the rate constants in Eq. (3-1). From Eqs. (3-1), (3-2), and (3-3) we see that this can be true if and only if $D_i = 0$.

At the other extreme there is the reversible electrode at which $J_i = 0$, implying $k_{if}c_il = k_{ib}c_i0$. In cases where α_i is zero we see from Eqs. (3-1) and (3-2) that $k_{if} = k_{ib}$, and therefore $c_il = c_i0$.

In cases where neither reversible nor blocking conditions exist at the boundaries, the matter of assigning reasonable values to the rate constants is complicated by the fact that it is necessary to know α_i in

Eqs. (3-2) and (3-3) in order to obtain values for the rate constants. The change in the value of α_i from its equilibrium value of zero to its nonequilibrium value is due entirely to the change in the value of the contact potential ($\Delta\phi$ in Eq. (3-4)), since the value of $\Delta\mu_i^o$ remains constant regardless of current flow. The change in the value of α is defined as the overpotential, and is not experimentally measurable. For two phase junctions in series

$$(\Delta\alpha_i^L + \Delta\alpha_i^R)/z_iF = \eta_L + \eta_R, \tag{3-6}$$

where the overpotentials (η_L and η_R) are

$$\eta_L = (\Delta\phi - \Delta\phi_{rev})_L, \tag{3-7}$$

and $$\eta_R = (\Delta\phi - \Delta\phi_{rev})_R. \tag{3-8}$$

The total overpotential loss ($\eta_L + \eta_R$) for a given electrode electrolyte system can be estimated from the analysis of the impedance frequency response of the system. This analysis is often aided by analogy with equivalent electrical circuits consisting of resistors and capacitors each associated with a single process (Sandifer and Buck [1975], Warburg [1899, 1901]). In Figure (3-3a), the bulk resistance is represented by R_b, while the resistance at the interface is represented by R_{if}. The charging of the double layers through the surface resistances is associated with surface capacitance C_{if}. Figures (3-3b), and (3-3c) show the equivalent circuit representations of ideally

polarized and depolarized electrode-electrolyte interfaces respectively. Impedance frequency response data (Braunshtein, Tannhauser and Riess [1981]) for a given system can then be used to assign values to the resistances and capacitances found in an equivalent circuit representation, which leads to estimates of the magnitude of the total overpotential given by Eq. (3-6).

C. Applications of the Boundary Conditions

Various workers have used these boundary conditions to simulate a variety of conditions. For liquid-liquid junction cells with blocking electrodes Leckey [1981] set the rate constants equal to zero at each end. He also used these boundary conditions to study charge injection into a one dimensional cell at a blocked interface containing a reversible electrode at the other boundary. For the reversible electrode simulation the rate constants were set to machine infinity. Chang and Jaffe [1952] studied the effect of changing the values of the rate constants on the conductance. Brumlevé and Buck [1978] simulated a variety of effects ranging from charge steps at blocked interfaces (k's = 0) to ion exchange membranes (k's finite). Their assignments for the rate constants were made from analyses of the impedance frequency responses of the systems as described above.

For the one dimensional solid state systems discussed in Chapters 4 and 5, it is convenient to break up the electrolyte into three regions (Figure (3-4)). In the vicinity of each electrode (regions I and II) there are reactions occurring, while in the bulk between regions I and

Figure (3-3). Circuit representations of solid-solid interfaces. (a) Partially blocking electrode, (b) ideally polarized electrode, (c) ideally depolarized electrode.

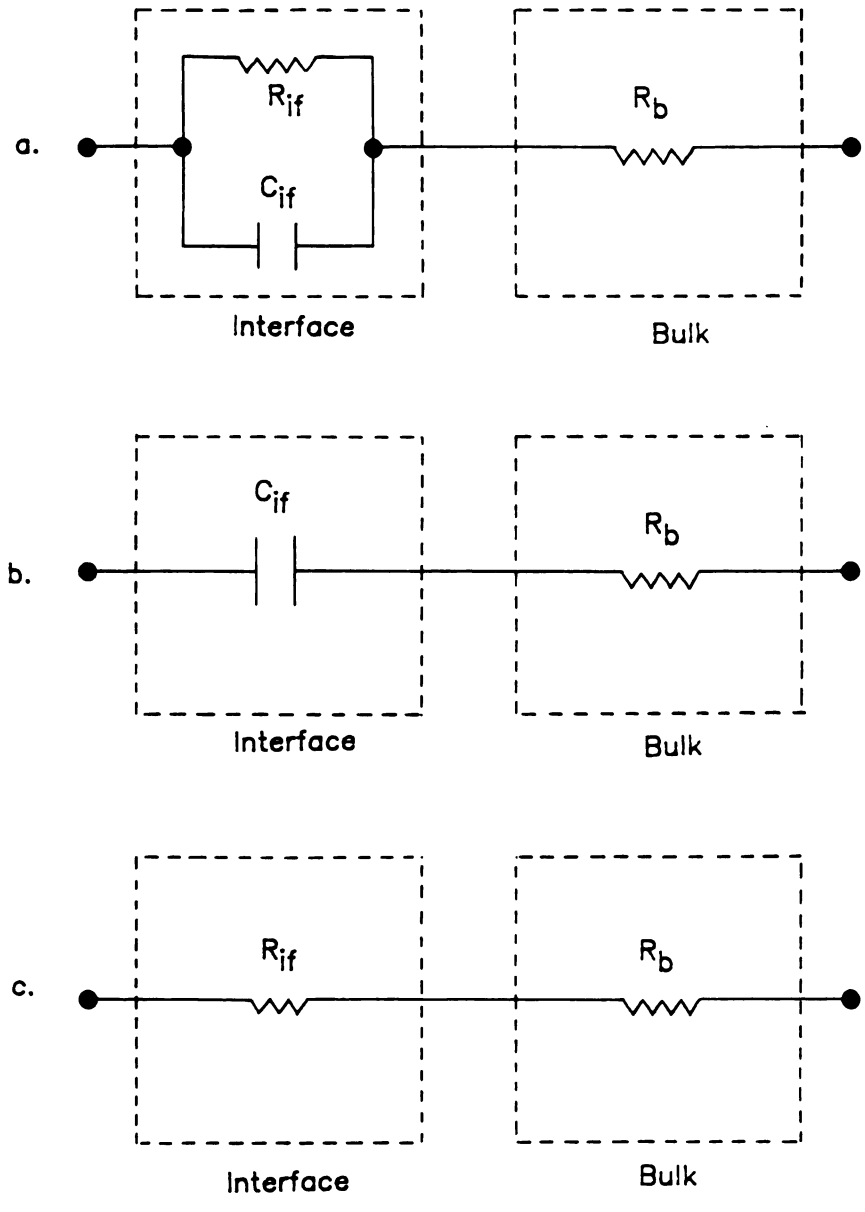

a.
R_{if}
C_{if}
R_b
Interface
Bulk
b.
C_{if}
R_b
Interface
Bulk
c.
R_{if}
R_b
Interface
Bulk

Figure (3-3)

Figure (3-4). Subdivision of the electrolyte into three pseudophases with pseudophase boundaries shown at $x = \pm L/2$.

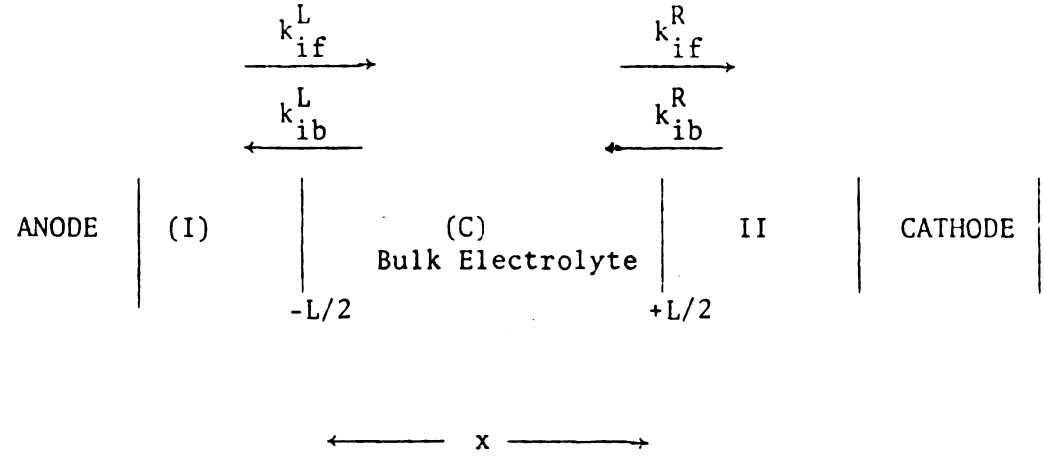

k^L_{if}
k^L_{ib}
k^R_{if}
k^R_{ib}
ANODE
(I)
(C)
Bulk Electrolyte
II
CATHODE
-L/2
+L/2
x

Figure (3-4)

II there are no reactions and only transport is occurring. The lines that separate the reaction regions from the bulk denote pseudophase boundaries. The term pseudophase is used here because there is no discontinuity in system properties at these boundaries, only a difference in the conservation of mass equations on either side with

$$\partial c_i/\partial t = -(\partial J_i/\partial x) \tag{3-9}$$

in the bulk and

$$\partial c_i/\partial t = -(\partial J_i/\partial x) + \sum v_{ir} b_r \tag{3-10}$$

in regions I and II. Therefore at the pseudophase boundaries $\Delta\mu_i^o = 0$ and $\Delta\phi = 0$, and by Eq. (3-4) $\alpha_i = 0$. From Eqs. (3-1), (3-2), (3-3), and (3-10) the flux of ion i at each boundary becomes

$$J_i = (D_i/\delta)(c_{i1} - c_{i0}), \tag{3-11}$$

$$k_{if} = k_{ib} = D_i/\delta. \tag{3-12}$$

Eq. (3-11) applies whether charge transfer between the electrode and electrolyte is reversible or irreversible. When the reactions are at equilibrium, $b_r = 0$ in Eq. (3-10), and $J_i(\text{Bulk}) = J_i(\text{I}) = J_i(\text{II}) = 0$ with $c_{i1} = c_{i0}$ by Eq. (3-11).

In general the manner in which the component fluxes in the reaction regions change from their bulk solution values to their values at the

electrode electrolyte interface is determined by the behavior of the electrode (overpotentials) and by the magnitude of the reaction rates in that region. At the steady state Eq. (3-10) gives

$$J_i(\text{I or II})) = \int \sum (v_{ir} b_r) dx, \tag{3-13}$$

where the integral is taken from the electrode to the bulk solution. Knowledge of the dependence of the reaction rates on distance from the electrode would allow one to obtain an analytical solution to Eq. (3-13), where the behavior of the electrode towards species i determines the integration constant.

High values for the rate constants used in Eqs. (3-11) and (3-12) imply electrodes behaving nearly reversibly with very little change in ionic concentrations between bulk and reaction phases, and hence very little double layer charging. From the equivalent circuit point of view the value of the interfacial rate constant is a measure of the resistance of the double layer. High rate constants mean low interfacial resistances and little double layer charging. Low values of the rate constants imply that significant concentration differences will arise across the pseudophase boundaries and double layer charging will occur. These rate constants correspond to high values of interfacial resistances. In Chapters 4 and 6 the effect of charging the double layer is examined through inclusion of the charge density terms in the boundary condition formulation.

CHAPTER 4

STEADY STATE TRANSPORT IN OPEN SYSTEMS

A. Introduction

In this chapter the equations of nonequilibrium thermodynamics are used to investigate the steady state behavior of energy conversion devices (batteries and fuel cells). Of special interest are solid state electrolytes into which a mobile species can enter from the static lattice of the electrodes. Intercalation electrodes (Whittingham [1979]) are useful for this purpose since they provide near reversibility of reaction. The equations are, however, quite general and can be applied with appropriate modification to other electrode and electrolyte systems.

B. Description of the system

The fuel cell arrangement (Figure 4-1) (Kiukkola and Wagner [1957]) consists of a solid electrolyte (C) sandwiched between two electrodes (B,B′) not necessarily at the same temperature. Each electrode is attached to a wire (A,A′) which leads to a terminal at some mean temperature T_A. The measurable EMF is $\Delta\phi = \phi_{VIII} - \phi_I$. The model electrolyte (Figure 3-4) extends from $x = -L/2$ to $x = +L/2$ and the voltage drop across it is $\phi_V - \phi_{IV}$ (Figure 4-1). In general there are

Figure (4-1). Nonisothermal galvanic cell.

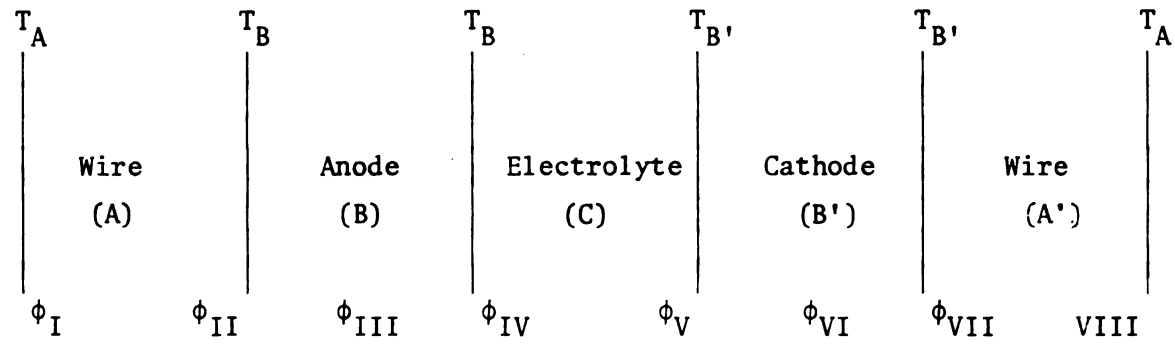

T_A
T_B
T_B
$T_{B'}$
$T_{B'}$
T_A
Wire
(A)
Anode
(B)
Electrolyte
(C)
Cathode
(B')
Wire
(A')
ϕ_I
ϕ_{II}
ϕ_{III}
ϕ_{IV}
ϕ_V
ϕ_{VI}
ϕ_{VII}
VIII

Figure (4-1)

reactions occurring near the electrode electrolyte interfaces which provide the driving forces (gradients of chemical potential and temperature) that cause the flux of material through the electrolye to occur. We assume in general a one dimensional problem with the goal of determining the voltage loss across the electrolyte ($\phi_V - \phi_{IV}$) using the equations of nonequilibrium thermodynamics. This voltage loss can then be subtracted from the theoretical or Nernst potential, and an estimate of the thermodynamic efficiency of such a device can be obtained. This estimate neglects overpotentials, which are changes in heterogeneous or contact potentials ($\phi_{VII} - \phi_{VI}$, $\phi_{VI} - \phi_V$, $\phi_{IV} - \phi_{III}$, and $\phi_{III} - \phi_{II}$) from their equilibrium values. Contact potentials arise as a consequence of charge transfer from one phase to another. Estimates of these contributions to the total voltage loss across any operating device can be obtained from the measurement of both the a.c. and d.c. properties of the system of interest. Such measurements lead to improved estimates of the true operating efficiency of such devices.

C. Steady State Equations

At the steady state the time derivatives of all intensive variables vanish and the fluxes defined by Eqs. (2-10) reduce to

$$-J_i^{\infty} = \sum D_{ij}(dc_j/dx) - (\lambda t_i/z_i F)E + l_{iq}(d\ln T/dx), \qquad (4-1)$$

where J_i^{∞} represents the constant steady state value of the flux of ion i. The sum and difference pseudo fluxes are defined in the same way as the sum and difference concentrations,

$$J_{\Delta}^{\infty} = (1/2)\left[(J_2^{\infty}/z_1) + (J_1^{\infty}/z_2)\right], \tag{4-2}$$

$$J_S^{\infty} = (1/2)\left[(J_2^{\infty}/z_1) - (J_1^{\infty}/z_2)\right]. \tag{4-3}$$

From Eqs. (2-34) through (2-36) we see that in terms of dependent variables and material parameters,

$$-J_S^{\infty} = Y_{SS}(dS/dx) + Y_{S\Delta}(d\Delta/dx) - Y_{sE}K^{-1}E + Y_{Sq}(dT/dx), \tag{4-4}$$

$$-J_{\Delta}^{\infty} = Y_{\Delta S}(dS/dx) + Y_{\Delta\Delta}(d\Delta/dx) - Y_{\Delta E}K^{-1}E + Y_{\Delta q}(dT/dx), \tag{4-5}$$

where

$$K = (2z_1z_2F)/\varepsilon. \tag{4-6}$$

The pseudo fluxes J_S^{∞} and J_{Δ}^{∞} are not true Onsager fluxes since there is no reciprocal relationship involving only the Y_{ij} of Eqs. (4-4) and (4-5).

Simplification of these equations results from simultaneously solving them for (dS/dx) and (dΔ/dx):

$$dS/dx = \alpha_S + \beta_S E + \gamma_S(dT/dx), \tag{4-7}$$

$$d\Delta/dx = \alpha_{\Delta} + \beta_{\Delta}E + \gamma_{\Delta}(dT/dx), \tag{4-8}$$

where the coefficients α, β, and γ are defined in terms of the Y_{ij} in

Appendix A. In general these coefficients incorporate all effects due to nonideality of the system and are themselves dependent upon the concentrations of all species present as well as the temperature. It is this dependence that gives rise to the nonlinearity of Eqs. (4-7) and (4-8). The α's are related to the fluxes at the boundaries and would be zero for the case of the system sandwiched between blocking electrodes. For ideal systems for which the Nernst Planck equations are valid the α's behave as constants, while the β's are linear functions of the ionic concentrations. The γ's incorporate nonisothermal effects such as the heats of transport of the ionic species. For systems in which there are small temperature gradients these coefficients are nearly constant, with values dependent upon the mean temperature of the system (Cowen [1979]).

It is possible to eliminate Δ as a variable by combining Eq. (4-8) with Poisson's equation to give

$$(d^2E/dx^2) - (K\beta_\Delta) = (K\alpha_\Delta) + K\gamma_\Delta(dT/dx). \qquad (4\text{-}9)$$

Eqs. (4-7) and (4-9) are the starting set of equations for the macroscopic investigation of the steady state problem. The only assumptions made up to this point are those implicit in the Onsager formulation of the transport equations of nonequilibrium thermodynamics (Haase [1969], Horne [1966], and Onsager [1931]). All effects due to nonideality are retained.

D. Solution to the isothermal problem

For the case of no temperature gradient, the nonisothermal terms in Eqs. (4-7) and (4-9) vanish, giving

$$(d^2E/dx^2) - (K\beta_\Delta)E = K\alpha_\Delta \tag{4-10}$$

$$dS/dx = \alpha_S + \beta_S E. \tag{4-11}$$

For ideal solutions Eq. (4-10) reduces to the Poisson-Boltzmann equation with $K\beta_\Delta$ the reciprocal of the Debye length squared,

$$K\beta_\Delta = (2F^2 I_c)/\varepsilon RT, \tag{4-12}$$

and I_c is the ionic strength of the solution.

The boundary conditions for the open system are

$$\int_x Sdx = \text{Constant}, \tag{4-13}$$

$$\Delta = \rho_L, \quad x = -L/2, \tag{4-14}$$

$$\Delta = \rho_R, \quad x = +L/2, \tag{4-15}$$

where ρ_L and ρ_R are the charge densities of the system at the left and right hand walls respectively. Their values will depend upon the speed of charge transfer across the interface separating the open system from the adjoining phase. The first boundary condition is simply a statement that the total mass of the system is fixed at the steady state.

Because of the nonlinearity of Eqs. (4-10) and (4-11), it is generally not possible to obtain solutions to them in closed form. For this reason a pertubation approach is used in which system parameters and variables are characterized according to their departures from their mean values. Before introducing this technique it is useful to transform the starting equations to dimensionless form in order to facilitate comparison with numerical results. The pertubation scheme is simplified simultaneously. The following dimensionless variables are introduced

$$\bar{S} = (S - S_m)/S_m, \quad \bar{\alpha}_j = (AA/S_m)\alpha_j, \quad j = S,\Delta,$$

$$\bar{\Delta} = \Delta/S_m, \quad \bar{\beta}_j = \left[(-2z_1z_2F(AA)^2)/\varepsilon_0\right]\beta_j, \quad j = S,\Delta,$$

$$\bar{x} = x/AA, \quad \bar{E} = -\left[\varepsilon_0/(2z_1z_2FS_m(AA))\right]E, \tag{4-16}$$

where S_m is the mean value of the sum concentration, ε_0 is the permittivity of a vacuum, and the barred quantities represent dimensionless variables. The value of AA in the above equations is chosen such that the reduced Debye length is fixed at a value of 5.0. This number has been found to give a convenient grid spacing length for numerical simulations (Brumlevé and Buck [1978]). The dimensionless variables used here are the same as those used in subsequent numerical simulations. In terms of reduced variables the starting equations become

$$(d^2\bar{E}/d\bar{x}^2) - (\bar{A}^2)\bar{E} = -\bar{\alpha}_\Delta/\overline{EPS}, \tag{4-17}$$

$$(d\bar{S}/d\bar{x}) = \bar{\alpha}_S\bar{x} + \bar{\beta}_S\bar{E}, \tag{4-18}$$

where $\overline{EPS}$ is the dielectric constant of the system (78.5 for water) and $\bar{A}$ is the reciprocal of the reduced Debye length of the system, given by

$$\bar{A} = -\bar{\beta}_\Delta/\overline{EPS} \tag{4-19}$$

In reduced variables the boundary conditions become

$$\int_{\bar{x}} \bar{S}d\bar{x} = 0, \tag{4-20}$$

$$\bar{\Delta} = \rho_L/S_m, \quad \bar{x} = -L/2AA, \tag{4-21}$$

$$\bar{\Delta} = \rho_R/S_m, \quad \bar{x} = +L/2AA. \tag{4-22}$$

The pertubation scheme is defined for the dependent variables as follows

$$S = S_0 + \delta S_1 + \delta S_2 + \cdots, \tag{4-23}$$

$$E = E_0 + \delta E_1 + \delta E_2 + \cdots, \tag{4-24}$$

where δ is a bookkeeping device that allows one to characterize the departure of Eqs. (4-17) and (4-18) from linearity. The barred notation has been omitted from Eqs. (4-23) and (4-24) for simplicity. The coefficients (L) are expanded in a Taylor's series about their mean

values according to

$$L(S,\Delta) = L_0 + \delta\left[L_S(S) + L_\Delta(\Delta)\right] + \cdots, \tag{4-25}$$

where L_0 represents the value of L at the mean values of S and Δ, and L_j ($j = S, \Delta$) is the derivative of L with respect to j evaluated at the mean values of S and Δ.

Substitution of Eqs. (4-23) through (4-25) into Eqs. (4-17) and (4-18) and subsequent ordering of the terms according to their power in δ results in sets of coupled linear ordinary differential equations solvable by standard techniques. Although in principle this set of equations is solvable, there is no guarantee of success in this technique, as the magnitude of higher order terms may increase leading to a divergent solution.

Collection of terms of order zero in δ results in

$$(d^2E_0/dx^2) - A_0^2E_0 = -\alpha_{\Delta 0}/EPS, \tag{4-26}$$

$$(dS_0/dx) = \alpha_{S0} + \beta_{S0}E_0, \tag{4-27}$$

where L_{ij} is the j^{th} order approximation to the coefficient L_i ($i = S,\Delta$, $j = 0,1,2,\cdots$). This system of equations would be the true description of the system if it were ideal.

To obtain E_0, we first solve Eq. (4-26). To obtain S_0, we use the

solution to Eq. (4-26) in Eq. (4-27). The zeroth order contribution to the charge density (Δ_0) is obtained by simple differentiation of E_0 in accordance with Poisson's equation. The general solution shown below results in the generation of three arbitrary constants whose values are fixed by application of the boundary conditions. We require that the zeroth order solution satisfy totally the charge density requirement at each wall while higher order solutions in charge density will be zero at the walls. The boundary conditions then become

$$\int_{\bar{x}} S_i dx = 0, \quad i = 0,1,2,\cdots, \tag{4-28}$$

$$\Delta_0 = \rho_L/S_m, \quad x = -L/2AA,$$

$$\Delta_0 = \rho_R/S_m, \quad x = +L/2AA,$$

$$\Delta_i = 0, \quad i = 1,2,\cdots, \quad \bar{x} = \pm(L/2AA). \tag{4-29}$$

The zeroth order solution is

$$E_0 = -(\alpha_{\Delta 0}/\beta_{\Delta 0}) - (\rho/A(EPS)) \left[\cosh(Ax)/\sinh(A\xi)\right],$$

$$S_0 = (\rho\beta_{S0}/\beta_{\Delta 0})(\sinh(Ax)/\sinh(A\xi)) + \left[(\alpha_{S0}\beta_{\Delta 0} - \alpha_{\Delta 0}\beta_{S0})/\beta_{\Delta 0}\right]x,$$

$$D_0 = \rho \left[\sinh(Ax)/\sinh(A\xi)\right], \tag{4-30}$$

where the dimensionless cell length defined by

$$\xi = (L/2AA) \tag{4-31}$$

and ρ the charge density

$$\rho \equiv -(\rho_L/S_m) = (\rho_R/S_m) \tag{4-32}$$

have been introduced.

It is apparent from the form of the solution that the redefinition of the concentration variables has served an exceedingly useful purpose in that each of the first two expressions is separated into two parts, one due to charge density and one due to bulk or electrically neutral behavior.

At 298 K, for an aqueous solution of ionic strength 0.01M, and a cell length of 1 cm, the value of ξ is on the order of 10^8. For solid electrolytes (where dielectric constants are much lower) at temperatures up to 1000 K and at cell lengths of up to 1 cm, the value of ξ is on the order of 10^8 or higher. This means that contributions to E_0 and S_0 due to nonelectroneutrality are going to be negligible everywhere except within approximately 5 Debye lengths of the walls. In the bulk solution a linear drop in concentration with a constant value for the electric field is found as expected.

Collection of terms of order one in δ gives

$$(d^2E_1/dx^2) - (A^2_0)E_1 = -(1/EPS)\left[\beta_{\Delta S}S_0 + \beta_{\Delta\Delta}\Delta_0\right]E_0, \tag{4-33}$$

$$(dS_1/dx) = \beta_{S0}E_1 + \left[\beta_{SS}S_0 + \beta_{S\Delta}\Delta_0\right]E_0, \qquad (4\text{-}34)$$

where the L_{ij}, $(i,j = S,\Delta)$ are the derivatives of L_i with respect to j evaluated at the mean concentrations of the system. Inclusion of terms involving derivatives of the α's is deferred until higher orders because of their expected smallness. The procedure for solving the first order set of equations is similar to that for the zeroth order, first the expressions for S_0 and E_0 are substituted into Eq. (4-33), and a solution for E_1 is obtained. Then, E_1, along with S_0 and E_0 are substituted into Eq. (4-34) to obtain S_1. As before Δ_1 results from simple differentiation of E_1 in accordance with Poisson's equation. The complete first order result is shown in Appendix B. Higher order solutions are obtained in the same way. The inclusion of more and more terms in the starting equations results in more and more complicated algebraic problems as one progresses to higher orders. This is already apparent in the first order case.

The way the problem was defined and the nature of the pertubation scheme result in solutions that alternate in parity. For the zeroth order case, E_0 is an even function while S_0 and Δ_0 are odd; at first order, E_1 is odd while S_1 and Δ_1 are even. This requires that one obtain a second order solution for the electric field in order to determine the first correction to the voltage drop $\Delta\phi$ across the electrolyte since, for E_1 odd,

$$\Delta\phi_1 = -\int_\xi E_1 dx = 0. \qquad (4\text{-}35)$$

The results are shown in Appendix B.

E. Determination of Efficiency

The current delivered to the load is $I = F \sum z_i J_i = I_1 + I_2$, where I_1 and I_2 are the individual ionic currents. The efficiency η defined here is the product of the voltage efficiency $(\Delta\phi)/(\Delta\phi_{rev})$ and the faradaic efficiency (I/I_m), where I_m is the maximum current that would be produced by the cell if it could operate ideally.

The power P delivered to the load by an ideally operating fuel cell (Bockris [1969]) is

$$P = I\Delta\phi = I\left[\Delta\phi_{rev} - IL/\lambda_m\right], \tag{4-36}$$

where λ_m is the mean specific conductance of the electrolyte. I_m is easily determined by setting the derivative of the power with respect to the current equal to zero, giving

$$I_m = \lambda_m \Delta\phi_{rev}/2L. \tag{4-37}$$

Measurement of the a.c. and d.c. properties of the electrode-electrolyte system of interest enables one to determine the value of λ_m and to calculate faradaic efficiencies as a function of total current produced by the cell.

The electrochemical contribution $\phi_V - \phi_{IV}$ to the total measured

voltage across the cell $\Delta\phi$ is obtained from integration of Eq. (4-30). In the isothermal case, $T_A = T_B = T_B$, so that $\phi_{II} = \phi_I$, and $\phi_{VII} = \phi_{VIII}$ (see Figure (4-1)). The measured EMF consists of the sum of the heterogeneous contributions $\Delta\phi_{het}$ and the homogeneous contributions $\Delta\phi_{hom}$.

$$\Delta\phi = \Delta\phi_{hom} + \Delta\phi_{het} = \phi_{VIII} - \phi_I, \tag{4-38}$$

where $$\Delta\phi_{hom} = \phi_V - \phi_{IV}, \tag{4-39}$$

$$\Delta\phi_{het} = (\phi_{VIII} - \phi_{VI}) + (\phi_{VI} - \phi_V) + (\phi_{IV} - \phi_{III}) + (\phi_{III} - \phi_I). \tag{4-40}$$

The assumption of electrochemical equilibrium across the wire/electrode interfaces allows us to write

$$\tilde{\mu}_e(A') = \tilde{\mu}_e(B'), \quad \tilde{\mu}_e(B) = \tilde{\mu}_e(A),$$

$$\tilde{\mu}_e(B) = \tilde{\mu}_e(x=-L/2), \quad \tilde{\mu}_e(B') = \tilde{\mu}_e(x=+L/2). \tag{4-41}$$

By substituting the full expression given by Eq. (2-6) for the electrochemical potentials above and solving for $\Delta\phi_{het}$, we obtain

$$F\Delta\phi_{het} = (RT)\ln\left[a_e(-L/2)/a_e(+L/2)\right], \tag{4-42}$$

where a_e, the activity of the electron, is different at either end of

the electrolyte. Because both the standard state chemical potential and the activity of the electron are equal in phases A and A' since the measurement of $\Delta\phi$ must take place between wires of the same phase, they do not appear in the final expression for the heterogeneous potential. The heterogeneous contribution is then added to the homogeneous contribution,

$$F\Delta\phi = F(\phi_V - \phi_{IV}) + (RT)\ln\left[a_e(-L/2)/a_e(+L/2)\right], \qquad (4\text{-}43)$$

which enables one to determine the voltage efficiency of the operating device. From a knowledge of the total efficiency of the operating device as a function of current given by the macroscopic description of the system, it becomes possible to predict under what external loads the cell operates most efficiently and how the material parameters affect cell performance.

F. Results and Discussion

1. Introduction

The results and ensuing discussion presented in this section are based upon the properties of the mixed (ionic-electronic) conductor solid electrolyte doped Cerium (IV) oxide. Choudhury and Patterson [1971], Tannhauser, [1978], and Riess [1981] have all derived analytical expressions relating the steady state voltage output of high temperature ($T \simeq 1100$ K) fuel cells employing this electrolyte to the current produced by the cell. Such relationships are termed "characteristics,"

and depend upon the material parameters of the electrolyte. Their calculations all share the common shortcomings of using the Nernst-Planck transport equations rather than the full set of Onsager flux equations, and at some point in their calculations all assume electroneutrality throughout the electrolyte. In addition they neglect the spatial dependence of the various system parameters (D, λ, and K) and in effect consider only the zeroth order solution for an ideally behaving system. These assumptions could, collectively, lead to a serious overestimation of the efficiency and hence of the economic performance of such systems. From the data acquired by the above workers and the more accurate expressions for the potential derived here it is possible to assess the importance of these effects and to arrive at a more realistic theoretical prediction of the economic feasibility of such devices.

2. The Mixed Conductor System

The electrolyte is a membrane of doped CeO_2, typically at high temperature, extending from x=-L/2 to x=+L/2. The arrangement and phase boundary sections are shown in Figures (3-1) and (3-4). The doping is done with a lower-valent metal, Ca^{2+}, creating vacancies $V_{\ddot{o}}$ in the oxide sublattice with an effective double positive charge above what exists in the undoped material. These charged vacancies conduct the ionic portion of the electrical current. The overall reaction which provides the driving force for the cell is given by the sum of the reactions occurring at the phase boundaries,

$$6Fe_2O_3 + 6FeO = 6Fe_3O_4. \qquad (4\text{-}44)$$

The oxygen partial pressures at the phase boundaries are fixed by the equilibria in the two phase electrode compartments,

$$\text{Anode: } 6FeO + O_2(g) = 2Fe_3O_4, \qquad (4\text{-}45)$$

$$\text{Cathode: } 6Fe_2O_3 = 4Fe_3O_4 + O_2(g). \qquad (4\text{-}46)$$

Substitution of Eqs. (4-45) and (4-46) into Eq. (4-44) produces

$$O_2(g,B) = O_2(g,B') \qquad (4\text{-}47)$$

with a ΔG° equal to that of the reaction given in Eq. (4-44). This value of ΔG° is the amount of reversible work required to displace one mole of $O_2(g)$ from its partial pressure at B' to its partial pressure at B. The reversible potential is therefore

$$\Delta\phi_{rev} = (RT/nF) \ln \left[P_{O_2(g,B')}/P_{O_2(g,B)}\right], \qquad (4\text{-}48)$$

where n is the number of equivalents of electrons required to displace one mole of O_2, and P_{O_2} is the partial pressure of oxygen. Due to the kinetic problems at the phase boundaries and the ohmic losses that occur in the electrolyte the useful voltage obtainable from such a cell will always be less than $\Delta\phi_{rev}$.

For the reactions given by Eqs. (4-45) and (4-46) the equilibrium

conditions at either end of the electrolyte are (Schmalzried [1974])

$$\text{phase I: } O^{2-} = 2e^- + (1/2)O_2(g) + V_{\ddot{o}}, \tag{4-49}$$

$$\text{phase II: } V_{\ddot{o}} + (1/2)O_2(g) + 2e^- = O^{2-}. \tag{4-50}$$

Since the partial pressures of oxygen are fixed in the two phase electrode compartments, the electrochemical potentials of the electrons, vacancies, and oxide anions will in general be different at each end of the electrolyte, and therefore a flux of each species occurs. The entropy production (θ) for this system is (Howard and Lidiard [1963])

$$\theta = J_{V_{\ddot{o}}}X_{V_{\ddot{o}}} + J_{e^-}X_{e^-} + J_{O^{2-}}X_{O^{2-}}, \tag{4-51}$$

where

$$X_i = -(\partial\tilde{\mu}_i/\partial x). \tag{4-52}$$

The conservation of lattice sites requires that $J_{O^{2-}} = -J_{V_{\ddot{o}}}$, since every jump of an oxide anion from one lattice site to another is accompanied by a vacancy jump in the opposite direction. Therefore θ becomes

$$-J_{V\ddot{o}}\left[(\partial\tilde{\mu}_{V_{\ddot{o}}}/\partial x)-(\partial\tilde{\mu}_{O^{2-}}/\partial x) \right] - J_{e^-}(\partial\tilde{\mu}_{e^-}/\partial x), \tag{4-53}$$

and Onsager thermodynamics yields

$$-J_1 = l_{11}\left[(\partial\mu_1/\partial x) - (\partial\mu_{O^{2-}}/\partial x) - z_{O^{2-}}F(\partial\phi/\partial x) \right]$$

$$+ l_{12} (\partial\mu_2/\partial x), \tag{4-54}$$

$$-J_2 = l_{21} \left[(\partial\mu_1/\partial x) - (\partial\mu_{O^{2-}}/\partial x) - z_{O^{2-}}F(\partial\phi/\partial x) \right]$$

$$+ l_{22} (\partial\mu_2/\partial x), \tag{4-55}$$

where the subscripts 1 and 2 denote vacancies and electrons respectively, and Eq. (2-7) has been used. Because the number of vacancies is far less than the number of oxide anions, the relative change in the oxide anion concentration will be far less than that of the vacancies. We therefore neglect the change in the oxide anion chemical potential. Eqs. (4-54) and (4-55) simplify to the prototype flux equations for isothermal transport given by Eqs. (2-2)

$$-J_i = \sum l_{ij}\left[\partial\tilde{\mu}_j/\partial x\right], \quad i,j = 1,2 \tag{4-56}$$

where $z_1 = z_{O^{2-}}$ is the effective charge on the vacancies.

3. Calculation of Efficiency

From the definition of efficiency and Eqs. (4-37) and (4-43) we write

$$\eta = \left[2IL/\lambda_m(\Delta\phi_{rev})^2\right] \left[(\phi_V - \phi_{IV}) + (RT/F) \right.$$

$$\left. \cdot \ln[c_2(-L/2)/c_2(+L/2)] \right] \tag{4-57}$$

where the activities have been replaced with concentrations. These concentrations subsequently serve as boundary conditions through the equilibrium constants for the reactions given by Eqs. (4-49) and (4-50). The value of $\phi_V - \phi_{IV}$ in Eq. (4-57) is determined by integration of Eq. (4-30) and allows us to determine the effect of selectively changing the value of ρ on the efficiency through Eq. (4-57). All effects due to the nonideality of the electrolyte are retained in the evaluation of $\phi_V - \phi_{IV}$.

The more mobile electrons enter and leave the electrolyte faster and therefore create a region of negative charge at the anodic end of the electrolyte and a positive charge at the cathodic end. Integration of Eq. (4-30) reveals a linear relationship between the voltage loss and this charge buildup, (ρ),

$$(\phi_V - \phi_{IV}) = a + b\rho, \qquad (4\text{-}58)$$

with the values of a and b displayed as a function of current in Table (4-1). These data highlight the importance of the inclusion of space charge upon voltage loss estimates. Only when one approaches complete charge separation ($\rho \rightarrow 1$) does this effect become important, but it is precisely at the charged surface of the electrode where one might expect complete separation of charge to occur. From Eq. (4-57) a linear relationship between the efficiency and the charge density results with

$$\eta = c + d\rho. \qquad (4\text{-}59)$$

The values of the coefficients c and d for Eq. (4-59) are tabulated alongside those of Eq. (4-58) in Table (4-1). These data demonstrate that the inclusion of space charge may be of great importance in theoretical determinations of efficiency. In Figure (4-2) a plot of efficiency versus current density shows that in the absence of overpotentials we expect behavior similar to that of an ideally operating fuel cell (see Eq. (4-16)). The ratio, (R), of the voltage loss obtained from Eq. (B-18) to that obtained from integration of Eq. (4-30) obeys the linear relationship

$$R = e + f\rho. \tag{4-60}$$

The coefficients e and f for Eq. (4-60) are displayed in Table (4-1). Figure (4-3) shows the relationship between R and the current. The increase in R with both ρ and the current is not surprising since the higher the current or charge density the greater the departure from linearity, where higher order solutions are expected to make a greater relative contribution.

TABLE 4-1. Least Squares Values of the Empirical Constants Given in the Equations $(\phi_V - \phi_{IV}) = a + b\rho$, $\eta = c + d\rho$, and $R = e + f\rho$ for Various Values of the Current.

Current Density ($A\text{-}cm^{-2}$)	a (volts)	$b \times 10^2$ (volts)	$c \times 10^2$	$d \times 10^2$	$e \times 10^3$	$f \times 10^3$
0.00	-0.135	-9.58	0.00	0.000	5.251	10.91
0.05	-0.167	-9.58	3.74	-0.400	5.982	12.40
0.10	-0.201	-9.54	7.19	-0.800	7.043	13.77
0.15	-0.241	-9.58	10.26	-1.169	8.44	16.04
0.20	-0.283	-9.52	13.02	-1.584	10.45	18.31
0.25	-0.330	-9.52	15.30	-1.980	13.01	21.63
0.30	-0.383	-9.52	17.02	-2.388	16.94	25.33

Figure (4-2). Dependence of efficiency on current density. (a) Ohm's Law behavior, (b) behavior predicted by Eq. (4-57).

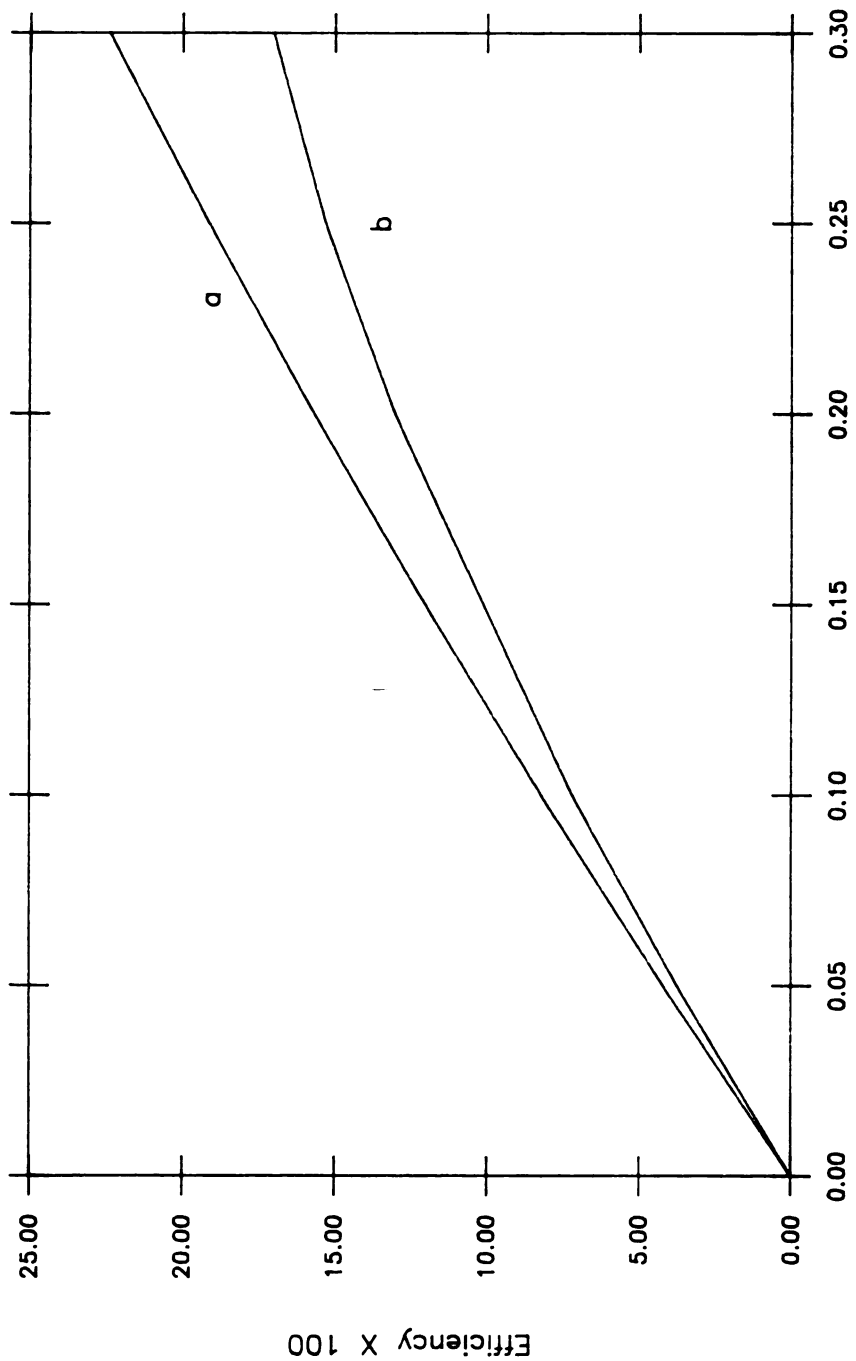

Efficiency X 100
25.00
20.00
15.00
10.00
5.00
0.00
0.00
0.05
0.10
0.15
0.20
0.25
0.30
Current Density (A-cm^{-2})
a
b

Figure (4-2)

Figure (4-3). Dependence of R on current density.

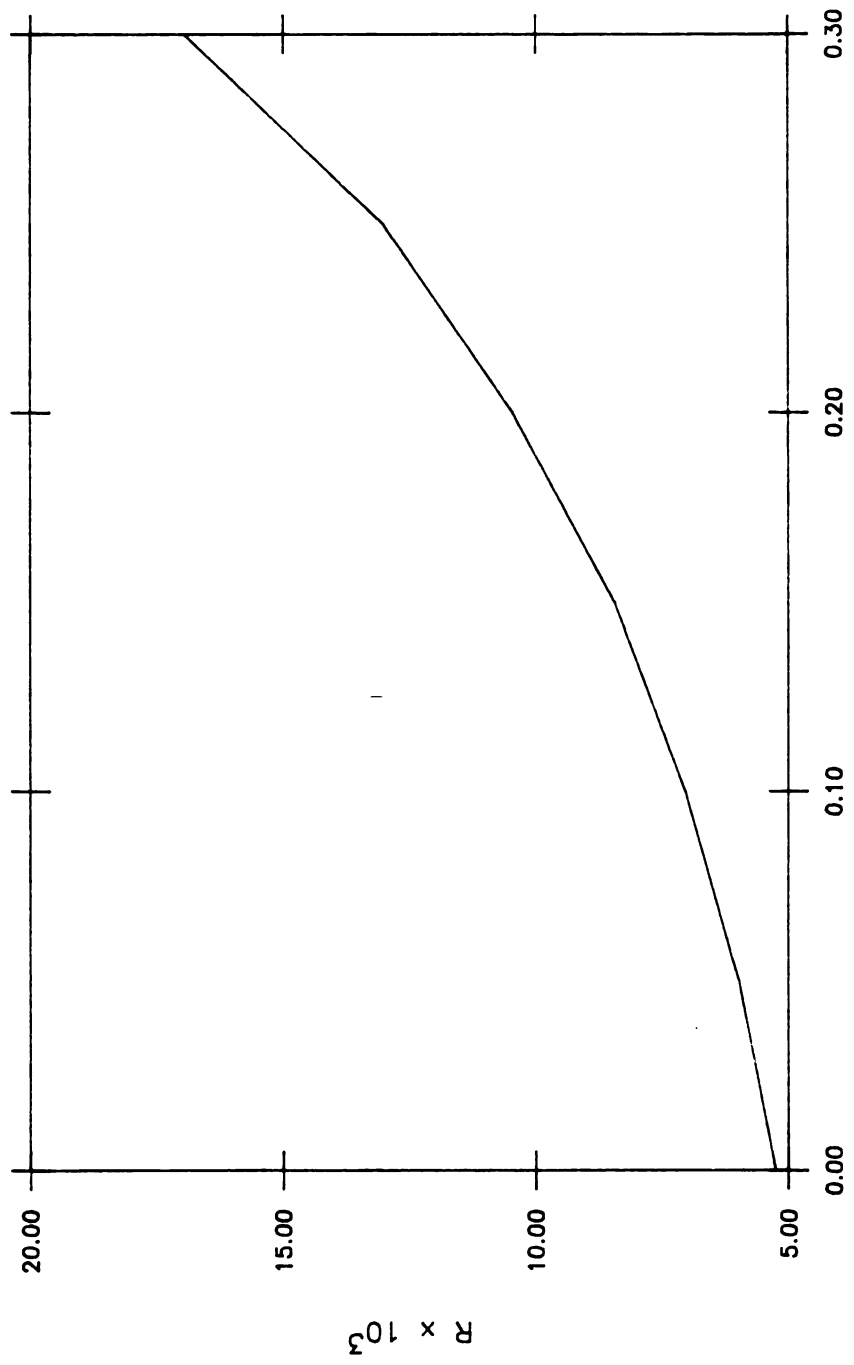

20.00
15.00
10.00
5.00
R x 10^3
0.00
0.10
0.20
0.30
Current Density (A-cm^-2)

Figure (4-3)

CHAPTER 5

STEADY STATE NONISOTHERMAL TRANSPORT IN OPEN SYSTEMS

A. Introduction

A nonisothermal cell or thermogalvanic cell is a galvanic cell in which the temperature is not uniform. The first experiments on nonisothermal liquid systems were done over 100 years ago by Ludwig [1859] and Soret [1879, 1880]. The possibility of using solid salt compounds as electrolytes in nonisothermal galvanic cells has been discussed by Sundheim [1960], Christy [1960], Howard and Lidiard [1964], and Wagner [1972]. One of the concerns of this chapter is to explore the relationship between EMF of such cells and the ionic properties that arise in nonisothermal systems, particularly the entropies of transport of the ions (S_i^*) and the Soret coefficient.

Thermoelectric effects in the metallic leads extending from the electrodes may also contribute to the EMF of such cells. By inserting reversible electrodes at suitable points as in Figure (4-1), the overall cell potential can be broken up into the sum of EMF's of successive terminals. We can thus break up the total EMF into the EMF of an isothermal cell at a known temperature and the EMF due to nonisothermal effects. It is upon the effect of these distinctly nonisothermal features on cell performance that we shall focus our attention in this chapter.

For nonisothermal systems the steady-state ion transport equations in dimensionless form are

$$(d^2\bar{E}/d\bar{x}^2) - (\bar{A}_0^2)\bar{E} = (-1/\overline{EPS})\left[\bar{\alpha}_\Delta + \bar{\gamma}_\Delta(d\bar{T}/d\bar{x})\right], \tag{5-1}$$

$$d\bar{S}/d\bar{x} = \bar{\alpha}_S + \bar{\beta}_S\bar{E} + \bar{\gamma}_S(d\bar{T}/d\bar{x}). \tag{5-2}$$

B. Temperature Distribution

At the steady-state, $\partial T/\partial t = 0$ and Eq. (2-21) becomes

$$0 = -I(d\phi/dx) - (dJ_q/dx) - \sum J_i(dH_i/dx) - \sum\sum \nu_{ir}b_r H_i. \tag{5-3}$$

The heat flux in Eq. (5-3) is eliminated through substitution of Eq. (2-3), while the electrostatic potential is eliminated by solving Eq. (2-2) for $d\phi/dx$, where

$$\tilde{\mu}_i = \mu_i + z_i F\phi, \tag{5-4}$$

and the elimination gives

$$0 = I^2/\lambda + (d/dx)[K_\infty(dT/dx)] - \sum J_i\left[(dQ_i^*/dx) + (dH_i/dx)\right.$$

$$\left. - (d\mu_i/dx)_T - (Q_i^*/T)(dT/dx)\right] - \sum\sum \nu_{ir}b_r(H_i + Q_i^*). \tag{5-5}$$

The entropy of transport S_i^* and enthalpy of transport H_i^* are defined by

$$S_i^* = S_i + (Q_i^*/T) \tag{5-6}$$

$$H_i^* = H_i + Q_i^*, \tag{5-7}$$

and

$$(\partial \mu_i/\partial x)_T = (\partial \mu_i/\partial x) + S_i(\partial T/\partial x). \tag{5-8}$$

Substitution of Eqs. (5-6-8) into Eq. (5-5) gives

$$0 = I^2/\lambda + (d/dx)\left[K_\infty(dT/dx)\right] - \sum J_i\Big[\, T(dS_i^*/dx)_T + T(\partial S_i^*/\partial T)(dT/dx) \,\Big] - \sum\sum \nu_{ir} b_r H_i^*. \tag{5-9}$$

The first two terms in the energy balance are the Joule heat (I^2/λ) and thermal conduction $(d/dx)[K_\infty(dT/dx)]$ respectively. The first summation contains terms related to the Peltier heat Q and Thomson heat τ defined as

$$Q = (IT/F) \sum (t_i/z_i)S_i^*, \tag{5-10}$$

$$\tau = (IT/F) \sum (t_i/z_i)(dS_i^*/dT), \tag{5-11}$$

where

$$J_i = (t_i/z_iF)I. \tag{5-12}$$

With Eq. (5-11) and (5-12) the energy balance becomes

$$0 = I^2/\lambda + (d/dx)\left[K_\infty(dT/dx)\right] + I\tau(dT/dx)$$

$$- (IT/F)\sum (t_i/z_iF)(dS_i^*/dx)_T. \qquad (5\text{-}13)$$

Comparison of Eqs. (5-10) and (5-13) shows that the summation term in Eq. (5-13) represents a continuous Peltier heat contribution. The Peltier and Thomson heats are cross effects and are of minor importance compared to the thermal conduction term and the Joule heating term in Eq. (5-9). In addition, if the cell electrodes are operating nearly reversibly the reaction terms will vanish ($b_r = 0$), leaving an energy conservation law of the form

$$0 = I^2/\lambda + (d/dx)\left[K_\infty(dT/dx)\right]. \qquad (5\text{-}14)$$

For the case of zero current and constant thermal conductivity, Eq. (5-14) reduces to the well known Fourier heat equation [1822]. Anderson and Horne, using a pertubation approach, have solved the time dependent energy balance equation, for the case of no current, in a binary liquid mixture. A similar approach is used here. We write the temperature as the sum of the mean temperature T_m and higher order pertubation terms T_i (i=0,1,2,$\cdots$), and we expand the thermal conductivity and electrical conductivity of the system in a Taylor's series about their values at the mean composition and temperature. This results in

$$T = T_m + T_0 + \delta T_1 + \delta T_2 + \cdots \tag{5-15}$$

$$L = L^0 + \delta\left[L_S(S-S_m) + L_\Delta(D) + L_T(T-T_m)\right] + \cdots \tag{5-16}$$

where $L = \lambda$ or K_∞, L_j ($j = S,\Delta,T$) is the derivative of L with respect to j evaluated at the mean system concentrations and temperature, and δ is the pertubation parameter.

Substitution of Eqs. (5-15) and (5-16) into Eq. (5-14) and collection of zeroth order terms results in

$$I^2 + \lambda_0 K_0 (d^2T_0/dx^2) = 0. \tag{5-17}$$

Eq. (5-17) is rendered dimensionless by introducing the dimensionless temperature $\bar{T} = (T - T_m)/T_m$ and using Eq. (4-16). The result is

$$(d^2\bar{T}_0/d\bar{x}^2) + I^2L^2/(4\xi^2\lambda_0 K_0 T_m) = 0. \tag{5-18}$$

The boundary conditions are $T(-L/2) = T_B$, and $T(+L/2) = T_B$,. In terms of dimensionless variables these are

$$\bar{T}_0(\xi) = (\Delta T/2T_m), \tag{5-19}$$

$$\bar{T}_0(-\xi) = (-\Delta T/2T_m), \tag{5-20}$$

$$\bar{T}_i(\pm\xi) = 0, \qquad i = 1,2,\cdots, \tag{5-21}$$

where $\Delta T = (T_{B'} - T_B)$ and $T_M = (T_B + T_{B'})/2$. The barred notation is dropped at this point with all subsequent references to the dependent variables in their dimensionless form.

The solution of Eq. (5-14) subject to Eqs. (5-15-16) is

$$T_0 = (\Delta T/T_m)(x/2\xi) + (\xi^2 - x^2)(I^2L^2/2\xi^2\lambda_0 K_0 T_m). \tag{5-22}$$

For solid electrolytes the thermal conductivity is about 10^{-1} $Jcm^{-1}K^{-1}s^{-1}$, while the electrical conductivity is about 10^{-1} $(\Omega cm)^{-1}$. For a cell 1 cm long at room temperature the maximum contribution of Joule heating occurs at the center of the cell and is

$$T_0(x = 0) = \left[(IL)^2/4\lambda_0 K_0 T_m\right] = 25(I/T_m). \tag{5-23}$$

For cells at low temperatures ($T_m \simeq 300K$) current densities as low as 1 amp/cm^2 result in contributions to the zeroth order temperature less than 9 percent of the mean temperature. For high temperature fuel cells ($T_m \simeq 1000K$), the same current density results in a contribution of less than 3 percent. Joule heating is less important at high temperatures and can safely be neglected for high temperature fuel cells operating at low current densities. Indeed, as is shown in Appendix D, inclusion of the Joule heating term in the temperature expression has no effect upon the <u>voltage</u> loss across the electrolyte considered in this work.

C. Solution to the Nonisothermal Problem

Substitution of Eq. (5-22) into Eq. (5-1) and collection of terms of order zero gives

$$(d^2E_0/dx^2) - (A_0^2)E_0 = -(1/EPS)\left[\ \alpha_{\Delta 0} + \gamma_{\Delta 0}(\Delta T/2\xi T_m)\right] \tag{5-24}$$

$$dS_0/dx = \alpha_{S0} + \beta_{S0}E_0 + \gamma_{S0}(\Delta T/2\xi T_m), \tag{5-25}$$

where the Joule heating contribution has been neglected. Comparison of the above set of equations to their isothermal analogs suggests the introduction of two new parameters,

$$\alpha'_{\Delta 0} = \alpha_{\Delta 0} + \gamma_{\Delta 0}(\Delta T/2T_m\xi), \tag{5-26}$$

$$\alpha'_{S0} = \alpha_{S0} + \gamma_{S0}(\Delta T/2T_m\xi). \tag{5-27}$$

When Eqs. (5-26) and (5-27) are substituted into Eqs. (5-24) and (5-25), the result is

$$(d^2E_0/dx^2) - A_0^2E_0 = -\alpha'_{\Delta 0}/EPS, \tag{5-28}$$

$$dS_0/dx = \alpha'_{S0} + \beta_{S0}E_0. \tag{5-29}$$

This set of equations has exactly the same form as Eqs. (4-26) and (4-27), and we can therefore write down their solutions by inspection. The complete set of first order equations and their solutions are shown in Appendix E.

D. Efficiency

The efficiency is defined as before as the product of faradaic and voltage efficiencies, written as

$$\eta = (I/I_m)(\Delta\phi/\Delta\phi_{rev}). \tag{5-30}$$

For the nonisothermal case $T_{B'} \neq T_B$ and thermal gradients are present in the wire phases (A, A'), as well as the electrolyte (C).

Assuming electrochemical equilibrium across each interface, we write for the heterogeneous potential contribution across the cell (Agar [1963], Watanabe [1980])

$$F\Delta\phi_{het} \equiv F\left[(\phi_{VII}-\phi_{VI}) + (\phi_{VI}-\phi_{V}) + (\phi_{IV}-\phi_{III}) + (\phi_{III}-\phi_{II})\right] =$$

$$[\mu_e(A)]_{T_{B'}} - [\mu_e(A)]_{T_B} + [\mu_e(C)]_{T_B}] - [\mu_e(C)]_{T_{B'}}, \tag{5-31}$$

where the chemical potential of the electron (μ_e) is written as $\mu_e = \mu_e^o + RT \ln c_e$, giving for the heterogeneous potential

$$F\Delta\phi_{het} = [\mu_e(A)]_{T_{B'}} - [\mu_e(A)]_{T_B} + [\mu_e^o(C)]_{T_B} - [\mu_e^o(C)]_{T_{B'}}$$

$$(RT_m)\ln\left[c_2{}^{(-L/2)}/c_{2(+L/2)}\right] - (R\Delta T/2)\ln\left[c_2{}^{(+L/2)}c_{2(-L/2)}\right], \tag{5-32}$$

where c_2 is the concentration of electrons in the electrolyte, and the definitions of ΔT and T_m are used. The homogeneous potential $\Delta\phi_{hom} \equiv$

$(\phi_{VIII} - \phi_{VII}) + (\phi_V - \phi_{IV}) + (\phi_{II} - \phi_I)$ is determined by the solution to the flux equations in the appropriate phases. The solution for the electrolyte $(\phi_V - \phi_{IV})$ has been given above. For the wire phases (A,A') only the electron is mobile, and there are no composition gradients present. The flux equations for these phases become

$$I = -\lambda(A)(d\phi/dx) + [\lambda(A)Q_e^*/FT](dT/dx)_A, \tag{5-33}$$

with an exactly analagous equation for phase A'. Rearrangement and integration gives

$$F\left[(\phi_{VIII}-\phi_{VII}) + (\phi_{II}-\phi_I)\right] = -F\int (I/\lambda(A))dx$$

$$+ \int (Q_e^*(A)/T)dT. \tag{5-34}$$

Since $\lambda(A)$ is large for metals ($\lambda(Ag) \simeq 10^5$ $(\Omega cm)^{-1}$), the ohmic drop across the wire phases can safely be neglected, and the homogeneous potential becomes

$$F\Delta\phi_{hom} = -\int (Q_e^*(A)/T)dT + F(\phi_V - \phi_{IV}). \tag{5-35}$$

The total measurable potential $\Delta\phi \equiv \Delta\phi_{hom} + \Delta\phi_{het}$ is given by the sum of Eqs. (5-32) and (5-35). Before combining Eqs. (5-32) and (5-35) to arrive at an expression for $\Delta\phi$, it is necessary to expand the chemical potential μ_e^o in Eq. (5-32) and the quantity Q_e^*/T in Eq. (5-35) in a Taylor's series about the mean temperature. The Taylor's

series expansion for μ_e^o has the form

$$\mu_e^o(T) = \mu_e^o(T_m) + (\partial\mu_e^o/\partial T)(T - T_m) + (1/2)[(\partial^2\mu_e^o/\partial T^2)(T - T_m)^2] + \cdots, \quad (5\text{-}36)$$

where all derivatives are evaluated at the mean values of the temperature. Truncation of the above power series beyond the linear terms and substitution into Eq. (5-32) gives

$$F\Delta\phi_{het} = -(S_e(A) - S_e^o(C))[T_B, - T_B] + (RT_m)\ \ln[c_2(-L/2)/c_2(+L/2)] - (R\Delta T/2)\ \ln[c_2(+L/2)c_2(-L/2)] \quad (5\text{-}37)$$

Similarly, we expand the quantity (Q_e^*/T) in a Taylor's series about the mean temperature and obtain

$$Q_e^*/T = (Q_e^*/T)_{T_m} + \left[\partial(Q_e^*/T)/\partial T\right]_{T_m}(T - T_m) + (1/2)\left[\partial^2(Q_e^*/T)/\partial T^2\right]_{T_m}(T - T_m)^2 + \cdots. \quad (5\text{-}38)$$

Truncation of the above series beyond terms linear in temperature and substitution of the result into Eq. (5-35) gives

$$F\Delta\phi_{hom} = -(Q_e^*/T)_{T_m}[T_B, - T_B] + F[\phi_V - \phi_{IV}]. \quad (5\text{-}39)$$

The measurable EMF is given by the sum of Eqs. (5-37) and (5-39),

$$F\Delta\phi = F(\phi_V - \phi_{IV}) - (S_e^*(A) - S_e(C))\Delta T + (RT_m)\ln[c_2(-L/2)/c_2(+L/2)]$$

$$- (R\Delta T/2)\ln\left[1 + [(c_e(+L/2) - c_e(-L/2))/2c_e^m]^2\right], \quad (5\text{-}40)$$

where the mean concentration (c_e^m) is defined as

$$c_e^m = [c_e(+L/2) + c_e(-L/2)]/2, \quad (5\text{-}41)$$

and $S_e^o - R\ln c_e^m = S_e$.

When the fluxes of both species are zero, the flux equations become

$$0 = \sum l_{ij}\left[(\partial\tilde{\mu}_j/\partial x)_T + (Q_j^*/T)(\partial T/\partial x)\right]. \quad (5\text{-}42)$$

Since the electrochemical potential and the temperature gradient are linearly independent forces, the term in brackets in Eq. (5-42) must be zero for all j, and substitution of Eq. (5-4) into Eq. (5-42) gives

$$(\phi_V - \phi_{IV}) = -(1/z_iF)\int\left[(\partial\mu_i/\partial x)_T + (Q_i^*/T)(\partial T/\partial x)\right]dx \quad (5\text{-}43)$$

where i is the species to which the electrode is reversible. Substitution of Eq. (5-43) into Eq. (5-35) results in

$$\Delta\phi_{hom} = -(1/F)\int\left[(Q_e^*(A)/T) - S_e^*(C)\right]dT$$

$$+ [\mu_e(C)]_{T_B} - [\mu_e(C)]_{T_B'}. \quad (5\text{-}44)$$

The overall potential which results by summing Eqs. (5-32) and (5-44) is known as the thermoelectric power (P_{C-A}) of the thermocouple C-A,

$$P_{C-A} = -(1/F) \int \left[\left(Q_e^*(A)/T\right) - S_e^*(C) \right] dT$$

$$+ [\mu_e(A)]_{T_B'} - [\mu_e(C)]_{T_B'} \qquad (5\text{-}45)$$

and is related to the difference in the entropy of transport of the electron between the two phases. This is more easily seen by expanding the chemical potential in Eq. (5-45) in a Taylor's series about the mean temperature and substituting Eq. (5-7) for $Q_e^*(A)$ into Eq. (5-45). The result is

$$P_{C-A} = [-S_e^*(A) + S_e^*(C)]\Delta T. \qquad (5\text{-}46)$$

With this result it is now possible to express the total measurable potential given by Eq. (5-40) in terms of experimentally measurable parameters. This is done by substituting Eq. (5-46) and the zeroth order result for $\phi_V - \phi_{IV}$ into Eq. (5-40). The result is

$$F\Delta\phi = F\Big[P_{C-A} + (\alpha_{\Delta 0}/\beta_{\Delta 0})L + (Q^*(C)\Delta T/T_m)K_q$$

$$+ RT_m \ln[c_e(-L/2)/c_e(+L/2)] - R\Delta T \ln[1 - (\Delta c_e/2c_e^m)^2] \Big] \qquad (5\text{-}47)$$

where K_q is given in Appendix A and $Q^* = v_1 Q_1^* + v_2 Q_2^*$ is the heat of transport of the electrolyte. Substitution of Eq. (5-47) into Eq.

(5-30) gives

$$\eta = [2IL/F\lambda_m \Delta\phi_{rev}^2] \left[P_{C-A} - RT \ln [1 - (\Delta c_e/2c_e^m)^2] \right]$$

$$+ (RT_m)\ln[c_e(-L/2)/c_e(+L/2)] + \alpha_{\Delta 0}L/\beta_{\Delta 0} + (Q^*(C)\Delta T/T_m)K_q, \quad (5\text{-}48)$$

which relates the efficiency to the current and the material parameters of the system. For the isothermal case $\Delta T = 0$, and both Eqs. (5-47) and (5-48) reduce to their isothermal analogs, Eqs. (4-43) and (4-57) respectively.

E. Results and Discussion

For the mixed conductor system described previously there is, in addition to the component fluxes, a heat flux as a result of the presence of a temperature gradient, and the entropy production becomes (Howard and Lidiard [1963])

$$\theta = J_q X_q + J_1 X_1 + J_2 X_2, \quad (5\text{-}49)$$

where component 1 represents vacancies and component 2 represents electrons, and

$$X_q = -\partial \ln T/\partial x. \quad (5\text{-}50)$$

The resulting transport equations take the form of Eqs. (2-2) and (2-3) where $z_1 = -z_O{}^{2-}$ as before.

The measurable EMF for the nonisothermal case is given by Eq. (5-47) and retains exactly the same form as for the isothermal case, in which Eq. (4-30) was integrated to obtain $\phi_V - \phi_{IV}$. The difference is that now the alphas are replaced with the alpha primes defined by Eqs. (5-26) and (5-27). It is these primed alphas that contain the heat of transport of the electrolyte. The reversible EMF for the nonisothermal cell is obtained from the Nernst equation

$$\Delta G^o = -nF\Delta\phi_{rev}, \tag{5-51}$$

where ΔG^o is the free energy change accompanying the reversible transfer of one mole of $O_2(g)$ from the electrode at T_B' to the electrode at T_B and n is the number of electrons accompanying the transfer. In terms of the material parameters this is

$$\Delta\phi_{rev} \simeq (RT/nF) \ln [P_{O_2}^{B'}/P_{O_2}^{B}] +$$

$$(R\Delta T/2nF) \ln [1 - (\Delta P_{O_2}/2P_{O_2}^{m})^2] - S_{O_2(g)}\Delta T. \tag{5-52}$$

where $P_{O_2}^{m}$ is the arithmetic mean of the electrode O_2 pressures.

By selectively altering the value for the heat of transport of the electrolyte, its effect on output performance for this system has been determined. A plot of efficiency as a function of current is shown in Figure (5-1). When the sign of $Q^*\Delta T < 0$ the upper curve results. There are two cases to consider. When $Q^*\Delta T < 0$ thermal diffusion reinforces the electrolytic flux. This corresponds to one of two situations.

Figure (5-1). Dependence of the efficiency on current density. (a) $Q^* \Delta T < 0$, (b) $Q^* \Delta T = 0$, (c) $Q^* \Delta T > 0$.

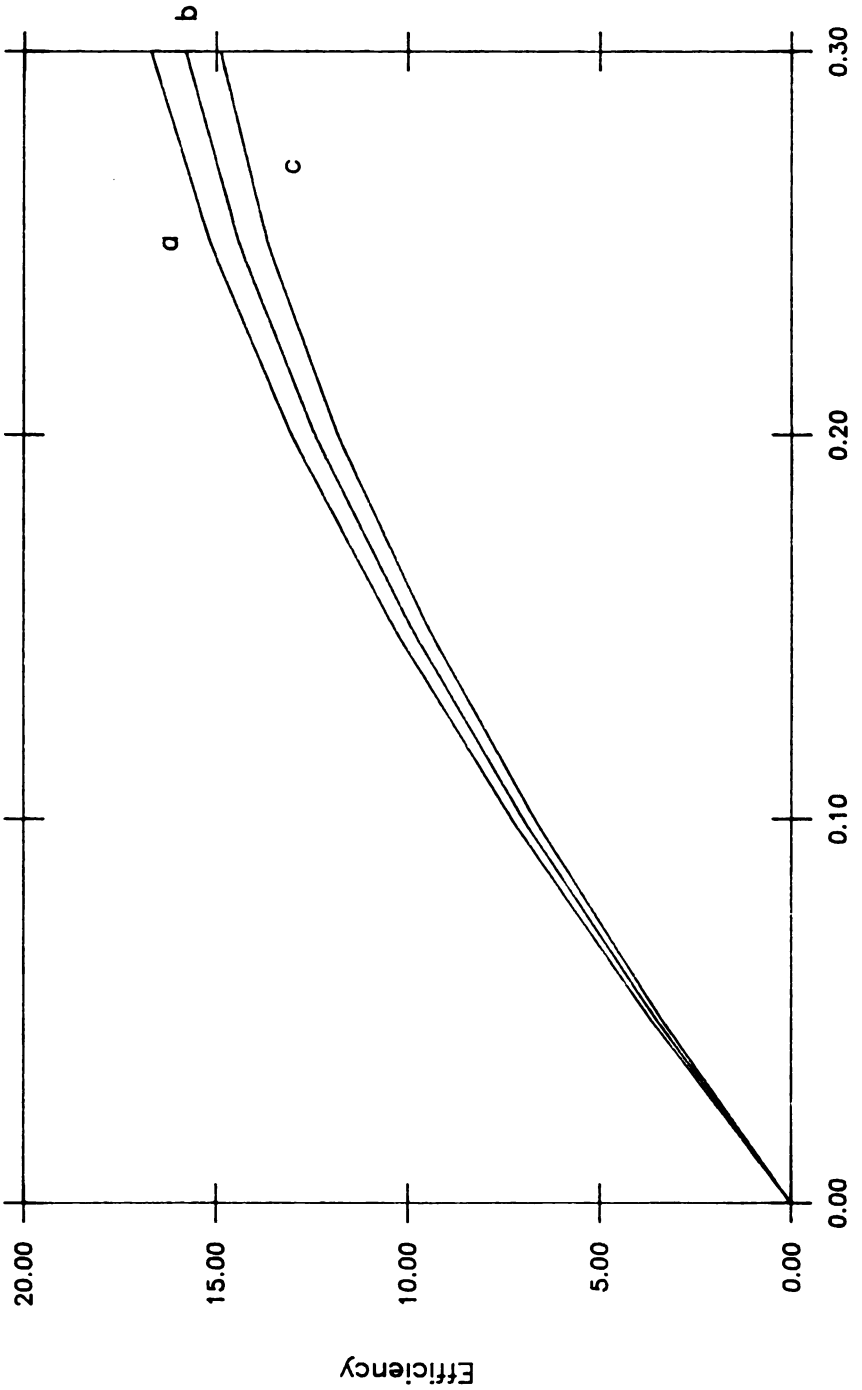

a
b
c
20.00
15.00
10.00
5.00
0.00
Efficiency
0.00
0.10
0.20
0.30
Current Density (A-cm^{-2})

Figure (5-1)

Either the cathode is cooler than the anode ($\Delta T < 0$, $Q^* > 0$), or the cathode is warmer than the anode ($\Delta T > 0$, $Q^* < 0$). In either event, because of its nonisothermal properties, the electrolyte prefers to be in the environment of the cathode. Therefore, to produce a current as great as the equivalent isothermal cell requires less ohmic loss across the electrolyte and results in an enhanced efficiency.

Exactly the opposite is true for the case of $Q^*\Delta T > 0$. Now, regardless of which direction the temperature gradient lies, the nonisothermal properties of the electrolyte dictate that it prefers the environment of the anode. Therefore, to produce the same current as the equivalent isothermal cell requires greater ohmic loss across the electrolyte and results in reduced efficiency.

For selected values of $Q^*\Delta T$ the efficiency has been calculated using Eq. (5-48), and the results fit to the empirical equation

$$\eta = a + b[Q^*\Delta T/T]. \qquad (5\text{-}53)$$

Although heat of transport data are not available for this electrolyte, the values of the empirical constants a and b displayed in Table (5-1) indicate that the greater the heat of transport of the electrolyte, the greater the potential for enhancing the efficiency, and the more profitable it becomes to exploit the nonisothermal properties of the electrolyte.

TABLE 5-1. Least Squares Values of the Empirical Constants Given in $\eta = a + b(Q^*\Delta T/T)$ for Various Values of the Current.

I ($A\text{-}cm^{-2}$)	a	b ($kcal^{-1}$ mol)
0.05	3.66	-5.00
0.10	6.98	-10.00
0.15	9.91	-14.84
0.20	12.42	-20.16
0.25	14.40	-25.00
0.30	15.79	-30.00

CHAPTER 6

NUMERICAL APPROACH

A. Introduction

The transport equations and boundary conditions described in Chapters 2 and 3 form a set of equations which are, in general, not solvable in closed analytical form. In an effort to verify the accuracy of the pertubation solutions obtained in Chapters 4 and 5 it is reasonable to resort to numerical techniques. Moreover numerical techniques can provide extremely accurate simulation results. The numerical technique of choice is the finite difference method. The details and theory behind the finite difference approach have been available for some time (Smith [1978] Rosenberg [1969]).

The essence of the finite difference approach is the replacement of the continuous space time domain with a discrete space time grid such as that depicted in Figure (6-1). In doing this the starting set of partial differential equations Eqs. (2-34) to (2-36), is converted to a set of algebraic, or finite difference, equations. In general, the grid spacing is nonuniform both in space and time. The nonuniformity in time allows one to expand the time steps as one approaches the steady state, where dependent variables are essentially constant, and to compress the time spacing at short times, when dependent variables are changing very rapidly. Nonuniformity in the space grid exists for a similar reason.

Figure (6-1). Nonuniform space and time grid.

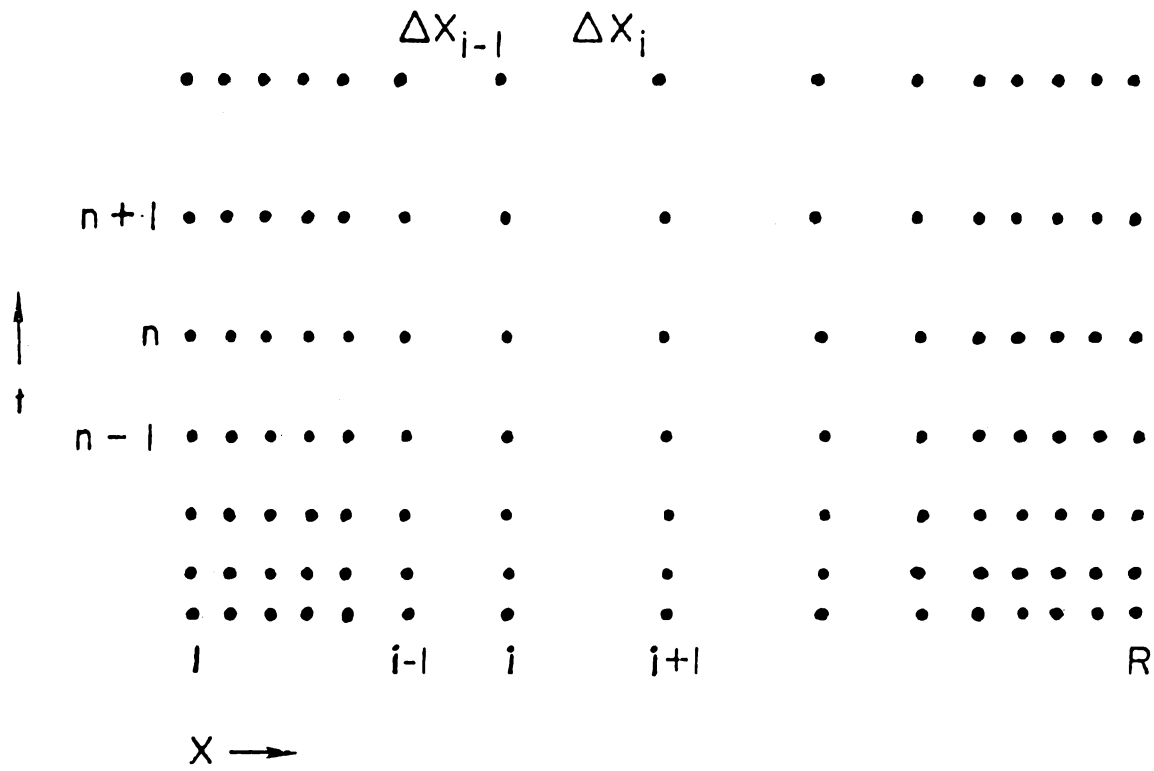


Figure (6-1)

It is expected that the dependent variables will exhibit their greatest spatial dependence in the vicinity of the boundaries, where charged surfaces exist. Therefore it is desirable to increase the density of space points in these regions at the expense of the bulk of the electrolyte, where dependent variables are expected to exhibit very little spatial dependence.

B. Finite Difference Formulation

Leckey [1981] was the first to transform the correct set of isothermal transport equations to finite difference form. The following discussion derives from that formulation, with appropriate modification for nonisothermal non uni-univalent systems.

The dependent variables, denoted by U (U = S, Δ, E) are specified in space and time with the indices i and n respectively. Thus, $U_{i,n}$ represents the value of U at space column i and time row n with

$$1 \leq i \leq R, \tag{6-1}$$

$$1 \leq n \leq Q, \tag{6-2}$$

where R is the number of space points per time row and Q is the number of time rows. There are therefore for J dependent variables, J·R unknowns and J·R equations at each time row.

The method for converting Eqs. (2-34) to (2-36) to their algebraic

analogs consists of expanding both $U_{i+1/2,n+1}$ and $U_{i-1/2,n+1}$ in Taylor's series about $U_{i,n+1}$. The weighted sum of the two series represents the second derivative approximation, and the weighted difference represents the first derivative approximation, with

$$(\partial U/\partial x)_{i,n+1} = 2 \left[U_{i+1/2,n+1}(\Delta x_{i-1})^2 + U_{i,n+1}[(\Delta x_{i-1})^2 - (\Delta x_i)^2] \right.$$

$$\left. - U_{i-1/2,n+1}(\Delta x_i)^2 \right]/[(\Delta x_i)(\Delta x_{i-1})(\Delta x_i + \Delta X_{i-1})], \qquad (6\text{-}3)$$

$$(\partial^2 U/\partial x^2)_{i,n+1} = 4 \left[U_{i+1/2,n+1}(\Delta x_{i-1}) + U_{i-1/2,n+1}(\Delta x_i) \right.$$

$$\left. - U_{i,n+1}[\Delta x_{i-1} - \Delta x_i] \right]/[(\Delta x_{i-1})(\Delta x_i)(\Delta x_{i-1} + \Delta x_i)], \qquad (6\text{-}4)$$

where $\Delta x_i = x_{i+1} - x_i$, and terms of order greater than $(\Delta x)^2$ are neglected.

Similarly, the time derivatives are approximated by expanding $U_{i,n}$ in a Taylor's series about $U_{i,n+1}$ and truncating beyond the linear terms. This results in little error if an appropriate time expansion scale is used. The resultant time derivative approximation is

$$(\partial U/\partial t)_{i,n+1} = [U_{i,n+1} - U_{i,n}]/\Delta t, \qquad (6\text{-}5)$$

where $\Delta t = t_{n+1} - t_n$. Eqs. (2-34) to (2-36) are converted to finite difference form by repeated application of Eqs. (6-3) to (6-5).

The first and last space points require special treatment. Strict

application of Eqs. (6-3) and (6-4) to the transport equations requires knowledge of both dependent variables and transport coefficients (Y_{SE}, $Y_{\Delta E}$) at the points i = 0, R+1, and transport coefficients (Y_{SS}, $Y_{\Delta\Delta}$, $Y_{S\Delta}$, $Y_{\Delta S}$) at grid points i = 1/2, R+1/2. In both cases these grid points lie outside the system boundaries. The treatment of these "image points" requires knowledge of the behavior of the transport coefficients in these regions. These coefficients are in turn dependent upon the concentrations of each species as well as the temperature. To determine exactly the nature of the behavior of these coefficients at the boundaries requires that the solution be available. Therefore we are forced to approximate their behavior by noting that for ideal systems the coefficients Y_{SS}, $Y_{\Delta\Delta}$, $Y_{S\Delta}$, and $Y_{\Delta S}$ are independent of concentration and can therefore be evaluated at grid points 1 and R instead of at 1/2 and R + 1/2. The electric field at the image points is eliminated through the use of Poisson's equation. The fluxes written in finite difference form are equated to the kinetic boundary flux equations, and both S and Δ at the image points are eliminated. The remaining coefficients Y_{SE} and $Y_{\Delta E}$ are determined by noting that for an ideal system they are linearly dependent on concentration. In the region of the left boundary we therefore write

$$(\partial Y_{SE}/\partial x)_{i=1} = \left[(Y_{SE})_{i=2} - (Y_{SE})_{i=0} \right]/2\Delta x_1$$

$$= K_S[S_{i=2} - S_{i=0}]/2\Delta x_1 + K_\Delta[\Delta_{i=2} - \Delta_{i=0}]/2\Delta x_1, \qquad (6\text{-}6)$$

where the constants K_S and K_Δ are the S and Δ derivatives of Y_{SE} evaluated at the mean system concentrations. From the solutions to $S_{i=0}$

and $D_{i=0}$ and Eq. (6-6) Y_{SE} at the image points is eliminated.

The full set of finite difference equations is shown in Appendix E. The finite difference procedure described above has been coded as a Fortran program for the purpose of checking the accuracy of the analytical results obtained in Chapters 4 and 5. A complete listing of the program is included in Appendix F.

C. Numerical Results

The data available for the doped CeO_2 electrolyte the steady state voltage loss across the electrolyte has been determined numerically. A comparison of the numerical results versus the analytical results obtained through integration of Eq. (4-30) is shown in Table 6-1. The relative deviation of the two solutions ($\Delta\phi_{num}/\Delta\phi_o$) increases with the current density. This is not surprising since $\Delta\phi_o$ represents the solution to the linearized problem and as the current density increases the starting equations (Eqs. (2-34) to (2-36)) become more nonlinear. It is for this same reason that the relative contribution of higher order solutions to the potential loss across the electrolyte increase as the current density increases.

As we saw in Chapters 3 and 4 the rate constants are dependent upon the behavior of the particular electrode-electrolyte system. In the numerical simulations the bulk potential drop is unaffected by the choice of rate constants. This does <u>not</u> mean that the cell performance is independent of the choice of rate constants, since as we saw in

TABLE 6-1. Comparison of $\Delta\phi_0$ Obtained from Integration of Eq. (4-30) and the Computer Simulation Results for the Doped Solid Electrolyte $CeO_2 + CaO$.

I ($A\text{-}cm^{-2}$)	$\Delta\phi_{NUM}$ (volts)	$\Delta\phi_0$ (volts)	$\Delta\phi_{NUM}/\Delta\phi_0$
0.00	-0.112	-0.110	1.02
0.05	-0.150	-0.147	1.02
0.10	-0.192	-0.187	1.03
0.15	-0.238	-0.232	1.03
0.20	-0.289	-0.280	1.03
0.25	-0.346	-0.334	1.04
0.30	-0.408	-0.394	1.04

Chapter 4 this choice is a reflection of the overpotential loss occurring at the interface, and is the primary cause of power loss. The numerical as well as the analytical results focus only on the bulk behavior which is independent of the properties of the interface. Thus although agreement between the numerical and analytical results based on the transport theory is good they are strictly valid only when no current is flowing, and give increasingly misleading results as the current density increases.

The ohmic loss across the electrolyte is defined as the potential drop that would be observed if only pure electric conduction were occurring and the potential drop across the electrolyte were given by

$$\Delta\phi_{ohmic} = -\int [I/\lambda(S,\Delta)]dx. \qquad (6\text{-}7)$$

The right hand side of Eq. (6-7) is integrated numerically and a plot of the ohmic potential drop versus current density is shown in Figure (6-2). For a conductor with homogeneous composition the specific conductance of the bulk is defined as (Levine [1978])

$$\lambda_b = IL/\Delta\phi, \qquad (6\text{-}8)$$

which is <u>not</u> a statement of Ohm's law but simply the definition of λ_b, and applies to all substances. From the plot in Figure (6-2) a value for λ_b of 0.117 $(ohm\text{-}cm)^{-1}$ is extracted by fitting the data to Eq. (6-8). This value compares quite favorably to a value of 0.113 $(ohm\text{-}cm)^{-1}$ measured for the same system using alternating current

Figure (6-2). Dependence of the ohmic voltage drop on current density.

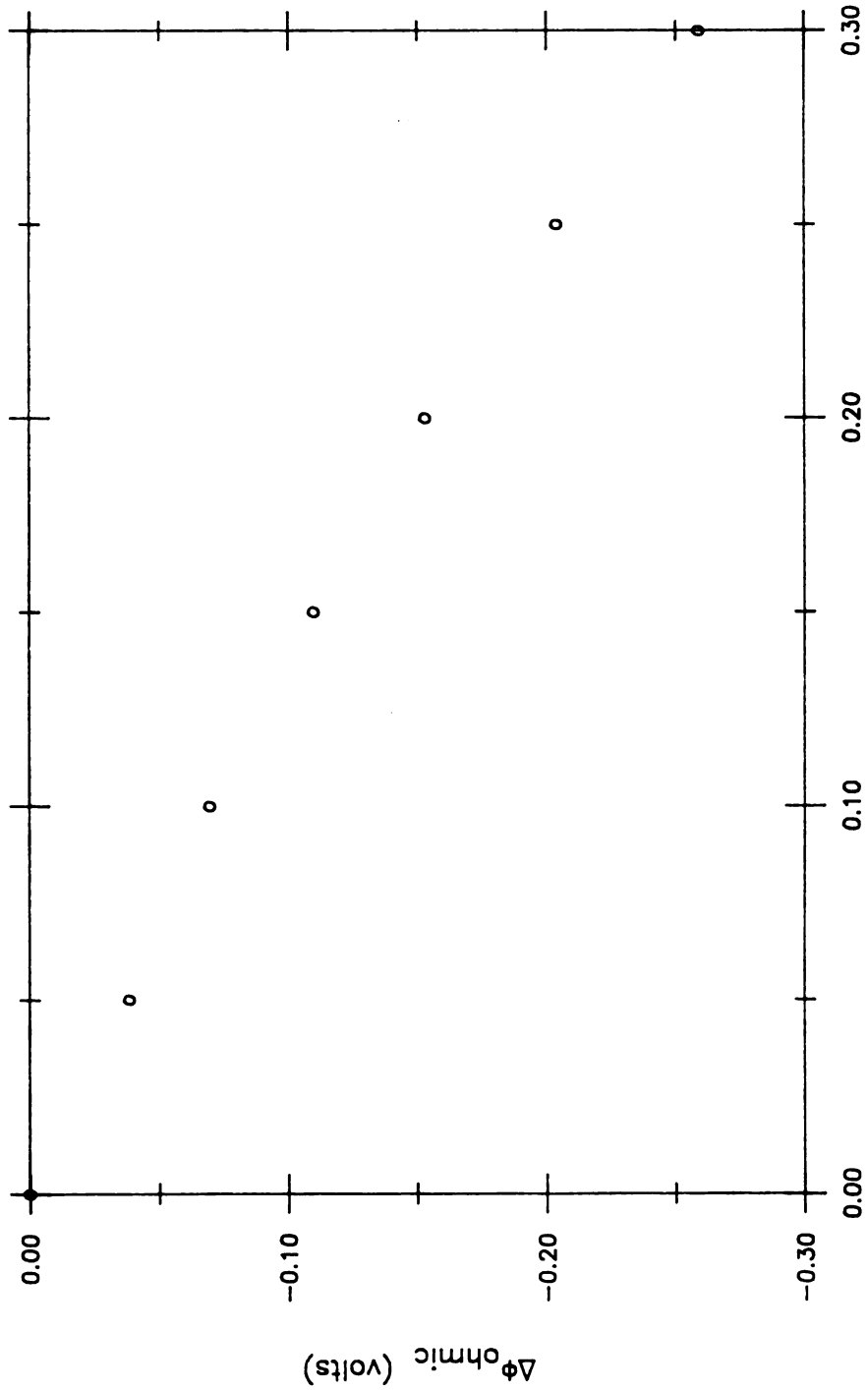

0.00
−0.10
−0.20
−0.30
0.00
0.10
0.20
0.30
Δφohmic (volts)
Current Density (A−cm−2)

Figure (6-2)

techniques (Braunshtein, Tannhauser, and Riess [1981]). The predictions of the transport equations are much more accurate when considering only bulk properties such as λ_b.

An important aspect of the analysis which has been neglected is the effect of overpotential losses on cell performance. Although overpotentials are not experimentally measurable their values can be estimated based upon measurements of the cell impedance $Z(\omega)$ or admittance $Y(\omega) = Z^{-1}(\omega)$ taken over a wide range of frequencies ω. Sluyters [1960, 1963, 1964, 1965] has used this technique extensively in his study of aqueous cell polarization phenomena. If one plots the imaginary part of these complex impedances or admittances versus the real part the resulting locus shows distinctive features for certain combinations of circuit components. Thus, these plots are useful for determining the appropriate equivalent circuit for the system under study. Examples of such plots for simple circuits are shown in Figure (6-3). The exact equations for these curves can be derived from a.c. circuit theory (Euler and Dehmelt [1957]). The resistance values in the circuit representations are related to the circular arc intercepts on the real axis, while the capacitance values are related to the frequencies at the peaks of the arcs. Once the appropriate equivalent circuit for the system has been selected, it is necessary to determine which portions of the equivalent circuit correspond to the bulk electrolyte properties, and which portions of the circuit correspond to the interfacial properties.

In their measurements on the doped CeO_2 platinum paste electrode

Figure (6-3). Equivalent circuits and their corresponding admittance plots. The conductance (G) is plotted versus the susceptability (B).

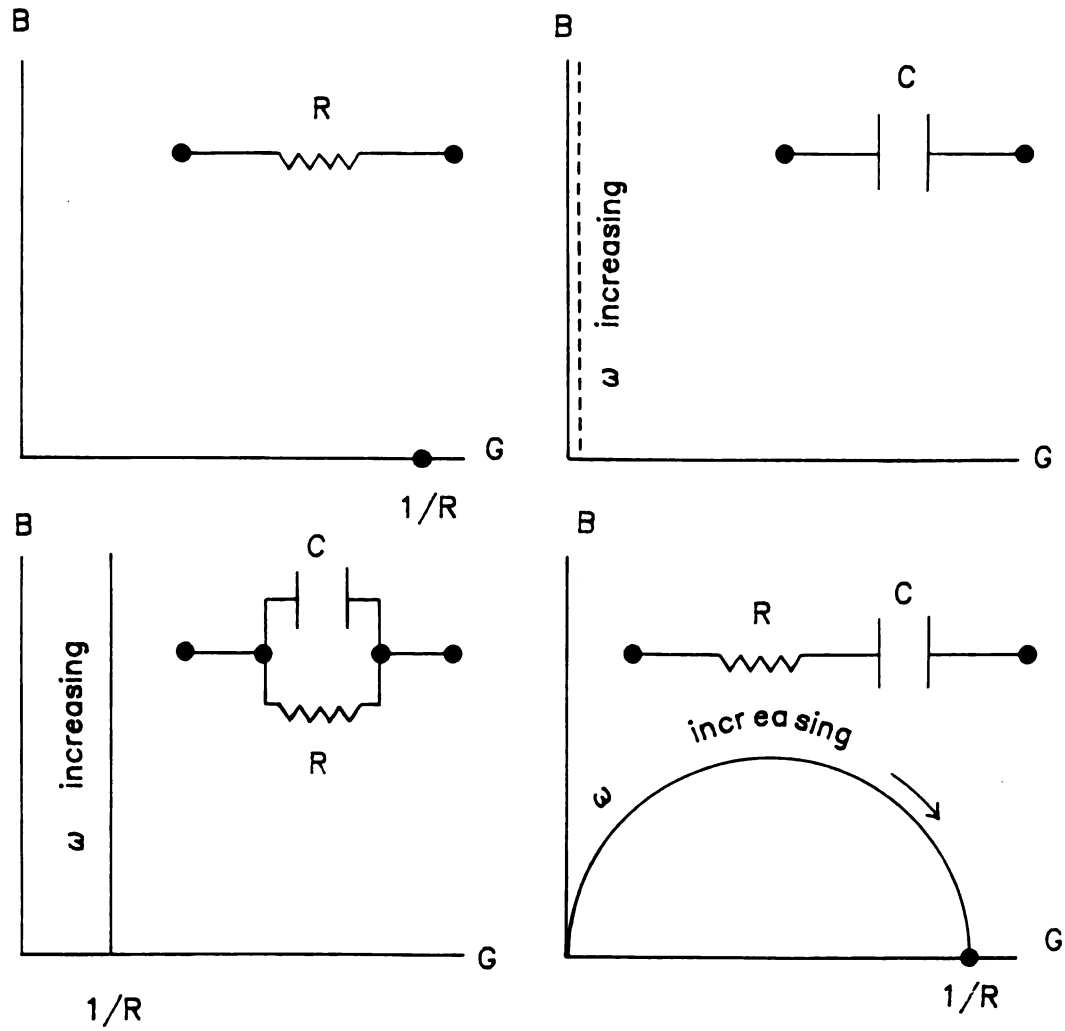

B
R
G
1/R
B
C
ω increasing
G
B
ω increasing
C
R
G
1/R
B
R
C
incr ea sing
ω
G
1/R

Figure (6-3)

electrolyte system, Braunshtein, Tannhauser, and Riess [1981] observed a clearly defined quarter circle, which corresponds to the circuit shown in Figure (6-4) (Bauerle [1969]). The Warburg impedance is the analog for a diffusive process. From the arc intercepts the values of R_1 and R_2 are obtained, with

$$R_\infty = R_1 R_2/(R_1 + R_2) \tag{6-9}$$

$$R_0 = R_1, \tag{6-10}$$

where R_∞ is the measured resistance for $\omega \to \infty$ and R_0 is the measured dynamic resistance for $\omega = 0$. The value of R_1 thus represents the resistance for current entering the solid electrolyte directly from the gas-electrode-electrolyte interface. The overpotential defined in Eqs. (3-7) and (3-8) is approximated by

$$\eta_L + \eta_R = IR_1. \tag{6-11}$$

Typical values for R_1 and R_2 for the CeO_2 platinum paste electrode as a function of temperature are shown in Table (6-2). Since $R_1 \gg R_2$, Eq. (6-9) reduces to

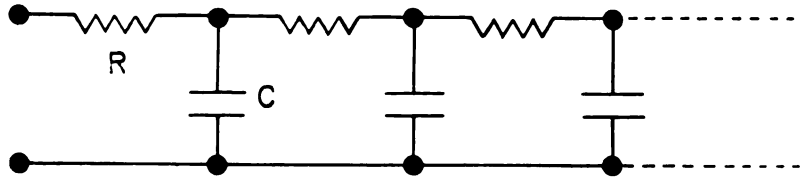
$$R_b = R_\infty \simeq R_2 \tag{6-12}$$

where R_b is the bulk resistance. It is from these resistance measurements that the literature value of 0.113 $(\text{ohm-cm})^{-1}$ for the specific conductance was extracted.

Figure (6-4). Warburg Impedance plot.

The "Warburg impedance" is designated by the symbol

and is equivalent to the infinite R–C line



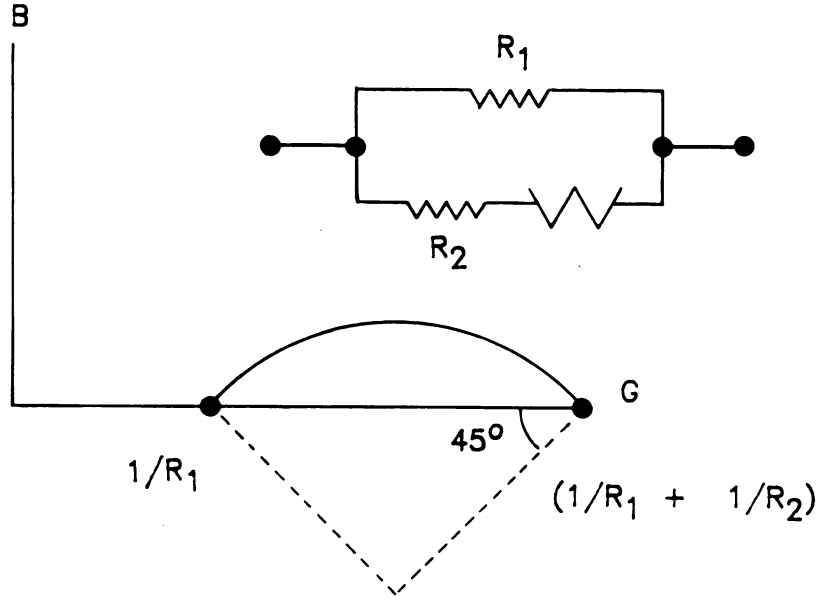


Figure (6-4)

Inclusion of the overpotentials estimated from Eq. (6-11) results in a far greater loss of power than that predicted by the transport equations alone. A comparison of the power output excluding overpotentials and including them is shown in Table (6-3), and a plot of efficiency versus output current illustrating this same comparison is shown in Figure (6-5). Comparison of these results with those shown in Table (4-2) and Figure (4-2) indicates that neglect of overpotentials is a far more serious error than neglect of space charge in predicting cell performance.

Figure (6-5). Dependence of the efficiency on the current density. (+) Neglecting overpotentials, (o) including overpotentials.

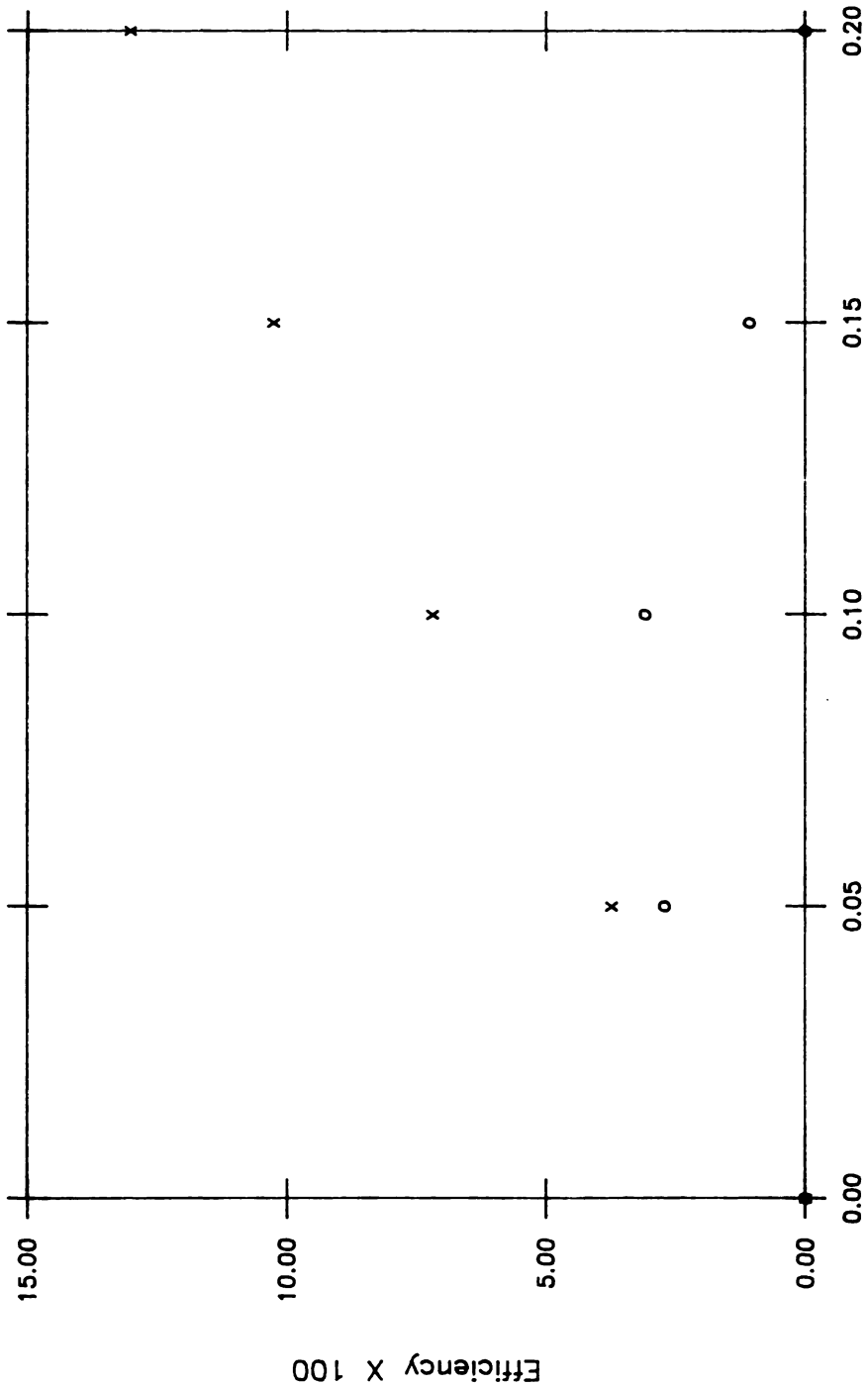

15.00
10.00
5.00
0.00
Efficiency X 100
0.00
0.05
0.10
0.15
0.20
Current Density (A-cm^{-2})

Figure (6-5)

TABLE 6-2. Comparison of the Values of R_1 and R_2 Measured at High Temperatures for the Doped Solid Electrolyte CeO_2 + CaO.

T (°C)	R_1 (ohms)	R_2 (ohms)
700	35.71	4.88
750	25.00	3.00
800	18.57	3.27
850	13.21	3.17
900	10.00	4.66

TABLE 6-3. Comparison of Power Densities With and Without Overpotentials.

	------Power ($W\text{-}cm^{-2}$) $\times 10^2$------	
I ($A\text{-}cm^{-2}$)	Without Overpotential	With Overpotential
0.00	0.00	0.00
0.05	4.49	3.26
0.10	8.63	3.71
0.15	12.35	1.29
0.20	15.63	—
0.30	20.44	—

CHAPTER 7

THE TIME DEPENDENT PROBLEM

A. Introduction

Throughout this work we have assumed that the transient period of operation of the fuel cell (the period from closing the circuit until the steady state is achieved) is short compared to the total operating period of the cell. To test the validity of this assumption it is necessary to examine the time dependent behavior of the system within the framework of nonequilibrium thermodynamics.

For systems with reversible electrodes the transient period of operation is determined by the time constant for the establishment of a steady state for mass transport across the bulk electrolyte. The bulk phase is essentially electrically neutral except within a few Debye lengths of the boundaries where kinetic effects dominate. Thus, for estimating the magnitude of the mass transport time constant, we treat the electrolyte as one mutually diffusing species under the influence of temperature and concentration fields. The rate of attainment of the steady state depends upon the magnitudes of the mutual diffusion coefficient, and the thermal conductivity of the solution. We suppress the dependence of this rate upon the thermal conductivity by noting that the thermal relaxation time is generally much shorter than the diffusive relaxation time. Thus we define time zero to be the point at which the

steady state thermal gradient has established itself but before appreciable chemical diffusion occurs. The transient period of operation of the cell thus becomes a function of the mutual diffusion coefficient.

For the doped solid state conductor CeO_2 + CaO, the transport of material occurs via a vacancy mechanism operating in the anion sublattice (Schmalzreid [1974]). We therefore choose as a reference species the Ca^{+2} dopant which is bound to the lattice positions of the essentially rigid cation framework, which results in a negligible reference velocity. The more nearly perfect the cation sublattice, the closer the reference velocity approaches zero, since there are fewer vacant sites to which the reference species can move. We choose the concentration as the composition variable because it allows us to formulate the time dependent problem directly in terms of the fundamental quantities σ and D, and results in an explicit dependence of the composition variable upon these quantities. This in turn leads to estimates of the length of the transient period of cell operation.

B. Formulation of the problem

Historically the Soret problem has been in a certain sense a zeroth order problem in that electroneutrality has always been assumed. As we saw previously, this assumption can lead to significant errors in the calculation of output voltages when the electrolyte approaches a charged surface such as an electrode.

Implicit in the electroneutrality assumption is the requirement that the velocities of the two ions are the same. If the positive ion moved faster than the negative ion, it would leave behind pockets of negative charge while creating pockets of positive charge, and the electroneutrality [assumption would be invalidated. By Eq. (2-1) the faradaic current (I_F) becomes, under the electroneutrality assumption,

$$I_F = F \sum (z_i c_i)(v_i - v_0) = F \sum (c_i z_i)(v_m - v_0) = 0 \qquad (7\text{-}1)$$

where $v_m = v_i$ $(i = 1,2)$ is the velocity of the mutually diffusing electrolyte. The total current defined by Eq. (2-29) then becomes

$$I = \varepsilon(\partial E/\partial t) = \varepsilon(dE/dt), \qquad (7\text{-}2)$$

which says that in the steady state the total current must vanish, and that the magnitude and duration of the displacement current is governed by the current produced by the cell as a function of time.

Dunlop and Gosting [1959] measured the thermopower of the thermocell

$$| \text{Pt} | \text{Ag} | \text{AgNO}_3(\text{aq}) | \text{Ag} | \text{Pt} |, \qquad (7\text{-}3)$$

and found that after imposition of a temperature gradient across a cell initially uniform in temperature several minutes elapsed before the displacement current vanished.

The initial value of the thermopower is taken to be the value of the thermopower measured at the time when the steady temperature field is established, but before appreciable chemical diffusion has occurred. The basis for assuming that the steady temperature field is established before noticeable diffusion occurs is that the rate of thermal conduction is ordinarily much greater than that of diffusion. The steady state temperature profile is linear since no Joule heating is present.

From Eq. (5-49) the entropy production for a nonisothermal binary electrolyte system is

$$\theta = J_q X_q + J_1 X_1 + J_2 X_2, \tag{7-4}$$

where the component fluxes are subject to the electroneutrality condition,

$$J_i = \nu_i J_m, \quad i = 1,2, \tag{7-5}$$

where J_m is the flux of the mutually diffusing electrolyte. In addition, the driving forces X_i are related through the definition of the chemical potential of a dissociated electrolyte,

$$\mu_m = \nu_1 \mu_1 + \nu_2 \mu_2, \tag{7-6}$$

and $X_m = -\partial \mu_m / \partial x$ is the driving force for the mutually diffusing electrolyte. From Eqs. (7-4) to (7-6),

$$\Theta = J_m X_m + J_q X_q, \tag{7-7}$$

and for the Hittorf diffusion fluxes,

$$-J_m = l_{mm}(\partial \mu_m/\partial x) + l_{mq}(\partial \ln T/\partial x), \tag{7-8}$$

$$-J_q = l_{qm}(\partial \mu_m/\partial x) + l_{qq}(\partial \ln T/\partial x), \tag{7-9}$$

where

$$l_{qm} = l_{mq}. \tag{7-10}$$

The Onsager coefficients are related to the Soret coefficient, the thermal conductivity, and the mutual diffusion coefficient, the three experimentally accessible quantities required to characterize this type of system.

The Hittorf diffusion flux defined by deGroot and coworkers [1953], is,

$$-J_m = (D/c_0 V_0)(\partial c_m/\partial x) - D[(\sigma x_m x_0 V_0/V^2) - (x_m \beta/V)](\partial T/\partial x), \tag{7-11}$$

where β is the thermal expansivity of the solute, x_i the mole fraction, c_i is the concentration, V_i is the partial molar volume, and V is the volume of the mixture. When the solvent velocity is neglected,

$$-J_m = D(\partial c_m/\partial x) - Dc_m(\sigma - \beta)(\partial T/\partial x), \tag{7-12}$$

where $x_i = c_i V$. From Eqs. (7-9) and (7-13),

$$D = 1_{mm}(\partial\mu_m/\partial c_m), \tag{7-13}$$

$$1_{mq}/T = (\beta - \sigma)c_m D = 1_{mm}Q^*/T. \tag{7-14}$$

From Eqs. (7-13) and (7-14) we recover the relationship expressed by Eq. (2-16),

$$\sigma c_m = -Q^*/T(\partial\mu_m/\partial c_m), \tag{7-15}$$

where the thermal expansivity of the electrolyte has been neglected.

The sum flux defined by Eq. (4-3) is related through Eq. (7-5) to the flux J_m by

$$J_s = [v/(z_1 - z_2)]J_m \tag{7-16}$$

and Eq. (7-12) can be rewritten in terms of the previously defined concentration variable S and flux J_s as

$$-J_s = D(\partial S/\partial x) - DS[\sigma - \beta](\partial T/\partial x), \tag{7-17}$$

where

$$S = \left[\ v/(z_1 - z_2)\ \right]c_m. \tag{7-18}$$

We now examine time dependent behavior and compare the steady state result to previously obtained steady state solutions. The general continuity equation (Eq. (2-20)) becomes

$$(\partial S/\partial t) - (\partial J_s/\partial x) = 0, \tag{7-19}$$

where J_s is given by Eq. (7-17), and the temperature distribution is given by Eq. (5-18).

C. Solution of the Soret Problem

The solution domain consists as before of a one dimensional electrolyte extending from $x = -L/2$ to $x = +L/2$ (see Figure 4-1). Time zero is defined as the time when the temperature field has been established with no appreciable diffusion having occurred. The initial concentration distribution is

$$S_0(x, t=0) = S_m. \tag{7-20}$$

The boundary conditions are in general time dependent because they reflect the behavior of the electrodes towards the system. For completely reversible electrodes, $J_i \equiv 0$, and by Eq. (7-17),

$$0 = D\left[(\partial S/\partial x) - S[\sigma - \beta](\partial T/\partial x) \right], \quad x = \pm L/2. \tag{7-21}$$

For nearly reversible electrodes, the time dependent boundary conditions

are approximated by

$$-J_s^{\infty} = D(\partial S/\partial x) + \omega S(\partial T/\partial x), \quad x = \pm L/2. \tag{7-22}$$

where J_s^{∞} is the steady state flux defined by Eq. (4-3), and $\omega \equiv [\beta - \sigma]D$. The pertubation expansions for S and the parameter $L = D,\omega$ are

$$S = S_m + S_0 + \delta S_1 + \delta^2 S_2 + \cdots, \tag{7-23}$$

$$L = L_0 + \delta\left[L_s(S-S_m) + L_T(T-T_m)\right] + \cdots \tag{7-24}$$

Since no current flows there is no Joule heating and the temperature distribution (Eq. (5-18)) is linear. Substitution of Eqs. (7-17), (7-23), and (7-24) into Eq. (7-22) and collection of terms of order zero gives

$$0 = (\partial S_0/\partial t) - D_0(\partial^2 S_0/\partial z^2) - \omega_0(\Delta T/L)(\partial S_0/\partial z), \tag{7-25}$$

where $z \equiv x + L/2$ has been introduced for convenience. We impose upon the zeroth order solution the requirement that it satisfy the boundary conditions while all higher order solutions vanish at the boundaries. Thus,

$$D_0(\partial S_0/\partial z) + \omega_0(\Delta T/L)(S_0 + S_m) = -J_s^{\infty}, \quad z = 0, L \tag{7-26}$$

$$S_0(z,0) = 0. \tag{7-27}$$

Although Eq. (7-25) lends itself easily to solution by separation of variables, the boundary conditions expressed by Eq. (7-26) do not. In order to separate variables it is necessary to transform Eqs. (7-25) to (7-27) so as to allow separation of both the resultant partial differential equation and boundary conditions. We utilize the Danckwerts transformation (Crank [1956]) and define the function U(z,t) as

$$U(z,t) = S_0 \exp[-(az + bt)], \tag{7-28}$$

where

$$a = -(\omega_0 \Delta T)/(2LD_0), \tag{7-29}$$

$$b = -\left[(\omega_0 \Delta T)/(2LD_0) \right]^2 D_0 = -a^2 D_0. \tag{7-30}$$

This transforms Eq. (7-25) to

$$(\partial U/\partial t) - D_0(\partial^2 U/\partial z^2) = 0 \tag{7-31}$$

with boundary conditions of the form

$$D_0(\partial U/\partial z) - aD_0 U = \left[-J_s^{\infty} + 2aD_0 S_m \right] \exp[-(az + bt)] \tag{7-32}$$

at z = 0,L with

$$U(z,0) = 0. \tag{7-33}$$

We transform the problem posed by Eqs. (7-31) to (7-33) to one with homogeneous boundary conditions (Boyce and Diprima [1977]) by subtracting from U(z,t) a function V(z,t) which satisfies both the boundary conditions given by Eq. (7-32) and the steady state equation given by

$$(\partial^2 V(z,t)/\partial z^2) = 0. \tag{7-34}$$

With

$$W(z,t) = U(z,t) - V(z,t), \tag{7-35}$$

$$V(z,t) \equiv [K_1 z + K_2]\exp(-bt), \tag{7-36}$$

$$K_1 = [-J_s^{\infty} + 2aS_m D_0][(1-\exp(-aL))/(aS_m D_0 L)], \tag{7-37}$$

$$K_2 = \left[[(1-\exp(-aL))/(aL)] - 1 \right][(-J_s^{\infty} + 2aS_m D_0)/(aS_m D_0)], \tag{7-38}$$

Eqs. (7-31-33) yield

$$(\partial W/\partial t) - D_0(\partial^2 W/\partial z^2) = b[K_1 z + K_2]\exp(-bt), \tag{7-39}$$

with the homogeneous boundary conditions

$$(\partial W/\partial z) - aW = 0, \qquad z = 0,L \tag{7-40}$$

and the initial condition

$$W(z,0) = -(K_1 z + K_2). \tag{7-41}$$

We solve the problem posed by Eqs. (7-39) to (7-41) by assuming that the solution can be expressed as a series of eigenfunctions of the form

$$W(z,t) = \sum b_n(t)\phi_n(z), \tag{7-42}$$

and then determine the coefficients $b_n(t)$. Moreover we expand the nonhomogeneous term in Eq. (7-39),

$$b(K_1 z + K_2)\exp(-bt) = \sum \gamma_n(t)\phi_n(z). \tag{7-43}$$

The first step in determining the coefficients in the eigenfunction expansion for $W(z,t)$ is to solve the analagous homogeneous problem

$$(\partial W^o/\partial t) - D_0(\partial^2 W^o/\partial z^2) = 0, \tag{7-44}$$

for which a Fourier series solution of the form

$$W^o(z,t) = \sum \alpha_n \phi_n(z) g_n(t) \tag{7-45}$$

exists where $g_n(t)$ and $\phi_n(z)$ are determined by substitution into Eqs. (7-44) and (7-40) respectively. The initial condition given by Eq. (7-41) is then used to determine α_n. From the homogeneous problem we

get

$$\phi_n(z) = \sin[(n\pi z)/L] + (n\pi/aL)\cos[(n\pi z)/L], \tag{7-46}$$

$$g_n(t) = \exp(\lambda_n t), \qquad \lambda_n = -(n\pi/L)^2 D_0, \tag{7-47}$$

$$\alpha_n = 2d^2[-J_s^\infty + 2aS_m D_0][1 - (-1)^n \exp(d\pi)]$$

$$\cdot[aS_m D_0(n^2 + d^2)n\pi]^{-1}, \tag{7-48}$$

$$d = -aL/\pi. \tag{7-49}$$

Substitution of Eqs. (7-42) and (7-43) into Eq. (7-39) gives

$$(db_n(t)/dt) - \lambda_n b_n(t) - \gamma_n(t) = 0. \tag{7-50}$$

Before solving Eq. (7-50) for $b_n(t)$, we obtain $\gamma_n(t)$ by appropriate integration of Eq. (7-43),

$$\gamma_n(t) = -b\exp(-bt)\alpha_n. \tag{7-51}$$

Substitution of Eq. (7-51) into Eq. (7-50) and integration from t=0 where $b_n(0) = \alpha_n$ to an arbitrary time t gives

$$b_n(t) = [\alpha_n/(\lambda_n + b)][\lambda_n \exp(\lambda_n t) + b\exp(-bt)]. \tag{7-52}$$

From Eqs. (7-46) to (7-48), (7-42), and (7-52) we have the complete solution to the problem posed by Eqs. (7-39) to (7-41) and are in a position to transform back to the original set of equations. When this is accomplished the final result for the zeroth order solution for S in terms of dimensionless variables is

$$S_0(z,t) = [(J_s^\infty - 2aS_mD_0)/2aS_mD_0]\left[1 + [2aL/(1-\exp(2aL))]\exp(2az)\right]$$

$$+ \exp(az) \sum [\alpha_n\lambda_n/(\lambda_n + b)]\phi_n(z)\exp[(\lambda_n + b)t]. \qquad (7\text{-}53)$$

For $\Delta T = 0$, two applications of L'Hopitals rule to Eq. (7-53) give

$$S_0(z,t) = -(LJ_s^\infty/S_mD_0)\left[(z/L) - (1/2)\right.$$

$$\left. + (4/\pi^2) \sum [\cos[(2n+1)\pi z/L)]/(2n+1)^2]\exp(\lambda_n t) \right] \qquad (7\text{-}54)$$

which corresponds to the solution to the diffusion equation given by Carslaw and Jaeger [1959]. As $t \to \infty$ in Eq. (7-54) the steady state solution

$$S_0(x,\infty) = -(J_s^\infty/S_mD_0)x \qquad (7\text{-}55)$$

is approached ($x = z - (L/2)$). From Eq. (4-30) we have, with $\rho = 0$,

$$S_0(x) = \left[\alpha_{s0}\beta_{\Delta 0} - \alpha_{\Delta 0}\beta_{s0} \right]x/\beta_{\Delta 0}. \qquad (7\text{-}56)$$

The solutions given by Eqs. (7-55) and (7-56) are equivalent. This is easily demonstrated by substituting Eq. (4-27) into the right hand side of Eq. (7-56), giving

$$S_0(x) = (dS_0/dx)(x/S_m). \tag{7-57}$$

By setting the two solutions given by Eqs. (7-55) and (7-56) equal to one another we regenerate with the help of Eq. (7-57) the diffusion equation

$$-J_s^{\infty} = D_0(dS_0/dx) \tag{7-58}$$

for an isothermal system.

The characteristic time (θ) governs the rate at which the steady state is approached, and is defined by Tyrell [1961] as

$$\theta = L^2/(\pi^2 D_0) \tag{7-59}$$

where L is the length of the system and D_0 is the zeroth order approximation to the diffusion coefficient. The terms in the sum of Eq. (7-53) converge rapidly and those for which $n > 1$ can be neglected when t/θ is sufficiently large. Indeed deGroot [1947] assumed this was always so and neglected higher order terms at all times. If we retain only the first term, Eq. (7-53) simplifies to

$$S_0(z,t) = S_0(z,\infty) - \exp(az+bt)(\alpha_1\lambda_1\phi_1/\theta)\exp(-t/\theta). \tag{7-60}$$

Weinberger [1965] defines an upper bound for the error made in approximating an infinite Fourier sum with a partial sum $S_m(z)$, where m is the number of terms included in the sum. For a generalized Fourier series of the form

$$f(z) = a_0/2 + \sum \left[a_n \cos(nz) + b_n \sin(nz) \right] \tag{7-61}$$

this error ($|f(z) - S_m(z)|$) is given by

$$|f(z) - S_m(z)| = \left[(1/\pi) \int [f'(z)]^2 dz - \sum n^2 [a_n^2 + b_n^2] \right]^{1/2}$$

$$\cdot \left[(\pi^2/6) - \sum (1/n^2) \right]^{1/2}. \tag{7-62}$$

Application of the above to Eq. (7-60) reveals an upper bound for error of 16 per cent. For purposes of estimating the time required for the system to reach the steady state Eq. (7-60) is sufficient since at $t > 5\theta$ the error involved in using Eq. (7-60) is less than 1 percent. Eq. (7-60) is, therefore, sufficient for estimating the length of transient behavior in cell operation. It also reveals the effect of the Soret coefficient upon the length of this transient period. From Eq. (7-30) we see that regardless of the algebraic sign of the Soret coefficient or the direction of the temperature gradient, b is always positive in Eq. (7-60), thus the time required to reach the steady state decreases as the magnitude of the nonisothermal effects increases. This decreased warm up time could be economically beneficial provided the nonisothermal effects are large enough.

CHAPTER 8

FUTURE WORK

To correctly model the time dependent behavior of electrolyte solutions, and gain information concerning single ion properties, it is necessary to know the dependence of the Onsager coefficients upon individual ionic concentrations. This requires making measurements in the first 10^{-8} s of a liquid junction potential experiment, (Leckey and Horne [1981]). Until such data become available it is difficult to make any statement concerning the validity of any given model in this time domain.

Measurements on electrolytes have been carried out on essentially neutral solutions, (Miller [1966]) and necessarily yield information only on the dependence of the Onsager coefficients on the total electrolyte concentration, and forces us to treat the electrolyte as if it were a singly diffusing neutral species. This poses no problem until one reaches a charged interface, where it is necessary to postulate some sort of single ion dependence for the Onsager coefficients.

Introduction of a temperature gradient has been suggested as a means of increasing the time available for observing single ion behavior. However this introduces additional parameters (G^*_i, and K_∞), raising to six the number of independent observations required to characterize a binary system in this time domain. An additional

complication is that the temperature dependence of these parameters must also be considered. The introduction of the temperature, and the energy balance equation brings to four the number of dependent variables and linearly independent equations respectively, that are required to characterize this system. The numerical treatment of this problem will require the redemensioning of program "IONFLO" and modeling of the dependence of the above parameters on the temperature and the single ion concentrations. Further experimental data are required in order to more fully develop this treatment.

Alternatively one can treat the electrolyte as one mutually diffusing species, reducing the number of equations and dependent variables to two. This treatment decouples the electric field from the dependent variables, (see Eq. 7-2), thus yielding information only on the temperature and concentration distribution of the system. "IONFLO" can be revised to simulate such a system, and the data necessary for carrying out the simulation, (Miller [1966], Longsworth [1957], Snowden and Turner [1960]), are available for liquid electrolytes. Similar data for solid electrolytes are virtually nonexistant. Experiments to determine the temperature and concentration dependence of the diffusion coefficient, Soret coefficient, and thermal conductivity of solids are needed.

The electrode/electrolyte/electrode system is not, in general, symmetrical. The solutions obtained in Chapters 4 and 5 can be further generalized by imposing nonsymmetrical boundary conditions of the type encountered in most real systems. This may result in predictions of

significant contributions to the voltage loss from Joule Heating.

Another area deserving of more theoretical and experimental attention is the effect of hydrostatic pressure upon transport phenomena in solids. One might expect large effects due to the stress gradients which may be present in many practical situations.

APPENDICES

APPENDIX A

TRANSPORT COEFFICIENTS

The Y_{ij} in Equations (2-34) to (2-36) are

$$Y_{SS} = (1/2)\left[(D_{11} + D_{22}) - [(z_1/z_2)D_{12} + (z_2/z_1)D_{21}] \right],$$

$$Y_{\Delta\Delta} = (1/2)\left[(D_{11} + D_{22}) + [(z_1/z_2)D_{12} + (z_2/z_1)D_{21}] \right],$$

$$Y_{S\Delta} = (1/2)\left[(D_{11} - D_{22}) - [(z_1/z_2)D_{12} - (z_2/z_1)D_{21}] \right],$$

$$Y_{\Delta S} = (1/2)\left[(D_{11} - D_{22}) + [(z_1/z_2)D_{12} - (z_2/z_1)D_{21}] \right],$$

$$Y_{SE} = (F^2/\varepsilon)\left[z_2^2 l_{22} - z_1^2 l_{11} \right],$$

$$Y_{\Delta E} = (F^2/\varepsilon)\left[z_1^2 l_{11} + 2z_1 z_2 l_{12} + z_2^2 l_{22} \right],$$

$$Y_{Sq} = (1/2z_1 z_2)\left[(-Q_1^*/T)(z_1 l_{11} - z_2 l_{12}) \right.$$

$$\left. + (Q_2^*/T)(z_2 l_{22} - z_1 l_{11}) \right],$$

and

$$Y_{\Delta q} = (1/2z_1 z_2)\left[(Q_1^*/T)(z_1 l_{11} + z_2 l_{12}) \right.$$

$$\left. + (Q_2^*/T)(z_1 l_{12} + z_2 l_{22}) \right], \qquad \text{(A-1)}$$

with

$$K_q = \text{Num}/\text{Den}, \tag{A-2}$$

where

$$\text{Num} = -Y_{SS}(z_1 l_{11} + z_2 l_{12}) - Y_{\Delta S}(z_1 l_{11} - z_2 l_{12}), \tag{A-3}$$

$$\text{Den} = v_1 F\Big[\, Y_{SS}(z_1^2 l_{11} + 2 z_1 z_2 l_{12} + z_2^2 l_{22}) - Y_{\Delta S}(z_2^2 l_{22} - z_1^2 l_{11}) \,\Big]. \tag{A-4}$$

For electrically neutral regions in an electrolyte, $\Delta = 0$, and

$$D = [Y_{SS}Y_{\Delta E} - Y_{SE}Y_{\Delta S}]/Y_{\Delta E}, \tag{A-5}$$

$$\text{with} \quad -\sigma S = Q^*/[T(\partial\mu/\partial S)] = [Y_{Sq}Y_{\Delta E} - Y_{SE}Y_{\Delta q}]/(DY_{\Delta E}) \tag{A-6}$$

where D and σ are the diffusion coefficient and Soret coefficient of the electrolyte respectively.

The α's, β's, and γ's in Equations (4-7) and (4-8) are

$$\alpha_S = [Y_{S\Delta}J_\Delta^\infty - Y_{\Delta\Delta}J_S^\infty]/[Y_{SS}Y_{\Delta\Delta} - Y_{\Delta S}Y_{S\Delta}],$$

$$\alpha_\Delta = [Y_{\Delta S}J_\Delta^\infty - Y_{SS}J_S^\infty]/[Y_{SS}Y_{\Delta\Delta} - Y_{\Delta S}Y_{S\Delta}],$$

$$\beta_S = \left[\; [Y_{SE}Y_{\Delta\Delta} - Y_{S\Delta}Y_{\Delta E}]/[Y_{SS}Y_{\Delta\Delta} - Y_{\Delta S}Y_{S\Delta}] \; \right](\varepsilon/2z_1z_2F),$$

$$\beta_\Delta = \left[\; [Y_{\Delta E}Y_{SS} - Y_{SE}Y_{\Delta S}]/[Y_{SS}Y_{\Delta\Delta} - Y_{\Delta S}Y_{S\Delta}] \; \right](\varepsilon/2z_1z_2F),$$

$$\gamma_S = [Y_{S\Delta}Y_{\Delta q} - Y_{Sq}Y_{\Delta\Delta}]/[Y_{SS}Y_{\Delta\Delta} - Y_{\Delta S}Y_{S\Delta}],$$

$$\gamma_\Delta = [Y_{\Delta S}Y_{Sq} - Y_{\Delta q}Y_{SS}]/[Y_{SS}Y_{\Delta\Delta} - Y_{\Delta S}Y_{S\Delta}]. \qquad \text{(A-7)}$$

APPENDIX B

FIRST ORDER SOLUTION FOR THE STEADY STATE ISOTHERMAL PROBLEM

Substitution of the zeroth order results into Eq. (4-33) results in the ordinary differential equation

$$(d^2E_1/dx^2) - (A_0^2)E_1 = C_1x + C_2\sinh(A_0x) + C_3\sinh(2A_0x), \qquad (B-1)$$

where the constants C_1, C_2, and C_3 are known from the zeroth order solution. In addition to the particular solution which satisfies the right hand side of Eq. (B-1) there is the complementary solution obtained by solving the homogeneous problem. The complementary solution introduces two new constants whose values are fixed by the boundary conditions. From Eq. (4-29), $\Delta_1 = 0$ at the walls, thereby fixing the values of the constants through Poisson's equation with

$$dE_1/dx = 0, \quad x = \pm L/2AA. \qquad (B-2)$$

The general first order solution for the electric field is thus given by

$$E_1 = T1 + T2 + T3 + T4 \qquad (B-3)$$

where

$$T1 = [\beta_{\Delta S}\alpha E^o/(A_0\beta_{\Delta 0})]\left[\ [\sinh(A_0x)/\cosh(A_0\xi)] - A_0x\ \right],$$

$$T2 = [\alpha\rho\beta_{\Delta S}/(4\beta_{\Delta 0}\sinh(A_0\xi))]\Big[\ (A_0x)^2\sinh(A_0x) - (A_0x)\cosh(A_0x)$$

$$- [(A_0\xi)^2 + (A_0\xi)\tanh(A_0\xi) - 1\ ]\sinh(A_0x)\ \Big],$$

$$T3 = [\rho E^o/(2\beta_{\Delta 0}\sinh(A_0\xi))][\beta_{\Delta\Delta} + (\beta_{S0}\beta_{\Delta S}/\beta_{\Delta 0})]\Big[\ (A_0x)\cosh(A_0x)$$

$$- [1 + (A_0\xi)\tanh(A_0\xi)]\sinh(A_0x)\ \Big],$$

$$T4 = [(\rho)^2A_0/(6(\beta_{\Delta 0})^2\sinh^2(A_0\xi))][\beta_{\Delta\Delta} + (\beta_{\Delta S}\beta_{S0}/\beta_{\Delta 0})]$$

$$\cdot\Big[\ \sinh(2A_0x) - 2[\cosh(2A_0\xi)/\cosh(A_0\xi)]\sinh(A_0x)\ \Big], \qquad \text{(B-4)}$$

with

$$\alpha = [\alpha_{S0}\beta_{\Delta 0} - \alpha_{\Delta 0}\beta_{S0}]/\beta_{\Delta 0}, \qquad \text{(B-5)}$$

$$E^o = -\alpha_{\Delta 0}/\beta_{\Delta 0}, \qquad \text{(B-6)}$$

and the L_{ij}, $(i,j = S,\Delta)$ are as defined in Chapter 4. The charge density Δ_1 is obtained from differentiation of Eq. (B-4) in accordance with Poisson's equation.

To obtain the first order solution for the total concentration S, the first order solution for E given by Eqs. (B-3) and (B-4) is substituted into Eq. (4-34), producing

$$(dS_1/dx) = C_1x + C_2\sinh(A_0x) + C_3\sinh(2A_0x) + C_4x^2\sinh(A_0x)$$

$$+ C_5 x\cosh(A_0 x), \qquad \text{(B-7)}$$

where the constants C_1 to C_5 are known from zeroth order results and E_1, and are not necessarily the same as the constants given in Eq. (B-1). Integration of Eq. (B-7) produces the first order solution for S along with an integration constant whose value is fixed by Eq. (4-28), which states that the total mass of the system is constant. The complete first order solution is

$$S_1 = T1 + T2 + T3 + T4 + T5 + T6, \qquad \text{(B-8)}$$

where

$$T1 = K_1[x^2 - \xi^2/3],$$

$$T2 = K_2[x\sinh(A_0 x) - (\cosh(A_0 x)/A_0) - (\cosh(A_0\xi)/A_0)$$

$$+ (2\sinh(A_0\xi)/(A_0^2\xi))],$$

$$T3 = K_3\Big[\ [(A_0 x^2) - (A_0\xi^2)]\cosh(A_0 x) - [5\sinh(A_0\xi)/(A_0^2\xi)]$$

$$- 3x\sinh(A_0 x) + (5\cosh(A_0\xi)/A_0) + (\sinh(A_0\xi)\tanh(A_0\xi)/A_0)$$

$$- \xi\tanh(A_0\xi)\cosh(A_0 x)\ \Big],$$

$$T4 = K_4\,[\cosh(2A_0x) - (\sinh(2A_0\xi)/(2A_0\xi))],$$

$$T5 = K_5\,[\cosh(A_0x) - (\sinh(A_0\xi)/(A_0\xi))],$$

$$T6 = K_6\,\Big[\,[1 - (\beta_{S0}/\beta_{\Delta 0})][(\cosh(A_0x)/A_0) - (\sinh(A_0\xi)/(2A_0^2\xi))]$$

$$+ (\beta_{S0}/2\beta_{\Delta 0})[x\sinh(A_0x) - \xi\tanh(A_0\xi)\cosh(A_0x)], \qquad \text{(B-9)}$$

where, moreover,

$$K_1 = [\beta_{SS} - (\beta_{S0}\beta_{\Delta S}/\beta_{\Delta 0})](\alpha E^o/2),$$

$$K_2 = \alpha\rho\beta_{SS}/[\beta_{\Delta 0}\sinh(A_0\xi)],$$

$$K_3 = \alpha\beta_{\Delta S}\beta_{S0}\rho/[4\beta_{\Delta 0}^2\sinh(A_0\xi)],$$

$$K_4 = [\rho^2/(4\beta_{\Delta 0}\sinh^2(A_0\xi))]\Big[\,[\beta_{S\Delta} + (\beta_{SS}\beta_{S0}/\beta_{\Delta 0})]$$

$$+ (\beta_{S0}/3\beta_{\Delta 0})[\beta_{\Delta\Delta} + (\beta_{\Delta S}\beta_{S0}/\beta_{\Delta 0})]\,\Big],$$

$$K_5 = -\rho^2\beta_{S0}[\beta_{\Delta\Delta} + (\beta_{\Delta S}\beta_{S0}/\beta_{\Delta 0})]/(3\beta_{\Delta 0}^2\sinh^2(A_0\xi)),$$

$$K_6 = \rho E^o[\beta_{SS} + (\beta_{S\Delta}\beta_{S0}/\beta_{\Delta 0})]/\sinh(A_0\xi). \qquad \text{(B-10)}$$

The solutions for E_1 and S_1 given by Eqs. (B-3) to (B-10) are easily simplified by noting that the argument of all of the sinh and cosh terms above contains the reciprocal of the Debye length of the system, which

is of the order of 10^8 cm^{-1}). Therefore, all of the terms in which ρ appears in both E_1 and S_1 vanish except within a few Debye lengths of the wall. The simplified expressions for E and S through first order, obtained by neglecting these terms, and valid everywhere except within a few Debye lengths of the walls are

$$E = E_0 + E_1 = E^o[1 - (\beta_{\Delta S}\alpha/\beta_{\Delta 0})x], \tag{B-11}$$

$$S = S_0 + S_1 = \alpha x + [\beta_{SS} - (\beta_{S0}\beta_{\Delta S}/\beta_{\Delta 0})][x^2 - \xi^2/3]. \tag{B-12}$$

The determination of the first order correction to the voltage drop across the electrolyte must be zero since E_1 is an odd function. Therefore in order to obtain the first correction to the voltage drop across the electrolyte it is necessary to determine the electric field to second order. The procedure for doing so is the same as outlined above and leads to extremely cumbersome expressions. Therefore an initial attempt at determining E_2 is undertaken by neglecting terms in which ρ appears. This leads to the result

$$E_2(\rho=0) = K_1\Big[\ (A_0)x\sinh(A_0x) - [(A_0)\xi\coth(A_0\xi) + 1]\cosh(A_0x)\ \Big]$$

$$+ K_2\Big[\ (A_0x)^2\cosh(A_0x) - (A_0x)\sinh(A_0x) - [(A_0\xi)^2$$

$$+ (A_0\xi)\coth(A_0\xi) - 1]\cosh(A_0x)\ \Big] + K_3[(Ax)^2 + 2$$

$$- (2A_0\xi)\cosh(A_0x)/\sinh(A_0\xi)] + K_4, \tag{B-13}$$

where

$$K_1 = [\alpha(E^o)^2\beta_{\Delta S}/(\beta_{\Delta 0}A_0^2\cosh(A_0\xi))][\beta_{\Delta\Delta} + (\beta_{\Delta S}\beta_{S0}/\beta_{\Delta 0})],$$

$$K_2 = [\beta_{\Delta S}^2 E^o\alpha^2/(4A_0^2\beta_{\Delta 0}^2\cosh(A_0\xi)],$$

$$K_3 = -[\beta_{\Delta S}E^o\alpha/(A_0^2\beta_{\Delta 0})]\Big[\ (E^o/2)[\beta_{SS} - (\beta_{\Delta S}\beta_{S0}/\beta_{\Delta 0})]$$

$$- (\beta_{\Delta S}\alpha/\beta_{\Delta 0})\Big],$$

$$K_4 = [\beta_{\Delta S}\alpha(E^o)^2/(A_0^2\beta_{\Delta 0})]\Big[\ \beta_{\Delta\Delta} + [\beta_{SS} - (\beta_{\Delta S}\beta_{S0}/\beta_{\Delta 0})][(A_0\xi)^2/6]$$

$$+ [\beta_{\Delta S}\beta_{S0}/\beta_{\Delta 0}][\tanh(A_0\xi)/(A_0\xi)], \qquad \text{(B-14)}$$

and

$$S_2(\rho = 0) = K_1(A_0x)^2\sinh(A_0x) + K_2(A_0x)\cosh(A_0x) + K_3\sinh(A_0x)$$

$$+ K_4x^3 + K_5x, \qquad \text{(B-15)}$$

where, moreover,

$$K_1 = [\beta_{\Delta S}\alpha/2\beta_{\Delta 0}]^2[\beta_{S0}E^o/(A_0^3\cosh(A_0\xi))],$$

$$K_2 = [\beta_{\Delta S}\alpha E^o/(A_0^3\beta_{\Delta 0}\cosh(A_0\xi))]\Big[\ (\alpha\beta_{SS}) + (\beta_{S0}\beta_{\Delta\Delta}E^o/2)$$

$$- [(\beta_{\Delta S}\beta_{S0}/2\beta_{\Delta 0})^2(\alpha\beta_{S0}E^o)]\ \Big],$$

$$K_3 = [\alpha E^o \beta_{\Delta S}/(A_0^3 \cosh(A_0\xi))]\Big[\ [\alpha\beta_{S0}\beta_{\Delta S}/4\beta_{\Delta 0}^2][1 + (A_0\xi)^2$$

$$+ (A_0\xi)\coth(A_0\xi)] - (E^0\beta_{S0}/\beta_{\Delta 0})[\beta_{\Delta\Delta} + (\beta_{\Delta S}\beta_{S0}/\beta_{\Delta 0})]$$

$$\cdot[1 + (A_0\xi/2)\coth(A_0\xi)] + [\beta_{S\Delta} + (\beta_{S0}\beta_{SS}/\beta_{\Delta 0})]E^o$$

$$- [\alpha\beta_{SS}/\beta_{\Delta 0}]\ \Big] + [2\xi\alpha E^o\beta_{S0}\beta_{\Delta S}/(A_0^2\beta_{\Delta 0}\sinh(A_0\xi))]$$

$$\Big[\ (E^o/2)[\beta_{SS} - (\beta_{\Delta S}\beta_{S0}/\beta_{\Delta 0})] - (\alpha\beta_{\Delta S}/\beta_{\Delta 0})\ \Big],$$

$$K_4 = (\alpha E^o/3)[\beta_{SS} - (\beta_{S0}\beta_{\Delta S}/\beta_{\Delta 0})]\Big[\ (E^o/2)[\beta_{SS} - (\beta_{S0}\beta_{\Delta S}/\beta_{\Delta 0})]$$

$$- (\alpha\beta_{\Delta S}/\beta_{\Delta 0})\ \Big],$$

$$K_5 = -[\alpha E^o/A_0^2][\beta_{SS} - (\beta_{\Delta S}\beta_{S0}/\beta_{\Delta 0})]\Big[\ [(A_0\xi)^2/6][\beta_{SS}$$

$$- (\beta_{\Delta S}\beta_{S0}/\beta_{\Delta 0})] + [\beta_{\Delta S}\beta_{S0}/(A_0\beta_{\Delta 0}\xi)]\tanh(A_0\xi)\ \Big]$$

$$+ [\beta_{\Delta S}E^o\alpha/A_0^2]\Big[\ E^o(\beta_{S0}/\beta_{\Delta 0})[\beta_{\Delta\Delta} - (\beta_{SS} - (\beta_{\Delta S}\beta_{S0}/\beta_{\Delta 0}))$$

$$- \beta_{S\Delta}] + (2\alpha\beta_{\Delta S}\beta_{S0}/\beta_{\Delta 0}^2)\ \Big]. \qquad \text{(B-16)}$$

The preceding results represent the second order contributions to the electric field and total concentration due to bulk behavior only. Integration of Eq. (B-13) from $x = -\xi$ to $+\xi$ produces

$$\Delta\phi_2(\rho=0) = (2E^o\xi^3/3)(\alpha\beta_{\Delta S}/\beta_{\Delta 0})^2, \qquad \text{(B-17)}$$

where terms of order ξ^2 and below have been neglected. It is from Eq. (B-17) that the voltage drops corresponding to the $\Delta/S_m = 0$ entries in Table (4-1) are calculated. Inclusion of terms linear in ρ enables us to examine the effect of non electrically neutral behavior upon the voltage loss across the electrolyte, and results in the expression

$$\Delta\phi_2 = \Delta\phi_2(\rho=0) - (\alpha\rho/\beta_{\Delta 0})(\beta_{\Delta S}\xi/\beta_{\Delta 0})^2\left[(3\alpha/8) - (E^o\beta_{S0}/3) \right], \quad \text{(B-18)}$$

where terms of order ξ^2 and below have been neglected. The second order contributions to the voltage drop as a function of charge density in Table (4-1) are computed from Eq. (B-18).

APPENDIX C

DIMENSIONLESS VARIABLES USED FOR COMPUTER SIMULATION

Dimensionless variables are denoted by an overline. The following list contains dimensionless variables used in addition to those introduced in Eq. (4-16). The definition of each variable is given in the comment section of the program "IONFLO."

$$epm = \varepsilon(\bar{S}=0,\bar{\Delta}=0),$$

$$\overline{EPS} = epm/\varepsilon_0,$$

$$Y^m_{\Delta E} = Y_{\Delta E}(\bar{S}=0,\bar{\Delta}=0),$$

$$\bar{t} = t[Y^m_{\Delta E}\overline{EPS}],$$

$$CON = \varepsilon_0/(2z_1z_2F),$$

$$GDE = epmY^m_{\Delta E}/(2z_1z_2F),$$

$$\overline{ZQ} = -Q(CON)/[\varepsilon_0(AA)S_m],$$

$$\overline{ZI} = -I(CON)/[(AA)S_mY^m_{\Delta E}epm],$$

$$\overline{EJ} = -\Delta\phi(CON)/[2(AA)^2S_m10^{-7}],$$

$$\overline{ZIJ} = Y_{ij}(CON)/[(AA)^2 GDE], \quad i,j = S,\Delta,q$$

$$\overline{KIJ} = k_{ij}(CON)/[(AA)GDE], \quad i = S,\Delta;\ j = L,0,A,R.$$

APPENDIX D

JOULE HEATING

Neglect of the Joule heating term in the energy balance equation (Eq. (5-10)) resulted in a linear temperature gradient. The resultant steady state equations for nonisothermal transport (Eqs. (5-24) and (5-25)) thus assumed a form identical to their isothermal analogs (Eqs. (4-26) and (4-27)). Inclusion of the Joule heating term in the energy balance equation transforms Eq. (5-24) to

$$(d^2E_0/dx) - (A_0^2)E_0 = -(1/EPS)\Big[\ \alpha'_{\Delta 0} - (2\gamma_{\Delta 0}x/(\lambda_0 K_0 T_m))$$

$$\cdot[IL/2\xi]^2\ \Big], \qquad \text{(D-1)}$$

which reduces to Eq. (5-24) when I = 0. The general solution to Eq. (D-1) is

$$E_0 = (IL/2\xi)^2[2\gamma_{\Delta 0}x/(\lambda_0 K_0 T_m \beta_{\Delta 0})] - (\alpha_{\Delta 0}/\beta_{\Delta 0})$$

$$+ C_1\cosh(A_0x) + C_2\sinh(A_0x), \qquad \text{(D-2)}$$

where the constants C_1 and C_2 are determined by the boundary conditions given by Eq. (4-29). Under the conditions of Eq. (4-32), which states that the charge density is equal but opposite in sign at either end of the cell, the constants become

$$C_1 = \rho/[A_0(EPS)\sinh(A_0\xi)], \tag{D-3}$$

$$C_2 = 2\gamma_{\Delta 0}(IL)^2/[(2\xi)^2\lambda_0 K_0 T_m A_0 \beta_{\Delta 0}\cosh(A_0\xi)]. \tag{D-4}$$

With C_1 and C_2 substituted into Eq. (D-2) the zeroth order expression for E_0 reduces to Eq. (4-30) when the current density vanishes. Integration of Eq. (D-2) across the electrolyte produces the same expression for $\Delta\phi_0$ as we obtain from Eq. (4-30) regardless of the value of the current density. This does not mean that the voltage loss across the electrolyte is independent of the current density: rather, it means that for the purpose of calculating the voltage loss across the electrolyte it is not necessary to include the Joule heating term in the energy balance equation, provided that the charge density distribution is symmetrical. If Eq. (4-32) is not valid ($\rho_L \neq -\rho_R$), then the constants C_1 and C_2 defined by the boundary conditions will change, thus altering the final expression for $\Delta\phi_0$ obtained by integration of Eq. (D-2). We would therefore expect Joule heating to be important in the determination of voltage loss for systems employing different kinds of electrodes where nonsymmetrical charge distributions are expected.

APPENDIX E

TRANSPORT EQUATIONS IN FINITE DIFFERENCE FORM

The following definitions are useful in simplifying the finite difference form of the transport equations.

$$A = 1/(\Delta x_i + \Delta x_{i-1}), \quad P = 4/(\Delta x_i + \Delta x_{i-1})^2,$$

$$Y_{UV} = Y_{UV}(S_{i,n+1}, \Delta_{i,n+1}), \quad Y^+_{UV} = Y_{UV}(S_{i+1/2,n+1}, \Delta_{i+1/2,n+1}),$$

$$Y^-_{UV} = Y_{UV}(S_{i-1/2,n+1}, \Delta_{i-1/2,n+1}), \quad Y^+_{UE} = Y_{UE}(S_{i+1,n+1}, \Delta_{i+1,n+1}),$$

$$Y^-_{UE} = Y_{UE}(S_{i-1,n+1}, \Delta_{i-1,n+1}), \; Y_{UE} = Y_{UE}(S_{i,n+1}, \Delta_{i,n+1}),$$

$$Rat = \Delta x_i/\Delta x_{i-1}, \quad Sub = \Delta x_i - \Delta x_{i-1},$$

$$Amul = (\Delta x_i)(\Delta x_{i-1}), \quad K = \varepsilon/(2z_1 z_2 F), \qquad \text{(E-1)}$$

where (U = S,Δ and V = S,Δ,q), with $U_{i,j}$ referring to the value of U at space point i and time row j.

Equation (2-34) becomes for $2 \leq i \leq R-1$,

$$S_{i,n}/\Delta t = -PY^-_{SS}S_{i-1,n+1} + [P(Y^+_{SS} + Y^-_{SS}) + 1/\Delta t]S_{i,n+1}$$

$$- PY^{+}_{SS}S_{i+1,n+1} - PY^{-}_{S\Delta}\Delta_{i-1,n+1} + P(Y^{-}_{S\Delta} + Y^{+}_{S\Delta})\Delta_{i,n+1}$$

$$- PY^{+}_{S\Delta}\Delta_{i+1,n+1} + (AK)(Rat)Y^{+}_{SE}E_{i+1,n+1} - (AK/Rat)E_{i-1,n+1}$$

$$+ [K(Sub)/Amul]Y_{SE}E_{i,n+1} - PY^{+}_{Sq}T_{i+1,n+1} - PY^{-}_{Sq}T_{i-1} + P(Y^{+}_{Sq}$$

$$+ Y^{-}_{Sq})T_{i,n+1}. \qquad \text{(E-2)}$$

Equation (2-35) becomes, for $2 \leq i \leq R-1$,

$$\Delta_{i,n}/\Delta t = - PY^{-}_{\Delta S}S_{i-1,n+1} + P(Y^{-}_{\Delta S} + Y^{+}_{\Delta S})S_{i,n+1}$$

$$- PY^{+}_{\Delta S}S_{i+1,n+1} - PY^{-}_{\Delta\Delta}\Delta_{i-1,n+1} + (PY^{-}_{\Delta\Delta} + PY^{+}_{\Delta\Delta} + 1/\Delta t)\Delta_{i,n+1}$$

$$+ (AK)(Rat)Y^{+}_{\Delta E}E_{i+1,n+1} - (AK/Rat)E_{i-1,n+1}$$

$$+ [K(Sub)/Amul]Y_{\Delta E}E_{i,n+1} - PY^{-}_{\Delta q}T_{i-1,n+1} + P(Y^{+}_{\Delta q}$$

$$+ Y^{-}_{\Delta q})T_{i,n+1} - PY^{+}_{\Delta q}T_{i+1,n+1}. \qquad \text{(E-3)}$$

Equation (2-36) becomes, for $2 \leq i \leq R-1$,

$$(I/\varepsilon) + E_{i,n}/\Delta t = E_{i,n+1}[(1/\Delta t) + Y_{\Delta E}] - (AY_{\Delta S}/K)$$

$$\cdot[(Rat)S_{i+1,n+1} - (S_{i-1,n+1}/Rat)] - (AY_{\Delta\Delta}/K)[(Rat)\Delta_{i+1,n+1}$$

$$- (\Delta_{i-1,n+1}/Rat)] - AY_{\Delta q}[(Rat)T_{i+1,n+1} - (T_{i-1,n+1}/Rat)]. \qquad \text{(E-4)}$$

The rate constants enter through the elimination of the values of S and Δ at the image points i = 0, R+1. The assumption of a linear temperature gradient being established at time zero, with $T_1 = T_0$ and $T_{R+1} = T_R$, results in the cancellation of all temperature terms from the transport equations at the boundaries. Thus for i = 1, Eq. (2-34) becomes

$$S_{i,n}/\Delta t + 4A[(KSL)SL + (K\Delta L)\Delta L] = -2PY_{SS}S_{2,n+1} - 2PY_{S\Delta}\Delta_{2,n+1}$$

$$+ [(1/\Delta t) + 2PY_{SS} + 4A(KS0)]S_{1,n+1} + [2PY_{S\Delta} + 4A(KD0)$$

$$+ Y_{SE}]\Delta_{1,n+1} + 2AKY_{SE}E_{1,n+1} + 2AKY^{+}_{SE}E_{1,n+1}. \qquad (E-5)$$

For i = 1, Eq. (2-35) becomes

$$\Delta_{i,n}/\Delta t + 4A[(KSL)\Delta L + (K\Delta L)SL] = -2PY_{\Delta S}S_{2,n+1} - 2PY_{\Delta\Delta}\Delta_{2,n+1}$$

$$+ [2PY_{\Delta S} + 4A(KD0)]S_{1,n+1} + [(1/\Delta t) + 2PY_{\Delta\Delta} + 4A(KS0) + Y_{\Delta E}]$$

$$(\Delta_{1,n+1}) + 2AKY_{\Delta E}E_{1,n+1} + 2AKY^{+}_{\Delta E}E_{1,n+1}. \qquad (E-6)$$

For i = 1, Eq. (2-36) becomes

$$(I/\varepsilon) + (E_{1,n}/\Delta t) - (1/K)[(K\Delta L)SL + (KSL)\Delta L] = (E_{1,n+1}/\Delta t)$$

$$- (1/K)[(KD0)S_{1,n+1} + (KS0)\Delta_{1,n+1}]. \qquad (E-7)$$

For i = R, Eq. (2-34) becomes

$$S_{1,n}/\Delta t + 4A[(KSR)SR + (K\Delta R)\Delta R] = - 2PY_{SS}S_{R-1,n+1} - 2PY_{S\Delta}\Delta_{R-1,n+1}$$

$$+ [2PY_{S\Delta} + 4A(K\Delta A) + Y_{SE}]\Delta_{R,n+1} + [(1/\Delta t) + 2PY_{SS} + 4A(KSA)]$$

$$\cdot S_{R,n+1} - 2AKY_{SE}E_{R,n+1} - 2AKY^{+}_{SE}E_{R,n+1}. \qquad \text{(E-8)}$$

For i = R, Eq. (2-35) becomes

$$\Delta_{1,n}/\Delta t + 4A[(K\Delta R)SR + (KSR)\Delta R] = -2PY_{\Delta S}S_{R-1,n+1} - 2PY_{\Delta\Delta}\Delta_{R-1,n+1}$$

$$+ [(1/\Delta t) + 2PY_{\Delta\Delta} + 4A(KSA) + Y_{\Delta E}]\Delta_{R,n+1} + [2PY_{\Delta S} + 4A(K\Delta A)]$$

$$\cdot S_{R,n+1} - 2AKY_{\Delta E}E_{R,n+1} - 2AKY^{+}_{\Delta E}E_{R,n+1}. \qquad \text{(E-9)}$$

For i = R, Eq. (2-36) becomes

$$(I/\varepsilon) + (E_{R,n}/\Delta t) + (1/K)[(K\Delta R)SR + (KSR)\Delta R] = (E_{R,n+1}/\Delta t)$$

$$+ (1/K)[(K\Delta A)S_{R,n+1} + (KSA)\Delta_{R,n+1}] \qquad \text{(E-10)}$$

APPENDIX F

LISTING OF PROGRAM "IONFLO"

The following is a listing of the program "IONFLO":

```
      PROGRAM IONFLO (INPUT,OUTPUT,TAPE 61=OUTPUT,TAPE 50=INPUT)
C
C     PROGRAM IONFLO SOLVES THE SYSTEM OF EQUATIONS, GENERALIZED NERNST-
C     PLANCK, POISSON, DISPLACEMENT CURRENT, FOR THE TRANSPORT OF A
C     BINARY ELECTROLYTE IN A FINITE SPACE DOMAIN.  DERIVATIVES ARE
C     APPROXIMATED USING FINITE DIFFERENCES.
C     2 TYPES OF BOUNDARY VALUE PROBLEMS ARE POSSIBLE. KEY=1 IS FOR THE
C     DIFFUSION POTENTIAL  KEY=2 IS FOR KINETIC ELECTRODE MODELING
C     BOTH EMPLOY A NON-UNIFORM SPACE MESH WHICH DEPENDS ON THE
C     MEAN CONCENTRATION OF THE ELECTROLYTE AND THE INPUT PARAMETER
C     RANGE.
C
C     INPUT
C
C     ALL INPUT IS READ THROUGH SUBROUTINE AIO.  THIS SUBROUTINE SHOULD
C     BE INSPECTED TO DETERMINE PROPER ORDER AND FORMAT OF INPUT
C     PARAMETERS.
C     THE FOLLOWING IS A LIST OF INPUT VARIABLES AND THEIR MEANING.
C
C     TITLE DESCRIPTION OF SIMULATION
C
C     KEY   1 FOR DIFFUSION POTENTIAL SIMULATION
C           2 FOR KINETIC ELECTRODE MODELING
C
C     R     NUMBER OF SPACE POINTS UP TO 100
C
C     Q     NUMBER OF TIME ROWS
C
C     ISET  NUMBER OF EQUAL INCREMENT SPACE POINTS AT EACH ELECTRODE
C           OR SIDE OF INTERFACE
C.
C     IJK   FRACTION OF TIME ROWS TO BE WRITTEN
C
C     ISTOP NUMBER OF TIME ROWS TIME STEP SIZES ARE CONSTANT
C
C     MMM   SPECIFIES A TIME ROW FOR WHICH MANY INTERNAL PARAMETERS WILL
C           OUTPUT AND SHOULD ONLY BE USED FOR DEBUGGING.  WHEN NOT IN
C           USE SET MMM GREATER THAN Q.
C
C     NPLT  FRACTION OF TIME ROWS THAT ARE WRITTEN THAT ARE TO BE
C           PLOTTED
C
```

```
C     IOFF  1 FOR COMPLETE ITERATION PROCEDURE
C           0 FOR NO ITERATION
C
C     IW    0 WRITES OUTPUT ONLY FOR LAST ITERATION OF EACH TIME ROW
C           SPECIFIED BY IJK
C           1 WRITES OUTPUT FOR EVERY ITERATION OF EACH TIME ROW
C           SPECIFIED BY IJK
C
C     ISTOP LAST TIME ROW THAT CURRENT IS TURNED ON FOR
C
C     RANGE DETERMINES RATE AT WHICH GRID SPACING EXPANDS FROM SMALL
C           STEP SIZES TO LARGE ONES.
C
C     DT    INITIAL TIME STEP SIZE IN SECONDS
C
C     F     DETERMINES RATE OF TIME STEP SIZE INCREASE.
C
C     TOL   MAXIMUM ALLOWABLE FRACTIONAL CHANGE FROM ONE ITERATION TO
C           THE NEXT FOR PROGRAM TO PROCEED TO THE NEW TIME ROW
C
C     ZP    CHARGE NUMBER FOR POSITIVE ION
C
C     ZM    CHARGE NUMBER FOR NEGATIVE ION
C
C     ZQ    FINAL CHARGE ON ELECTRODE IN C/CM**2
C
C     ALF   TIME CONSTANT FOR CHARGE INJECTION
C
C     A     CHARACTERISTIC LENGTH IN CM
C
C     GDE   MEAN ZDE VALUE IN MOL*S*C/G*CM**3
C
C     SIZE  LENGTH OF SYSTEM IN CM
C
C     EPM  PERMITTIVITY OF A VACUUM IN C*C*S*S/G*CM**3.
C
C     SM    MEAN ELECTROLYTE CONCENTRATION IN MOLES/CM**3
C
C     KDO,KSO,KDA,KSA,  RATE CONSTANTS FOR TRANSPORT ACROSS
C           ELECTRODE-ELECTROLYTE INTERFACES.
C
C     SR,SL,DR,DL, RESERVOIR CONCENTRATIONS.
C
C     C(1)  THROUGH C(10)  EXPANSION COEFFICIENTS FOR ONSAGER
C           COEFFICIENTS AND ACTIVITY COEFFICIENT DERIVATIVES.
C           C(1) AND C(2) FOR L++, C(3) AND C(4) FOR L--, C(5) AND C(6)
C           FOR L+-, C(7) AND C(8) FOR M, C(9) AND C(10) FOR B
C           UNITS ARE S*MOL*MOL/(G*CM**3) FOR ONSAGER
C           COEFFICIENTS.  M AND B ARE IN CM**3/MOLE.
C           EXPANSIONS ARE OF THE FORM:
C           L++ = C1*CP + C2*CP**1.5
C           L-- = C3*CM + C4*CM**1.5
C           L+- = C5*S**1.5 + C6*S**2
```

```
C           M = C7*S - C8/S**(0.5)
C           B = C9 + C10*S
C
C     NAME(1,2,3)  TITLES FOR PLOTS
C
C     JNAME(1,2,3)  TITLES FOR PLOTS
C
C     POINT(1,2,3)  SYMBOLS FOR PLOTS
C
C     OUTPUT
C
C     ALL OF THE INPUT PARAMETERS, THE DEBYE LENGTH OF THE SYSTEM,
C     AND THE TRANSPORT COEFFICIENTS IN DIMENSIONLESS FORM ARE WRITTEN
C     BEFORE THE FIRST TIME ROW IS EXECUTED
C
C     S      SUM CONCENTRATION.  WRITTEN FOR EVERY TIME ROW AS INDICATED
C            BY IJK AND EVERY SPACE POINT AS INDICATED BY IW.  UNITS
C            ARE MOLES/CM**3
C            SM IS SUBTRACTED FROM S FOR THE OUTOUT
C
C     D      CHARGE DENSITY  LABELED RHO ON OUTPUT.  WRITTEN FOR EVERY
C            TIME ROW AS INDICATED BY IJK AND EVERY SPACE POINT AS
C            INDICATED BY IW.  UNITS ARE C/CM**3
C
C     E      SAME COMMENT AS FOR D. UNITS ARE VOLTS/CM
C
C     PSI    SAME COMMENT AS FOR D.  UNITS ARE VOLTS RELATIVE TO THE
C            POTENTIAL AT X=0.
C
C     CP      POSITIVE ION CONCENTRATION
C
C     CM      NEGATIVE ION CONCENTRATION
C
C     X      SPACE POSITION IN CM RELATIVE TO NEAREST WALL.
C
C     T      TIME IN UNITS OF SECONDS
C
C     EJ     CELL POTENTIAL DIFFERENCE IN VOLTS
C
C     ZI     DIFFERENCE IN CURRENT DENSITY BETWEEN ARBITRARY TIME
C            T AND STEADY STATE, AMPS/CM**2.
C
C     CLE    TOTAL CHARGE IN SYSTEM IN COULOMBS
C
C     RCOND SEE LINPACK DOCUMENTATION
C           IF SUBROUTINE SGBFA IS USED BY IONFLO RCOND IS MEANINGLESS
C
C     RTEST ARBITRARY CUTOFF VALUE TO TELL COMPUTER THAT MATRIX IS
C           NEARLY SINGULAR AND TO STOP ATTEMPTING A SOLUTION. A VALUE
C           OF 10**(-25) HAS BEEN USED SUCCESSFULLY.
C     EPS   RATIO OF PERMITTIVITY OF ELECTROLYTE TO THAT OF A VACUUM.
C     SO    INITIAL CONDITION ON S.
C     DO    INITIAL CONDITION ON D.
```

```
C     EO    INITIAL CONDITION ON E.
C     QDELT IS THE QUANTITY Q*(TR - TL)/TM IN CALORIES PER MOLE.
C     V1 AND V2 ARE THE STOICHIOMETRIC COEFFICIENTS OF SPECIES 1 AND 2.
C     DELT IS THE TEMPERATURE DIFFERENCE, TR-TL, IN KELVIN.
      INTEGER R,RR,Q
      DOUBLE XER,DEL,SIZE,DEBL
      DIMENSION B(300),IPVT(300),BB(300),Z(300)
      DIMENSION Y(300),DEL(100),XER(100),YY(300)
      DIMENSION ABD(16,300)
      DIMENSION NPT(10),JNAME(10),NAME(10)
      COMMON /ELEC/ EPS,ZI
      COMMON /GREEK/ C(24)
      COMMON /PARAM/ KEY,R,Q,DT,F,TOL,RANGE,ISET
      COMMON/UNITS/SM,DF,GDE,EPM,A,ZP,ZM,CON,TM,DIM,CREF,ZREF
      COMMON /BOX/ IW,NPLT,IJK
      COMMON/ICOND/SO,DO,EO
      COMMON /PLTPTS/POINT(10)
      COMMON /CHRG/ ZQ,ALF
      COMMON/MATRIX/RTEST,BCOND
C
C     SUBROUTINE AIO READS THE INPUT DATA AND CONVERTS VARIABLES TO
C     DIMENSIONLESS FORM.  MOST OF THE INPUT DATA IS ALSO WRITTEN
C
      CALL AIO (IOFF,ISTOP,SIZE,DEBL,NPT,NAME,JNAME,MMM)
C     IF BCOND IS ZERO THEN THE PROGRAM WILL SOLVE ONLY THE
C     STEADY STATE PROBLEM.
      IF (BCOND .EQ. 0.0)GO TO 335
C
C     SUBROUTINE GRIDXX, WHERE XX IS PR FOR ONE BLOCKING ELECTRODE,
C     RR FOR TWO BLOCKING ELECTRODES, AND RR FOR LIQUID JUNCTION
C     SIMULATIONS, GENERATES THE NONUNIFORM SPACE MESH ACCORDING TO R,
C     GAUGE, AND KEY. DEL IS THE INCREMENT VECTOR AND XER HOLDS THE
C     SPACE POSITIONS OF THE GRID PTS.
C
      CALL GRIDPR (DEL,XER,SIZE,DEBL)
C
C     SHIFTING ORIGIN FOR KEY=1 PROBLEM
C
      IF (KEY .EQ. 2) GO TO 13
      DO 15 I=1,R
      XER(I)=XER(I)-(0.5*SIZE)
 15   CONTINUE
 13   CONTINUE
      RR=3*R
      TIME=0.0
      RCOND=1.0
      ZI = 0.0
      M = 0
C
C     KOUNT IS THE NUMBER OF ITERATIONS PERFORMED AT EACH TIME ROW.
C
      KOUNT=0
C
```

```
C     SUBROUTINE IC ASSEMBLES THE INITIAL CONDITIONS FOR S,D, AND E.
C
      CALL IC (KEY,Y,R)
C
C     OUTPUTTING THE INITIAL CONDITIONS
C
      CALL IANDW(Y,TIME,KOUNT,RCOND,XER,NPT,NAME,JNAME,M,KFLAG,SIZE)
C
C     SAVING F AS FF FOR USE AFTER CHARGING IS COMPLETE.
C
      FF = F
C
C     BEGINNING OF TIME LOOP
C
      DO 17 M=1,Q
      ZI = ALF*ZQ*EXP(-ALF*TIME)
C
C     IN GENERAL TIME(N,F,DT)=DT*((1+F)**N-1)/F
C
      TIME=TIME+DT
C
C     SUBROUTINE RHSVO COMPUTES THE PORTION OF THE RHS-VECTOR GENERATED
C     BY THE SOLUTIONS FROM THE PREVIOUS TIME ROW. RHSVO IS CALLED ONLY
C     ONCE FOR EACH TIME ROW. THE RHS-VECTOR IS RETURNED AS B.
C
      CALL RHSVO (R,DEL,DT,Y,B,M,MMM)
C
C     THE UNCHANGING PORTION OF B IS SAVED AS BB FOR USE WITH EACH
C     SUBSEQUENT ITERATION.
      DO 18 I=1,RR
      BB(I)=B(I)
 18   CONTINUE
C
C     SUBROUTINE COEMAT ASSEMBLES THE COEFFICIENT MATRIX, ABD, IN BAND
C     STORAGE FORM.
C
 21    CALL COEMAT (R,DEL,DT,Y,ABD,M,MMM)
C
C     IF RCOND LESS THAN RTEST THEN MATRIX WILL BE NEAR SINGULAR.
C     RTEST IS SUPPLIED BY THE USER BY OBTAINING THE CONDITION
C     OF THE MATRIX NEAR THE STEADY STATE.
C
      IF (ABS(RCOND) .LE. RTEST) GO TO 333
C
C
C     SUBROUTINE RHSVN COMPUTES THE PORTION OF THE RHS-VECTOR DUE TO
C     THE SOLUTION TO THE PREVIOUS ITERATION. THIS VECTOR IS RETURNED AS
C     B. THE VECTOR B+BB IS THE COMPLETE RHS-VECTOR FOR ANY GIVEN
C     ITERATION.
C
      CALL RHSVN (R,DEL,DT,Y,B)
      DO 19 J=1,RR
      B(J)=B(J) + BB(J)
```

```
      YY(J)=Y(J)
 19   CONTINUE
C
C     LDA IS THE LEADING DIMENSION OF ABD, ML IS THE NUMBER OF DIAGONALS
C     ABOVE THE MAIN, MU IS THE NUMBER OF DIAGONALS BELOW THE MAIN.
C
      LDA=16
      ML=5
      MU=5
C
C     SGBCO FACTORIZES THE MATRIX  ABD. RCOND IS RETURNED AS 1/COND.
C     WHERE COND IS THE CONDITION OF THE MATRIX.
C     IF RCOND IS NOT NEEDED, SUBROUTINE SGBFA MAY BE USED TO DECREASE
C     EXECUTION TIME
C
      JOB=0
      CALL SGBCO (ABD,LDA,RR,ML,MU,IPVT,RCOND,Z)
C
C     SGBSL SOLVES THE MATRIX EQUATION ABD*Y=B. WHERE ABD IS THE BAND
C     MATRIX FACTORIZED BY SGBCO, B IS FORMED FROM RHSVO AND RHSVN,
C     AND Y IS THE SOLUTION VECTOR RETURNED AS B. THE ENTERING
C     RHS-VECTOR, B, IS DESTROYED.
C
      CALL SGBSL (ABD,LDA,RR,ML,MU,IPVT,B,JOB)
      DO 20 K=1,RR
      Y(K)=B(K)
 20   CONTINUE
C
C     CMPR COMPARES THE CURRENT ITERATION SOLUTIONS WITH THE PREVIOUS
C     ONES. IF THE RELATIVE CHANGE IS LESS THAN TOL FOR EACH VARIABLE,
C     KFLAG IS RETURNED AS ZERO AND THE MAIN PROGRAM CONTINUES TO THE
C     NEXT TIME ROW. OTHERWISE KFLAG=1 AND ANOTHER ITERATION IS
C     PERFORMED.
C
      CALL CMPR (Y,YY,TOL,R,KFLAG)
C
C     THE NEXT CARD REDUCES EXECUTION TIME FOR SMALL PERTURBATIONS
C     BY ELIMINATING THE ITERATION PROCEDURE
C
      KFLAG=IOFF*KFLAG
      KOUNT=KOUNT+1
C
C     IF KOUNT REACHES 11 ITERATION IS PROBABLY DIVERGING SO PROGRAM
C     IS TERMINATED.
C
      IF (KOUNT .EQ. 11) GO TO 16
      DO 27 J=1,RR
      Y(J)=YY(J)
 27    CONTINUE
C
C     IF M IS NOT EQUAL TO 1 OR A MULTIPLE OF IJK, THE OUTPUT
C     AT THAT TIME ROW WILL NOT BE WRITTEN
C
```

```
      L=MOD (M,IJK)
      IF (L .NE. 0 .AND. M .NE. 1) GO TO 14
      IF (IW .EQ. 0) GO TO 11
C
C     IANDW CALCULATES THE CHARGE AND MASS IN THE SYSTEM, THE POTENTIAL
C     AS A FUNCTION OF X, WRITES EVERY IJK TH TIME ROW  AND PLOTS
C     S,D,AND E AS A FUNCTION OF X.
C
      CALL IANDW(Y,TIME,KOUNT,RCOND,XER,NPT,NAME,JNAME,M,KFLAG,SIZE)
 11   CONTINUE
 14   CONTINUE
      IF (KFLAG .EQ. 1) GO TO 21
      IF (L .NE. 0 .AND. M .NE. 1) GO TO 12
      IF (IW .NE. 0 ) GO TO 12
      CALL IANDW(Y,TIME,KOUNT,RCOND,XER,NPT,NAME,JNAME,M,KFLAG,SIZE)
 12   CONTINUE
C
C     DT IS INCREMENTED AT EACH TIME ROW ACCORDING TO THE VALUE OF F
C     THAT IS SPECIFIED IN THE INPUT DATA
C
C     F KEEPS TIME STEP SIZES CONSTANT WHILE ELECTRODE
C     IS BEING CHARGED
C
      IF (M .LE. ISTOP) F = 0.0
C
C     AFTER ELECTRODE CHARGE IS COMPLETED TIME STEP SIZES ARE
C     GRADUALLY INCREASED IF F IS SET POSITIVE
C
      IF (M .GT. ISTOP) F = ABS(FF)
C
C     IF F IS SET BETWEEN 0 AND -1 TIME STEP SIZES WILL BE
C     DECREASED BY ABS(FF) FOR TIME ROW ISTOP+1 AND THEN
C     GRADUALLY INCREASED THEREAFTER AS USUAL
C
      IF (M .EQ. ISTOP .AND. FF .LT. 0.0) DT = ABS(FF)*DT
      DT=(F+1.0)*DT
      KOUNT=0
 17   CONTINUE
      STOP
 16   CONTINUE
      WRITE (61,10)
 10   FORMAT (1X,28HSOLUTION VECTOR IS DIVERGING)
      GO TO 335
 333   WRITE (61,334)
 334   FORMAT (1X,23HMATRIX IS NEAR SINGULAR)
 335   CONTINUE
      END



      SUBROUTINE AIO (IOFF,ISTOP,SIZE,DEBL,NPT,NAME,JNAME,MMM)
```

```
C
C     SUBROUTINE A10 READS IN ALL THE DATA NEEDED BY IONFLO.  ALL
C     INPUT DATA IS ALSO WRITTEN BY A10.  ALL INPUT FORMAT IS EITHER
C     I5 OR E10.3 EXCEPT NAME AND JNAME WHICH ARE A5 AND TITLE1
C     AND TITLE2 WHICH ARE A10.
C
      DIMENSION NPT(10),JNAME(10),NAME(10)
      REAL I1,I2,ITOT
      DOUBLE SIZE,DEBL
      REAL KSL,KDL,KSO,KDO,KSA,KDA,KSR,KDR
      INTEGER R,Q
      COMMON/CURRENT/I1,I2
      COMMON /ELEC/ EPS,ZI
      COMMON /GREEK/ C(24)
      COMMON/UNITS/SM,DF,GDE,EPM,A,ZP,ZM,CON,TM,DIM,CREF,ZREF
      COMMON /PARAM/ KEY,R,Q,DT,F,TOL,RANGE,ISET
      COMMON /PLTPTS/ POINT(10)
      COMMON /BOX/ IW,NPLT,IJK
      COMMON/ICOND/SO,DO,EO
      COMMON /CHRG/ ZQ,ALF
      COMMON/RATES/KSL,KDL,KSO,KDO,KSA,KDA,KSR,KDR
      COMMON/BNDRY/SL,SR,DL,DR
      COMMON/MATRIX/RTEST,BCOND
      COMMON/DIFF/D1,D2,DELTA
      COMMON/THERM/QDELT,V1,V2
C     DOO,AND DA ARE THE DIFFERENCE CONCENTRATIONS AT X=-L/2 AND
C     X=+L/2 RESPECTIVELY
      READ (50,37) TITLE1,TITLE2
      READ (50,10) KEY,R,Q,ISET,IJK,NPLT,IOFF,IW,MMM,ISTOP,RANGE,DT,F
      READ (50,13) ZP,ZM,ZQ,ALF,EPS,TOL,TM,RTEST
      READ (50,13) EPM,ZREF,SIZE,CREF,SO,DO,EO,BCOND
      READ (50,13) CRESL2,CRESR2,DL,DR
      READ (50,13) I1,ITOT,D1,D2,DELTA,DOO,DA
      READ (50,13) (C(I),I=1,10)
      READ (50,13) QDELT,V1,V2
      READ (50,11) (POINT(J),J=1,3)
      READ (50,12) (NAME(J),J=1,3)
      READ (50,12) (JNAME(J),J=1,8)
      CRESL1 = (2*ZP*ZM*DL - CRESL2*ZM - CREF*ZREF)/ZP
      CRESR1 = (2*ZP*ZM*DR - CRESR2*ZM - CREF*ZREF)/ZP
      SL = 0.5*((CRESL2/ZP) - (CRESL1/ZM))
      SR = 0.5*((CRESR2/ZP) - (CRESR1/ZM))
      SM = (SL+SR)/2.0
      SL = (SL-SM)/SM
      SR = (SR-SM)/SM
      DR = DR/SM
      DL = DL/SM
      DOO = DOO/SM
      DA = DA/SM
      DF=-ZREF*CREF/(ZP*ZM*2.0)
      F111=C(1)*(ZM*(DF-SM))
      F112=C(2)*(((ZM*(DF-SM)))**1.5)
      F121=C(5)*((((ZP+ZM)/2.0)*DF + ((ZP-ZM)/2.0)*SM)**1.5)
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```
      F122=C(6)*((((ZP+ZM)/2.0)*DF + ((ZP-ZM)/2.0)*SM)**2.0)
      F221=C(3)*(ZP*(DF+SM))
      F222=C(4)*(((ZP*(DF+SM)))**1.5)
      G11=(F111 + F112)*ZP*ZP
      G12=2.0*ZP*ZM*(F121 + F122)
      G22=ZM*ZM*(F221 + F222)
      GDE=(96485.0/(2.0*ZP*ZM))*(G11 + G12 + G22)
      SC = (ZP*ZM*SM/2.0)*(((ZP+ZM)*(DF/SM)) + (ZM-ZP) +
     + ((ZREF*ZREF)*CREF/(ZP*ZM*SM)))
      DEBL=((8.314E7*EPS*EPM*TM)/(2.0*(96485.0**2.0)*SC))**0.5
      A=DEBL/5.0
      KSL= (D2+D1)/(2.0*DELTA)
      KDL = (D2-D1)/(2.0*DELTA)
      KSA = KSL
      KSO = KSL
      KSR = KSL
      KDA = KDL
      KDO = KDL
      KDR = KDL
      WRITE (61,33) TITLE1,TITLE2
      WRITE (61,28) R,Q,KEY
      WRITE (61,35) DT,F,TOL,RANGE,RTEST
      WRITE (61,32) A,ALF
      WRITE (61,31) IJK,ISET,IW,IOFF,ISTOP,NPLT
      WRITE (61,40) GDE,EPM,SM,DF,ZQ,SIZE
      WRITE (61,41) CREF,EPS
      WRITE (61,38)KSO,KDO,KSA,KDA
      WRITE (61,83)KSL,KDL,KSR,KDR
      WRITE (61,53)DELTA
      WRITE (61,27) C(1),C(2)
      WRITE (61,26) C(3),C(4)
      WRITE (61,25) C(5),C(6)
      WRITE (61,14)
      WRITE (61,15) C(7),C(8)
      WRITE (61,16) C(9),C(10)
      WRITE (61,29) DEBL,TM
      WRITE (61,68)SL,SR,DL,DR
10    FORMAT (1015,3E10.3)
11    FORMAT (3A1)
12    FORMAT (8A10)
13    FORMAT (8E10.3)
14    FORMAT (///,2X,19H M AND B EXPANSIONS,/)
15    FORMAT (3X,3HM =,E10.3,5H/S - ,E10.3,7H*S**1.5,/)
16    FORMAT (3X,3HB =,E10.3,3H + ,E10.3,2H*S,/)
22    FORMAT (//,2X,31H ONSAGER COEFFICIENT EXPANSIONS,/)
25    FORMAT (3X,5HLPM =,E10.3,12H*(S)**1.5 + ,E10.3,7H*(S)**2,/)
26    FORMAT (3X,5HLMM =,E10.3,11H*(S + D) + ,E10.3,13H*(S + D)**1.5,/)
27    FORMAT (3X,5HLPP =,E10.3,11H*(S - D) + ,E10.3,13H*(S - D)**1.5,/)
28    FORMAT (/,1X,14,10H SPACE PTS,4X,14,10H TIME ROWS,
     12X,6H KEY =,12,//)
29    FORMAT (////,2X,15H DEBYE LENGTH =,E10.3,7X,5H TM =,E10.3,//)
31    FORMAT (2X,6H IJK =,13,8X,7H ISET =,13,6X,5H IW =,13,10X,7H IOFF =
     1,13,10X,8H ISTOP =,13,10X,7H NPLT =,13,//)
```

```
 32   FORMAT (2X,4H A =,E10.3,3X,7H ALF  =,E10.3,//)
 33   FORMAT (1H1,60X,2A10,///)
 35   FORMAT (2X,4H DT=,E10.3,3X,3H F=,E10.3,3X,5H TOL=,E10.3,3X,7H RANG
     1E=,E10.3,3X,7H RTEST=,E10.3,//)
 53    FORMAT (3X,7HDELTA =,E10.3,//)
 68    FORMAT (//,3X,4HSL =,E10.3,3X,4HSR =,E10.3,3X,4HDL =,E10.3,
     + 3X,4HDR =,E10.3,//)
119   FORMAT (1X,6HCOMP =,E10.3,3X,5HSUM =,E10.3,//)
 37   FORMAT (2A10)
 38    FORMAT (3X,5HKSO =,E10.3,2X,5HKDO =,E10.3,2X,5HKSA =,E10.3,.
     + 2X,5HKDA =,E10.3,/)
 83    FORMAT (3X,5HKSL =,E10.3,2X,5HKDL =,E10.3,2X,5HKSR =,E10.3,
     + 2X,5HKDR =,E10.3,/)
 40   FORMAT (2X,5H GDE=,E10.3,2X,5H EPM=,E10.3,1X,5H SM =,E10.3,
     +3X,5H DF =,E10.3,5X,5H ZQ =,E10.3,7H SIZE =,E10.3,//)
 41    FORMAT(2X, 6H CREF=,E10.3,2X,4HEPS=,E10.3,///)
C
C     CONVERSION OF DT, ZQ, ALF, AND THE C-EXPANSION COEFFICIENTS TO
C     DIMENSIONLESS QUANTITIES FOR USE IN THE MAIN PROGRAM
C
      CON = EPM/(2.0*96485.0*ZP*ZM)
      DIM=CON/(A*GDE)
      DT = GDE*DT/CON
      ZQ = -CON*ZQ/(A*SM*EPM)
      ALF = CON*ALF/GDE
      DO 50 I=1,6
      C(I) = (8.314E7)*TM*C(I)*CON/(A*A*GDE*2.0)
 50   CONTINUE
      C(2) = C(2)*(SM)**0.5
      C(4) = C(4)*(SM)**0.5
      C(5) = C(5)*(SM)**0.5
      C(6) = C(6)*SM
      C(7) = C(7)*SM
      C(8) = C(8)*SQRT(SM)
      C(9) = C(9)*SM
      C(10) = C(10)*SM**2.0
C     DETERMINATION OF THE STEADY STATE ANALYTICAL SOLUTION.
C
      IF (BCOND .EQ. 0.0)CALL BCONDIT(I1,ITOT,DOO,DA,SIZE)
      I2 = ITOT-I1
      KDO=KDO*DIM
      KSO=KSO*DIM
      KDA=KDA*DIM
      KSA=KSA*DIM
      KDL=KDL*DIM
      KDR=KDR*DIM
      KSR=KSR*DIM
      KSL=KSL*DIM
      RETURN
      END
```

```
      SUBROUTINE IANDW (Y,TIME,KOUNT,RCOND,XER,NPT,NAME,JNAME,M
     + ,KFLAG,SIZE)
C     IANDW CALCULATES THE POTENTIAL AS A FUNCTION OF X, THE TOTAL
C     CHARGE AND MASS IN THE SYSTEM, AND WRITES THE OUTPUT FOR EACH
C     TIME ROW SPECIFIED BY IJK.
C
      DIMENSION Y(300),XER(100),PSI(100),YER(100)
      DIMENSION E(100),YI(100),YJ(100)
      DIMENSION NPT(10),JNAME(10),NAME(10)
      DIMENSION ZXARAY(100,3),ZARAY(100,3)
      DIMENSION PD(150),PDT(150)
      COMMON /ELEC/ EPS,ZI
      COMMON /PARAM/ KEY,R,Q,DT,F,TOL,RANGE,ISET
      COMMON/UNITS/SM,DF,GDE,EPM,A,ZP,ZM,CON,TM,DIM,CREF,ZREF
      COMMON /BOX/ IW,NPLT,IJK
      COMMON /PLTPTS/ POINT(10)
      COMMON/CURRENT/I1,I2
      COMMON/DIFF/D1,D2,DELTA
      COMMON/BNDRY/SL,SR,DL,DR
      INTEGER R,RR,Q,RSTOP,RSTART
      DOUBLE XER,XLO,XUP,AVINT,TMS,TCS,PSI,SIZE
      REAL I1,I2
      DATA IO/61/,MAX/100/,ISCALE/1/,NF/3/
      DATA ZXARAY/300*0.0/
      RR=3*R
      RSTOP=R/2
      RSTART=RSTOP+1
C
C     STRIPPING OUT THE MASS CHARGE,AND ELECTRIC FIELD VECTORS FOR
C     INTEGRATION AND FORMING THE + AND - ION CONCENTRATIONS FOR PLOTS.
C
      DO 16 K=1,R
      ZARAY(K,1)=ZM*SM*(Y(3*K-1) - Y(3*K-2) + (DF/SM) - 1.0)*1.0E-6
      ZARAY(K,2)=ZP*SM*(Y(3*K-1) + Y(3*K-2) + (DF/SM) + 1.0)*1.0E-6
      ZARAY(K,3) = Y(3*K)*1.0E-11*A*SM/CON
      YI(K) = Y(3*K-1)
      YJ(K) = Y(3*K-2)
      E(K) = Y(3*K)
 16   CONTINUE
C
C     LOWER AND UPPER BOUNDS FOR INTEGRATION
C
      XLO = XER(1)
      XUP = XER(R)
C
C     CALCULATING THE TOTAL CHARGE AND EXCESS MOLES OF IONS IN THE
C     SYSTEM
C
      TCS=AVINT(XER,YI,R,XLO,XUP,IND)
      TMS= (ZP+ZM)*AVINT(XER,YI,R,XLO,XUP,IND)
     + + (ZP-ZM)*AVINT(XER,YJ,R,XLO,XUP,IND)
```

```
C
C      CALCULATING THE POTENTIAL AS A FUNCTION OF X
C
       DO 26 J=1,R
       XUP=XER(J)
       PSI(J)= (1.0E-07*A*SM/CON)*AVINT(XER,E,R,XLO,XUP,IND)
 26    CONTINUE
       RJ = PSI(R)
       ZJD = -DIM*(I2+I1)/(2.0*ZP*ZM*96485.0*SM)
C      COMPUTING THE POTENTIAL LOSS DUE TO OHMIC DROP.
       PSOM = 0.0
       PSOD = 0.0
       DO 231 J = 2,R
       SMM = Y(3*J-5)
       SPP = Y(3*J-2)
       DMM = Y(3*J-4)
       DPP = Y(3*J-1)
       S = 0.5*(SMM + SPP)
       D = 0.5*(DMM + DPP)
C      SETTING ARGUMENTS FOR THE FUNCTION SUBROUTINE.
       T1 = ZIJ(S,D)
       SPAC = XER(J) - XER(J-1)
       PSOD = PSOD - (ZI+ZJD)*(1.0E-07*A*SM/CON)*SPAC/ZDE(S,D)
       PSOM = PSOD + PSOM
 231    CONTINUE
       PD(1+M/IJK) = PSI(R) - PSOM
       IF (M .EQ. 0 .OR. M .EQ. 1)GO TO 232
       CHNG = (PD(1+M/IJK) - PD(1+(M-1)/IJK))/PD(1+M/IJK)
       CHNG = ABS(CHNG)
       IF (CHNG .LT. 0.001)Q=M
C
C      CONVERTING EJ TO VOLTS, TIME TO SECONDS, TCS TO COULOMBS, TMS TO
C      MOLES, AND ZI TO AMPS PER CM**2
C
 232    RIME = TIME*CON/GDE
       PDT(1 + M/IJK) = RIME
       RI = -A*SM*GDE*EPM*ZI/CON**2
       TCS = TCS*2.0*ZP*ZM*96485.0*SM
       TMS=SM*TMS
       WRITE (61,24) RIME,KOUNT,TMS
       WRITE (61,25) RJ,TCS,RI
       WRITE (61,444) RCOND
 24    FORMAT (1H1,/,7X,1HX,10X,3HSUM,9X,3HRHO,9X,2HC+,10X,2HC-,10X,1HE,
      110X,3HPSI,6X,3H T=,E10.3,2X,7H KOUNT=,I2,7X,6H TMS =,E10.3,/)
 25    FORMAT (86X,4H EJ=,E10.3,1X,5H TCS=,E10.3,1X,4H ZI=,E10.3,/)
 444    FORMAT (86X,8H RCOND =,E10.3)
C
C      AY IS THE SUM CONCENTRATION LESS THE BULK CONCENTRATION
C      BY IS THE CHARGE DENSITY IN COULOMBS/CC
C      CY IS THE ELECTRIC FIELD IN VOLTS/CM
C      CP IS THE  POSITIVE ION CONCENTRATION
C      CM IS THE  NEGATIVE ION CONCENTRATION
C
```

```
      DO 888 K=1,RSTOP
      YER(K) = XER(K) + 0.5*SIZE
 888   CONTINUE
      DO 999 K=RSTART,R
      YER(K)=0.5*SIZE - XER(K)
 999   CONTINUE
      JR = RR - 2
      DO 11 I=1,JR,3
      AY = Y(I)*SM
      BY = Y(I+1)*SM*ZP*ZM*2.0*96485.0
      CY = -Y(I+2)*1.0E-07*A*SM/CON
      CP=ZM*((Y(I+1)+(DF/SM)) - (Y(I)+(1.0)))*SM
      CM=ZP*((Y(I+1)+(DF/SM)) + (Y(I)+(1.0)))*SM
      WRITE (61,23) YER((I+2)/3),AY,BY,CP,CM,CY,PSI((I+2)/3)
 23   FORMAT (7E12.5)
 11   CONTINUE
      IF (M .EQ. Q) GO TO 15
      RETURN
 15   MQ = 1 + Q/IJK
      WRITE (61,28)
      WRITE (61,27) (PDT(I),PD(I),I=1,MQ)
      CPO = ZM*((Y(2)+(DF/SM)) - (Y(1)+(1.0)))*SM
      CMO = ZP*((Y(2)+(DF/SM)) + (Y(1)+(1.0)))*SM
      CPA = ZM*((Y(RR-1)+(DF/SM)) - (Y(RR-2)+(1.0)))*SM
      CMA = ZP*((Y(RR-1)+(DF/SM)) + (Y(RR-2)+(1.0)))*SM
      CPL = ZM*((DL+(DF/SM)) - (SL+(1.0)))*SM
      CML = ZP*((DL+(DF/SM)) + (SL+(1.0)))*SM
      CPR = ZM*((DR+(DF/SM)) - (SR+(1.0)))*SM
      CMR = ZP*((DR+(DF/SM)) + (SR+(1.0)))*SM
      Z11L = (D1*ZP*96485.0/DELTA)*(CPL-CPO)
      Z12L = (D2*ZM*96485.0/DELTA)*(CML-CMO)
      Z11R = (D1*ZP*96485.0/DELTA)*(CPA-CPR)
      Z12R = (D2*ZM*96485.0/DELTA)*(CMA-CMR)
      WRITE (61,789)Z11L,Z12L,Z11R,Z12R
 789   FORMAT (//,1X,5H11L =,E12.5,3X,5H12L =,E12.5,3X,5H11R =,E12.5,
     + 3X,5H12R =,E12.5,//)
 27   FORMAT (2X,2E13.6)
 28   FORMAT (//,1X,46H POTENTIAL DIFFERENCE CORRECTED FOR OHMIC DROP,/)
      RETURN
      END



      SUBROUTINE BCONDIT (I1,ITOT,DOO,DA,SIZE)
      REAL I1,I2,ITOT
      COMMON /ELEC/ EPS,ZI
      COMMON/GREEK/C(24)
      COMMON/UNITS/SM,DF,GDE,EPM,A,ZP,ZM,CON,TM,DIM,CREF,ZREF
      COMMON/THERM/QDELT,V1,V2
      I2 = ITOT-I1
C
```

```
C      DETERMINATION OF STEADY STATE PARAMETERS
C
       ZJS = -DIM*(I2-I1)/(2.0*ZP*ZM*96485.0*SM)
       ZJD = -DIM*(I2+I1)/(2.0*ZP*ZM*96485.0*SM)
       S = 0.0
       D = 0.0
       T1 = ZIJ(S,D)
       ZZ = (ZSS(S,D)*ZDD(S,D)) - (ZSD(S,D)*ZDS(S,D))
       BDO = ((ZSS(S,D)*ZDE(S,D)) - (ZSE(S,D)*ZDS(S,D)))/ZZ
       BSO = ((ZDD(S,D)*ZSE(S,D)) - (ZSD(S,D)*ZDE(S,D)))/ZZ
       ADO = -((ZDS(S,D)*ZJS) - (ZSS(S,D)*ZJD))/ZZ
       ASO = -((ZSD(S,D)*ZJD) - (ZDD(S,D)*ZJS))/ZZ
       AA = (-BDO/(A*A*EPS))**0.5
C
C      CALCULATION OF FIRST ORDER TERMS.
C
       BSD = ((ZDD(S,D)*ZSED(S,D)) - (ZSD(S,D)*ZDED(S,D)))/ZZ
       BSS = ((ZDD(S,D)*ZSEP(S,D)) - (ZSD(S,D)*ZDEP(S,D)))/ZZ
       BDD = ((ZSS(S,D)*ZDED(S,D)) - (ZDS(S,D)*ZSED(S,D)))/ZZ
       BDS = ((ZSS(S,D)*ZDEP(S,D)) - (ZDS(S,D)*ZSEP(S,D)))/ZZ
       ZZP = ZSS(S,D)*ZDDP(S,D) + ZSSP(S,D)*ZDD(S,D)
      + - ZSD(S,D)*ZDSP(S,D) - ZSDP(S,D)*ZDS(S,D)
       ZZD = ZSS(S,D)*ZDDD(S,D) + ZSSD(S,D)*ZDD(S,D)
      + - ZSD(S,D)*ZDSD(S,D) - ZSDD(S,D)*ZDS(S,D)
       T1 = -((ZDSP(S,D)*ZJS) - (ZSSP(S,D)*ZJD))
       T2 = -((ZDS(S,D)*ZJS) - (ZSS(S,D)*ZJD))
       ADOP = (ZZ*T1 - ZZP*T2)/(ZZ**2.0)
       T1 = -((ZDSD(S,D)*ZJS) - (ZSSD(S,D)*ZJD))
       ADOD = (ZZ*T1 - ZZD*T2)/(ZZ**2.0)
       T1 = -((ZSDP(S,D)*ZJD) - (ZDDP(S,D)*ZJS))
       T2 = -((ZSD(S,D)*ZJD) - (ZDD(S,D)*ZJS))
       ASOP = (ZZ*T1 - ZZP*T2)/(ZZ**2.0)
       T1 = -((ZSDD(S,D)*ZJD) - (ZDDD(S,D)*ZJS))
       ASOD = (ZZ*T1 - ZZD*T2)/(ZZ**2.0)
C
C       CALCULATION OF THE THERMAL TERMS.
C
       Y=D+(DF/SM)-S-1.0
       Z= D + S + 1.0 + (DF/SM)
       IF (Y.GE.0.0) Y=-1.0E-10
       IF (Z.LE.0.0) Z=1.0E-10
       SUM=((ZM*ZM)*Y - (ZP*ZP)*Z)/(ZM-ZP)
       ZPP=C(1)*(ZM*(Y)) + C(2)*(ZM*(Y))**1.5
       ZMM=C(3)*(ZP*(Z)) + C(4)*(ZP*(Z))**1.5
       ZPM=C(5)*(SUM**1.5) + C(6)*(SUM**2.0)
       T1 = ZSS(S,D)*(ZP*ZPP+ZM*ZPM) + ZDS(S,D)*(ZP*ZPP-ZM*ZPM)
       T2 = ZSS(S,D)*(ZP*ZP*ZPP + 2.0*ZP*ZM*ZPM + ZM*ZM*ZMM)
       T3 = -ZDS(S,D)*(ZM*ZM*ZMM - ZP*ZP*ZPP)
       T5 = QDELT/(SIZE*V1)
       T4 = T1*T5*CON*BDO*1.0E+07/(A*96485.0*4.184*SM*(T2+T3))
       ADO = ADO + T4
C      THE FOLLOWING ARE ELECTROLYTE CONCENTRATIONS AT THE WALLS,
C      AND NOT RESERVOIR CONCENTRATIONS.
```

```
      SA1 = (((ASO*BDO)-(ADO*BSO))/BDO)*(SIZE/(2.0*A))
      SA2=(BSO/BDO)*(DA-DOO)/2.0
C     THE ZEROTH ORDER SUM CONCENTRATION AT THE WALLS.
      SRO = SA1 + SA2
      SLO=-SRO
      ALPHA = ((ASO*BDO) - (ADO*BSO))/BDO
      GAMMA = SIZE/A
      SA1 = (ALPHA*(GAMMA**2.0)/12.0)*(-ADO/BDO)
      SA1 = SA1*(BSS-(BDS*BSO/BDO))
      SA2 = ALPHA*GAMMA/2.0
      SA2 = SA2*(BSS-(BDS*BSO/BDO))*(DA/BDO)
      SA3 = 2.0*((DA/2.0)**2.0)/BDO
      SA3 = SA3*((BSD+(BSS*BSO/BDO)) - ((BSO/BDO)*(BDD+(BDS*BSO/BDO))))
C     THE FIRST ORDER CONTRIBUTION TO THE SUM CONCENTRATION AT
C     THE WALLS.
      SR1 = SA1 + SA2 + SA3
      SL1 = SR1
      SSR = SRO + SR1
      SSL = SLO + SL1
C     COMPUTATION OF SECOND ORDER CONTRIBUTION TO THE POTENTIAL
C     DROP ACROSS THE ELECTROLYTE.
      T1 = (BDS*SIZE*ALPHA/(BDO*A))**2.0
      T2 = -ADO*SIZE/(A*12.0*BDO)
      T3 = T1*T2
      T4 = 3.0*ALPHA*BDS/2.0
      T5 = -BDS*BSO*ADO/(3.0*BDO)
      T6 = BDS*ALPHA*(DA-DOO)/(8.0*BDO)
      T7 = (SIZE/(A*BDO))**2.0
      T8 = T6*T7*(T4-T5)
      T9 = T8 + T3
      PHI2 = (1.0E-07)*A*A*SM*T9/CON
      WRITE (61,111)BDO,BSO,ADO,ASO
      WRITE (61,112)BSD,BSS,BDD,BDS
      WRITE (61,114)ADOP,ASOP,ADOD,ASOD
C     THE VALUE OF PHI REPRESENTS THE ZEROTH ORDER CONTRIBUTION
C     TO THE TOTAL POTENTIAL DIFFERENCE ACROSS THE CELL.
      PHI = -(1.0E-07*A*A*SM/(CON*BDO))*((DOO-DA) + ADO*SIZE/A)
      WRITE (61,113)AA,PHI
      WRITE(61,67) I1,I2
      WRITE (61,555)SLO,SRO,SL1,SR1,SSL,SSR
C     THE VALUE OF PHI2 REPRESENTS THE SECOND ORDER CONTRIBUTION TO
C     THE POTENTIAL DROP ACROSS THE ELECTROLYTE.
      WRITE (61,478)PHI2
 478   FORMAT (2X,6HPHI2 =,E10.3,//)
 111   FORMAT (1H1,1X,5HBDO =,E10.3,2X,5HBSO =,E10.3,2X,5HADO =,E10.3,
     + 2X,5HASO =,E10.3,//)
 112   FORMAT (2X,5HBSD =,E10.3,2X,5HBSS =,E10.3,2X,5HBDD =,E10.3,
     + 2X,5HBDS =,E10.3,//)
 114   FORMAT (2X,6HADOP =,E10.3,2X,6HASOP =,E10.3,2X,6HADOD =,E10.3,
     + 2X,6HASOD =,E10.3,//)
 113   FORMAT (2X,4HAA =,E10.3,3X,5HPHI =,E10.3,5HVOLTS,//)
 67    FORMAT (2X,15HIONIC CURRENT =,E12.5,3X,20HELECTRONIC CURRENT =
     +,E12.5,//)
```

```
555   FORMAT (2X,5HSLO =,E10.3,3X,5HSRO =,E10.3,3X,5HSL1 =,E10.3,
     + 3X,5HSR1 =,E10.3,3X,5HSSL =,E10.3,3X,5HSSR =,E10.3,//)
      RETURN
      END




      SUBROUTINE GRIDPR (DEL,XER,SIZE,DEBL)
C
C     GRIDPR GENERATES A NONUNIFORM SPACE  MESH WITH INCREASING
C     DISTANCE BETWEEN GRID POINTS AS X INCREASES.  IT IS
C     DESIGNED FOR SIMULATIONS USING A POLARIZABLE ELECTRODE
C     AT X=0 AND A REVERSIBLE ELECTRODE AT X=1.
C     THE VALUE OF RANGE SHOULD BE SELECTED WITH CARE TO
C     AVOID UNDERFLOW AND OVERFLOW FROM THE EXPONENTIAL FUNCTION
C
      DIMENSION DEL(100),XER(100)
      INTEGER R
      DOUBLE DEL,XER,SIZE,DEBL,GAUGE
      COMMON/UNITS/SM,DF,GDE,EPM,A,ZP,ZM,CON,TM,DIM,CREF,ZREF
      COMMON /PARAM/ KEY,R,Q,DT,F,TOL,RANGE,ISET
      GAUGE = DEBL/5.0
      DO 10 I = 1,ISET
      DEL(I) = GAUGE
10    CONTINUE
      JSET = ISET + 1
      L=MOD(R,2)
      IF (L.EQ.0)GO TO 70
      JR=(R-1)/2
80     DO 20 J=JSET,JR
      DEL(J)=GAUGE*EXP((J-ISET)*RANGE)
20     CONTINUE
      KSET=JR+2-L
      LSET=R-1
      DO 90 J=KSET,LSET
      DEL(J)=DEL(R-J)
90     CONTINUE
      GO TO 100
70     JR=(R/2)-1
      DEL(R/2)=GAUGE*EXP(((R/2)-ISET)*RANGE)
      GO TO 80
100    JR=R-1
      SUM = 0.0
      DO 30 M = 1,JR
      SUM = SUM + DEL(M)
30    CONTINUE
      DO 40 L = 1,JR
      DEL(L) = DEL(L)*SIZE/(A*SUM)
40    CONTINUE
      XER(1) = 0.0
      DO 50 M = 2,R
```

```
      XER(M) = XER(M-1) + DEL(M-1)
 50   CONTINUE
      DO 60 N=2,JR
      XER(N) = A*XER(N)
 60   CONTINUE
      XER(R)=SIZE
      RETURN
      END


      SUBROUTINE COEMAT (R,DEL,DT,Y,ABD,M,MMM)
C
C     SUBROUTINE COEMAT ASSEMBLES THE CORE MATRIX FOR USE IN THE
C     NEWTON-RAPHSON ITERATION PROCEDURE.  THE MATRIX IS ASSEMBLED
C     DIRECTLY INTO BAND STORAGE FORM FOR USE IN THE LINPAC SUBROUTINE
C     SGBCO.  R IS THE NUMBER OF SPACE GRID POINTS.  RR IS THE TOTAL
C     NUMBER OF DEPENDENT VARIABLES.  DEL IS THE GRID SPACING VECTOR.
C     DT IS THE TIME STEP. ABD(LDA,RR) IS THE MATRIX IN BAND STORAGE
C     FORM. LDA=2*ML+MU+1   ML-NUMBER OF DIAGONALS ABOVE THE MAIN.
C     MU-NUMBER OF DIAGONALS BELOW THE MAIN.  Y IS THE SOLUTION VECTOR
C     FROM THE PREVIOUS TIME ROW OR PREVIOUS ITERATION.  COEMAT CALLS
C     THE Z COEFFICIENT FUNCTION SUBPROGRAMS.
C     FOR THIS ROUTINE, THE CONVERSION FROM BAND FORM TO BAND STORAGE
C     IS    ABD(I-J+11,J)=A(I,J)
C     THE BAND STORAGE MATRIX IS PASSED TO THE MAIN PROGRAM THROUGH
C     THE COMMON BLOCK COE.  THE RATE CONSTANTS ARE PASSED TO COEMAT
C     THROUGH THE COMMON BLOCK RCNSTS.
C     IF THERE WERE 15 SPACE GRID PTS. THE A AND ABD MATRICES WOULD LOOK
C     LIKE THE FOLLOWING BLOCKS.
C
C                     A                                ABD
C
C     6 5 4 3 2 1 0 0 0 0 0 0 0 0 0 0    0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
C     7 6 5 4 3 2 0 0 0 0 0 0 0 0 0 0    0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
C     8 7 6 5 4 3 0 0 0 0 0 0 0 0 0 0    0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
C     9 8 7 6 5 4 3 2 1 0 0 0 0 0 0 0    0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
C     A 9 8 7 6 5 4 3 2 0 0 0 0 0 0 0    0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
C     B A 9 8 7 6 5 4 3 0 0 0 0 0 0 0    0 0 0 0 0 0 1 0 0 1 0 0 1 0 0 1
C     0 0 0 9 8 7 6 5 4 3 2 1 0 0 0 0    0 0 0 0 2 2 0 2 2 0 2 2 0 2 2 2
C     0 0 0 A 9 8 7 6 5 4 3 2 0 0 0 0    0 0 0 3 3 3 3 3 3 3 3 3 3 3 3 3
C     0 0 0 B A 9 8 7 6 5 4 3 0 0 0 0    0 0 4 4 4 4 4 4 4 4 4 4 4 4 4 4
C     0 0 0 0 0 0 9 8 7 6 5 4 3 2 1 0    0 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
C     0 0 0 0 0 0 A 9 8 7 6 5 4 3 2 0    6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6
C     0 0 0 0 0 0 B A 9 8 7 6 5 4 3 0    7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 0
C     0 0 0 0 0 0 0 0 0 9 8 7 6 5 4 0    8 8 8 8 8 8 8 8 8 8 8 8 8 8 0 0
C     0 0 0 0 0 0 0 0 0 A 9 8 7 6 5 0    9 9 9 9 9 9 9 9 9 9 9 9 0 0 0 0
C     0 0 0 0 0 0 0 0 0 B A 9 8 7 6 0    A A 0 A A 0 A A 0 A A 0 0 0 0 0
C                                        B 0 0 B 0 0 B 0 0 B 0 0 0 0 0 0
C
      INTEGER R,RR,RSTOP
```

```
      REAL KDL,KSL,KDO,KSO,KDA,KSA,KDR,KSR
      DOUBLE DEL
      DIMENSION DEL(100),Y(300),ABD(16,300)
      COMMON/UNITS/SM,DF,GDE,EPM,A,ZP,ZM,CON,TM,DIM,CREF,ZREF
      COMMON /ELEC/ EPS,ZI
      COMMON/RATES/KSL,KDL,KSO,KDO,KSA,KDA,KSR,KDR
      RR = 3*R
      RSTOP = RR - 5
C
C     INITIALIZING THE ABD MATRIX TO ZERO
C
      DO 100 I=1,16
      DO 100 J=1,RR
      ABD(I,J) = 0.0
  100 CONTINUE
C
C     ASSEMBLING THE MATRIX ELEMENTS ARISING FROM THE BOUNDARY
C     CONDITIONS AT X=0
C
      D2 = DEL(1)/2.0
      D22 = DEL(1)*DEL(1)/2.0
      S = Y(1)
      D = Y(2)
      SP = Y(4)
      DP = Y(5)
C
C     SETTING THE COEFFICIENT ARGUMENTS FOR THE FUNCTION ROUTINES.
C
      T1 = ZIJ(S,D)
      T2 = ZIJUP(SP,DP)
C
      F1 = 1.0/DT
      F2 = KSO/D2
      F3 = ZSS(S,D)/D22
      T1 = F1 + F2 + F3
      T2 = ZSSP(S,D)*Y(1)/D22
      F1 = ZSDP(S,D)/D22
      F2 = -ZSEP(S,D)/EPS
      T3 = (F1 + F2)*Y(2)
      T4 = ZSEP(S,D)*Y(3)/(2.0*D2)
      T5 = -ZSSP(S,D)*Y(4)/D22
      T6 = -ZSDP(S,D)*Y(5)/D22
      ABD(11,1) = T1 + T2 + T3 + T4 + T5 + T6
      F1 = KDO/D2
      F2 = ZDS(S,D)/D22
      T1 = F1 + F2
      T2 = ZDSP(S,D)*Y(1)/D22
      F1 = ZDDP(S,D)/D22
      F2 = -ZDEP(S,D)/EPS
      T3 = (F1 + F2)*Y(2)
      T4 = ZDEP(S,D)*Y(3)/(2.0*D2)
      T5 = -ZDSP(S,D)*Y(4)/D22
      T6 = -ZDDP(S,D)*Y(5)/D22
```

```
      ABD(12,1) = T1 + T2 + T3 + T4 + T5 + T6
      ABD(13,1) = KDO/EPS
      T1 = KDO/D2
      T2 = ZSD(S,D)/D22
      T3 = -ZSE(S,D)/EPS
      T4 = ZSSD(S,D)*Y(1)/D22
      T5 = ZSDD(S,D)*Y(2)/D22
      T6 = -ZSSD(S,D)*Y(4)/D22
      T7 = -ZSDD(S,D)*Y(5)/D22
      T8 = -ZSED(S,D)*Y(2)/EPS
      T9 = ZSED(S,D)*Y(3)/(2.0*D2)
      ABD(10,2) = T1+T2+T3+T4+T5+T6+T7+T8+T9
      T1 = 1.0/DT
      T2 = KSO/D2
      T3 = ZDD(S,D)/D22
      T4 = -ZDE(S,D)/EPS
      T5 = ZDSD(S,D)*Y(1)/D22
      T6 = ZDDD(S,D)*Y(2)/D22
      T7 = -ZDSD(S,D)*Y(4)/D22
      T8 = -ZDDD(S,D)*Y(5)/D22
      T9 = -ZDED(S,D)*Y(2)/EPS
      T10 = ZDED(S,D)*Y(3)/(2.0*D2)
      ABD(11,2) = T1+T2+T3+T4+T5+T6+T7+T8+T9+T10
      ABD(12,2) = KSO/EPS
      T1 = ZSE(S,D)/(2.0*D2)
      T2 = ZSEUP(SP,DP)/(2.0*D2)
      ABD(9,3) = T1 + T2
      T1 = ZDE(S,D)/(2.0*D2)
      T2 = ZDEUP(SP,DP)/(2.0*D2)
      ABD(10,3) = T1 + T2
      ABD(11,3) = 1.0/DT
      ABD(8,4) = -ZSS(S,D)/D22 + (0.5*ZSEPUP(SP,DP)/D2)*Y(3)
      ABD(9,4) = -ZDS(S,D)/D22 + (0.5*ZDEPUP(SP,DP)/D2)*Y(3)
      ABD(10,4) = 0.0
      ABD(7,5) = -ZSD(S,D)/D22 + (0.5*ZSEDUP(SP,DP)/D2)*Y(3)
      ABD(8,5) = -ZDD(S,D)/D22 + (0.5*ZDEDUP(SP,DP)/D2)*Y(3)
      ABD(9,5) = 0.0
      ABD(6,6) = 0.0
      ABD(7,6) = 0.0
      ABD(8,6) = 0.0
C
C     ASSEMBLING THE INTERIOR MATRIX ELEMENTS
C     IT IS CONVENIENT TO LOOP IN MULTIPLES OF 3 BECAUSE THERE ARE 3
C     EQUATIONS AT EVERY GRID POINT
C
      DO 101 K=4,RSTOP,3
      KM = (K-1)/3
      KK = (K+2)/3
      SF = (Y(K-3) + Y(K))/2.0
      SMM = Y(K-3)
      SPP = Y(K+3)
      S = Y(K)
      SP = (Y(K+3) + Y(K))/2.0
```

```
      DM = (Y(K-2) + Y(K+1))/2.0
      DMM = Y(K-2)
      D = Y(K+1)
      DP = (Y(K+4) + Y(K+1))/2.0
      DPP = Y(K+4)
      AD = DEL(KM) + DEL(KK)
      DENM = DEL(KM)*AD/2.0
      DENK = DEL(KK)*AD/2.0
      RAT = DEL(KK)/DEL(KM)
      AMUL = DEL(KK)*DEL(KM)
      SUB = DEL(KK) - DEL(KM)
C
C     SETTING THE COEFFICIENT ARGUMENTS FOR THE FUNCTION ROUTINES.
C
      T1 = ZIJ(S,D)
      T2 = ZIJUP(SP,DP)
      T3 = ZIJDN(SF,DM)
      T4 = PPZIJ(SPP,DPP)
      T5 = DDZIJ(SMM,DMM)
C
      T1 = -ZSSDN(SF,DM)/DENM
      T2 = -ZSSPDN(SF,DM)*Y(K-3)/DENM
      T3 = -ZSDPDN(SF,DM)*Y(K-2)/DENM
      T4 = ZSSPDN(SF,DM)*Y(K)/DENM
      T5 = ZSDPDN(SF,DM)*Y(K+1)/DENM
      T6 = -DDZSEP(SMM,DMM)*RAT*Y(K+2)/AD
      ABD(14,K-3) = T1 + T2 + T3 + T4 + T5 + T6
      T1 = -ZDSDN(SF,DM)/DENM
      T2 = -ZDSPDN(SF,DM)*Y(K-3)/DENM
      T3 = -ZDDPDN(SF,DM)*Y(K-2)/DENM
      T4 = ZDSPDN(SF,DM)*Y(K)/DENM
      T5 = ZDDPDN(SF,DM)*Y(K+1)/DENM
      T6 = -DDZDEP(SMM,DMM)*RAT*Y(K+2)/AD
      ABD(15,K-3) = T1 + T2 + T3 + T4 + T5 + T6
      ABD(16,K-3) = -ZDS(S,D)*RAT/(EPS*AD)
      T1 = -ZSDDN(SF,DM)/DENM
      T2 = -ZSSDDN(SF,DM)*Y(K-3)/DENM
      T3 = -ZSDDDN(SF,DM)*Y(K-2)/DENM
      T4 = ZSSDDN(SF,DM)*Y(K)/DENM
      T5 = ZSDDDN(SF,DM)*Y(K+1)/DENM
      T6 = -DDZSED(SMM,DMM)*RAT*Y(K+2)/AD
      ABD(13,K-2) = T1 + T2 + T3 + T4 + T5 + T6
      T1 = -ZDDDN(SF,DM)/DENM
      T2 = -ZDSDDN(SF,DM)*Y(K-3)/DENM
      T3 = -ZDDDDN(SF,DM)*Y(K-2)/DENM
      T4 = ZDSDDN(SF,DM)*Y(K)/DENM
      T5 = ZDDDDN(SF,DM)*Y(K+1)/DENM
      T6 = -DDZDED(SMM,DMM)*Y(K+2)*RAT/AD
      ABD(14,K-2) = T1 + T2 + T3 + T4 + T5 + T6
      ABD(15,K-2) = -ZDD(S,D)*RAT/(EPS*AD)
      ABD(12,K-1) = 0.0
      ABD(13,K-1) = 0.0
      ABD(14,K-1) = 0.0
```

```
T1 = 1.0/DT
T2 = ZSSUP(SP,DP)/DENK
T3 = ZSSDN(SF,DM)/DENM
T4 = -ZSEP(S,D)*Y(K+1)/EPS
T5 = ZSEP(S,D)*SUB*Y(K+2)/AMUL
ABD(11,K) = T1 + T2 + T3 + T4 + T5
T1 = ZDSUP(SP,DP)/DENK
T2 = ZDSDN(SF,DM)/DENM
T3 = -ZDEP(S,D)*Y(K+1)/EPS
T4 = ZDEP(S,D)*Y(K+2)*SUB/AMUL
ABD(12,K) = T1 + T2 + T3 + T4
T1 = -ZDSP(S,D)*Y(K-3)*RAT/(EPS*AD)
T2 = -ZDDP(S,D)*Y(K-2)*RAT/(EPS*AD)
T3 = ZDSP(S,D)*Y(K)*SUB/(EPS*AMUL)
T4 = ZDDP(S,D)*Y(K+1)*SUB/(EPS*AMUL)
T5 = -ZDEP(S,D)*Y(K+2)/EPS
T6 = ZDSP(S,D)*Y(K+3)/(RAT*EPS*AD)
T7 = ZDDP(S,D)*Y(K+4)/(RAT*EPS*AD)
T8 = ZDS(S,D)*SUB/(EPS*AMUL)
ABD(13,K) = T1 + T2 + T3 + T4 + T5 + T6 + T7 + T8
T1 = ZSDUP(SP,DP)/DENK
T2 = ZSDDN(SF,DM)/DENM
T3 = -ZSE(S,D)/EPS
T4 = -ZSED(S,D)*Y(K+1)
T5 = ZSED(S,D)*SUB*Y(K+2)/AMUL
ABD(10,K+1) = T1 + T2 + T3 + T4 + T5
T1 = 1.0/DT
T2 = ZDDUP(SP,DP)/DENK
T3 = ZDDDN(SF,DM)/DENM
T4 = -ZDE(S,D)/EPS
T5 = -ZDED(S,D)*Y(K+1)
T6 = ZDED(S,D)*SUB*Y(K+2)/AMUL
ABD(11,K+1) = T1 + T2 + T3 + T4 + T5 + T6
T1 = -ZDSD(S,D)*Y(K-3)*RAT/(EPS*AD)
T2 = -ZDDD(S,D)*Y(K-2)*RAT/(EPS*AD)
T3 = ZDSD(S,D)*Y(K)*SUB/(EPS*AMUL)
T4 = ZDDD(S,D)*Y(K+1)*SUB/(EPS*AMUL)
T5 = -ZDED(S,D)*Y(K+2)/EPS
T6 = ZDSD(S,D)*Y(K+3)/(RAT*EPS*AD)
T7 = ZDDD(S,D)*Y(K+4)/(RAT*EPS*AD)
T8 = ZDD(S,D)*SUB/(EPS*AMUL)
ABD(12,K+1) = T1 + T2 + T3 + T4 + T5 + T6 + T7 + T8
T1 = -DDZSE(SMM,DMM)*RAT/AD
T2 = PPZSE(SPP,DPP)/(RAT*AD)
T3 = ZSE(S,D)*SUB/AMUL
ABD(9,K+2) = T1 + T2 + T3
T1 = -DDZDE(SMM,DMM)*RAT/AD
T2 = PPZDE(SPP,DPP)/(RAT*AD)
T3 = ZDE(S,D)*SUB/AMUL
ABD(10,K+2) = T1 + T2 + T3
T1 = 1.0/DT
T2 = -ZDE(S,D)/EPS
ABD(11,K+2) = T1 + T2
```

```
      T1 = -ZSSUP(SP,DP)/DENK
      T2 = ZSSPUP(SP,DP)*Y(K)/DENK
      T3 = ZSDPUP(SP,DP)*Y(K+1)/DENK
      T4 = -ZSSPUP(SP,DP)*Y(K+3)/DENK
      T5 = -ZSDPUP(SP,DP)*Y(K+4)/DENK
      T6 = PPZSEP(SPP,DPP)*Y(K+2)/(AD*RAT)
      ABD(8,K+3) = T1 + T2 + T3 + T4 + T5 + T6
      T1 = -ZDSUP(SP,DP)/DENK
      T2 = ZDSPUP(SP,DP)*Y(K)/DENK
      T3 = ZDDPUP(SP,DP)*Y(K+1)/DENK
      T4 = -ZDSPUP(SP,DP)*Y(K+3)/DENK
      T5 = -ZDDPUP(SP,DP)*Y(K+4)/DENK
      T6 = PPZDEP(SPP,DPP)*Y(K+2)/(AD*RAT)
      ABD(9,K+3) = T1 + T2 + T3 + T4 + T5 + T6
      ABD(10,K+3) = ZDS(S,D)/(EPS*RAT*AD)
      T1 = -ZSDUP(SP,DP)/DENK
      T2 = ZSSDUP(SP,DP)*Y(K)/DENK
      T3 = ZSDDUP(SP,DP)*Y(K+1)/DENK
      T4 = -ZSSDUP(SP,DP)*Y(K+3)/DENK
      T5 = -ZSDDUP(SP,DP)*Y(K+4)/DENK
      T6 = PPZSED(SPP,DPP)*Y(K+2)/(AD*RAT)
      ABD(7,K+4) = T1 + T2 + T3 + T4 + T5 + T6
      T1 = -ZDDUP(SP,DP)/DENK
      T2 = ZDSDUP(SP,DP)*Y(K)/DENK
      T3 = ZDDDUP(SP,DP)*Y(K+1)/DENK
      T4 = -ZDSDUP(SP,DP)*Y(K+3)/DENK
      T5 = -ZDDDUP(SP,DP)*Y(K+4)/DENK
      T6 = PPZDED(SPP,DPP)*Y(K+2)/(AD*RAT)
      ABD(8,K+4) = T1 + T2 + T3 + T4 + T5 + T6
      ABD(9,K+4) = ZDD(S,D)/(EPS*RAT*AD)
      ABD(6,K+5) = 0.0
      ABD(7,K+5) = 0.0
      ABD(8,K+5) = 0.0
  101 CONTINUE
C
C     ASSEMBLING THE MATRIX ELEMENTS ARISING FROM THE BOUNDARY
C     CONDITIONS AT X=A
C
      D2 = DEL(R-1)/2.0
      D22 = DEL(R-1)*DEL(R-1)/2.0
      S = Y(RR-2)
      SF = Y(RR-5)
      D = Y(RR-1)
      DM = Y(RR-4)
C
C     SETTING THE COEFFICIENT ARGUMENTS FOR THE FUNCTION ROUTINES.
C
      T1 = ZIJ(S,D)
      T2 = ZIJDN(SF,DM)
C
      ABD(14,RR-5) = -ZSS(S,D)/D22 - (0.5*ZSEPDN(SF,DM)/D2)*Y(RR)
      ABD(15,RR-5) = -ZDS(S,D)/D22 - (0.5*ZDEPDN(SF,DM)/D2)*Y(RR)
      ABD(16,RR-5) = 0.0
```

```
ABD(13,RR-4) = -ZSD(S,D)/D22 - (0.5*ZSEDDN(SF,DM)/D2)*Y(RR)
ABD(14,RR-4) = -ZDD(S,D)/D22 - (0.5*ZDEDDN(SF,DM)/D2)*Y(RR)
ABD(15,RR-4) = 0.0
ABD(12,RR-3) = 0.0
ABD(13,RR-3) = 0.0
ABD(14,RR-3) = 0.0
F1 = 1.0/DT
F2 = KSA/D2
F3 = ZSS(S,D)/D22
T1 = F1 + F2 + F3
T2 = -ZSSP(S,D)*Y(RR-5)/D22
T3 = -ZSDP(S,D)*Y(RR-4)/D22
T4 = ZSSP(S,D)*Y(RR-2)/D22
F1 = ZSDP(S,D)/D22
F2 = -ZSEP(S,D)/EPS
T5 = (F1 + F2)*Y(RR-1)
T6 = -ZSEP(S,D)*Y(RR)/(2.0*D2)
ABD(11,RR-2) = T1 + T2 + T3 + T4 + T5 + T6
F1 = KDA/D2
F2 = ZDS(S,D)/D22
T1 = F1 + F2
T2 = -ZDEP(S,D)*Y(RR)/(2.0*D2)
T3 = -ZDDP(S,D)*Y(RR-4)/D22
T4 = ZDSP(S,D)*Y(RR-2)/D22
F1 = ZDDP(S,D)/D22
F2 = -ZDEP(S,D)/EPS
T5 = (F1 + F2)*Y(RR-1)
T6 = -ZDSP(S,D)*Y(RR-5)/D22
ABD(12,RR-2) = T1 + T2 + T3 + T4 + T5 + T6
ABD(13,RR-2) = -KDA/EPS
T1 = KDA/D2
T2 = ZSD(S,D)/D22
T3 = -ZSE(S,D)/EPS
T4 = -ZSSD(S,D)*Y(RR-5)/D22
T5 = -ZSDD(S,D)*Y(RR-4)/D22
T6 = ZSSD(S,D)*Y(RR-2)/D22
T7 = ZSDD(S,D)*Y(RR-1)/D22
T8 = -ZSED(S,D)*Y(RR-1)/EPS
T9 = -ZSED(S,D)*Y(RR)/(2.0*D2)
ABD(10,RR-1) = T1+T2+T3+T4+T5+T6+T7+T8+T9
T1 = 1.0/DT
T2 = KSA/D2
T3 = ZDD(S,D)/D22
T4 = -ZDE(S,D)/EPS
T5 = -ZDSD(S,D)*Y(RR-5)/D22
T6 = -ZDDD(S,D)*Y(RR-4)/D22
T7 = ZDSD(S,D)*Y(RR-2)/D22
T8 = ZDDD(S,D)*Y(RR-1)/D22
T9 = -ZDED(S,D)*Y(RR-1)/EPS
T10 = -ZDED(S,D)*Y(RR)/(2.0*D2)
ABD(11,RR-1) = T1+T2+T3+T4+T5+T6+T7+T8+T9+T10
ABD(12,RR-1) = -KSA/EPS
ABD(9,RR) = -ZSE(S,D)/(2.0*D2) - ZSEDN(SF,DM)/(2.0*D2)
```

```
      ABD(10,RR) = -ZDE(S,D)/(2.0*D2) - ZDEDN(SF,DM)/(2.0*D2)
      ABD(11,RR) = 1.0/DT
      IF (M .NE. MMM) GO TO 103
      DO 102 IM = 1,16
      DO 102 JM = 1,RR
      WRITE (61,1) ABD(IM,JM)
 1    FORMAT (2X,E14.7)
 102  CONTINUE
 103  CONTINUE
      RETURN
      END



      SUBROUTINE RHSVN (R,DEL,DT,Y,B)
C
C     WHEN IFLAG=0 (THE FIRST TIME RHSV IS CALLED AT A GIVEN TIME ROW)
C     SUBROUTINE RHSV COMPUTES THE RHS VECTOR FOR THE MATRIX EQUATION AT
C     THE N+1 TH TIME ROW FROM THE SOLUTION TO THE MATRIX EQUATION AT
C     THE N TH TIME ROW.  WHEN IFLAG=1, RHSV COMPUTES THE CURRENT
C     VALUE OF THE AUXILLARY VECTOR.  IN THE MAIN PROGRAM THIS VECTOR
C     WILL BE ADDED TO THE RHS VECTOR TO FORM THE CURRENT RHS VECTOR
C     FOR A GIVEN ITERATION.  R IS THE NUMBER OF SPACE PTS.  RR IS THE
C     TOTAL NUMBER OF DEPENDENT VARIABLES.  DT IS THE TIME STEP SIZE.
C     DEL IS THE NON-UNIFORM GRID SPACING VECTOR.  Y(RR) IS THE SOLUTION
C     VECTOR FROM THE N TH TIME ROW IF IFLAG=0 AND THE SOLUTION TO THE
C     PREVIOUS ITERATION STEP IF IFLAG=1.  B(RR) IS THE RIGHT HAND SIDE
C     VECTOR IF IFLAG=0 AND THE AUXILLARY VECTOR IF IFLAG=1.
C     THE ONLY DIFFERENCES BETWEEN THE RHS VECTOR AND THE AUX VECTOR
C     ARE IN THE TERMS INVOLVING DT AND IN THE BOUNDARY TERMS.
C
      INTEGER R,RR,RSTOP
      REAL KDL,KSL,KDO,KSO,KDA,KSA,KDR,KSR
      DOUBLE DEL
      DIMENSION DEL(100),Y(300),B(300)
      COMMON/UNITS/SM,DF,GDE,EPM,A,ZP,ZM,CON,TM,DIM,CREF,ZREF
      COMMON /ELEC/ EPS,ZI
      COMMON/RATES/KSL,KDL,KSO,KDO,KSA,KDA,KSR,KDR
      RR = 3*R
      RSTOP = RR - 5
C
C     VECTOR ELEMENTS ARISING FROM THE BOUNDARY CONDITIONS AT X=0
C
      D2 = DEL(1)/2.0
      D22 = DEL(1)*DEL(1)/2.0
      S = Y(1)
      SP = Y(4)
      D = Y(2)
      DP = Y(5)
C
C     SETTING THE COEFFICIENT ARGUMENTS FOR THE FUNCTION ROUTINES.
```

```
C
      T1 = ZIJ(S,D)
      T2 = ZIJUP(SP,DP)
C
      F1 = -1.0/DT
      F2 = -ZSS(S,D)/D22
      F3 = -KSO/D2
      T1 = (F1 + F2 + F3)*Y(1)
      T2 = (-ZSD(S,D)/D22 + ZSE(S,D)/EPS - KDO/D2)*Y(2)
      T3 = -(ZSE(S,D)/(2.0*D2) + ZSEUP(SP,DP)/(2.0*D2))*Y(3)
      T4 = (ZSS(S,D)/D22)*Y(4)
      T5 = (ZSD(S,D)/D22)*Y(5)
      B(1) = T1 + T2 + T3 + T4 + T5
      T1 = (-KDO/D2 - ZDS(S,D)/D22)*Y(1)
      F1 = -1.0/DT
      F2 = -ZDD(S,D)/D22
      F3 = ZDE(S,D)/EPS
      F4 = -KSO/D2
      T2 = (F1 + F2 + F3 + F4)*Y(2)
      T3 = -(ZDE(S,D)/(2.0*D2) + ZDEUP(SP,DP)/(2.0*D2))*Y(3)
      T4 = (ZDS(S,D)/D22)*Y(4)
      T5 = (ZDD(S,D)/D22)*Y(5)
      B(2) = T1 + T2 + T3 + T4 + T5
      T1 = (-1.0/DT)*Y(3)
      T2 = -KSO*Y(2)/EPS
      T3 = -KDO*Y(1)/EPS
      B(3) = T1 + T2 + T3
C
C     VECTOR ELEMENTS FROM THE INTERIOR SPACE POINTS
C     THE DO-LOOP IS IN MULTIPLES OF 3 SINCE THERE
C     ARE 3 EQUATIONS AT EACH SPACE POINT
C
      DO 101 K=4,RSTOP,3
      KM = (K-1)/3
      KK = (K+2)/3
      SF = (Y(K-3) + Y(K))/2.0
      SMM = Y(K-3)
      SPP = Y(K+3)
      S = Y(K)
      SP = (Y(K+3) + Y(K))/2.0
      DM = (Y(K-2) + Y(K+1))/2.0
      DMM = Y(K-2)
      D = Y(K+1)
      DP. = (Y(K+4) + Y(K+1))/2.0
      DPP = Y(K+4)
      AD = DEL(KM) + DEL(KK)
      DENM = DEL(KM)*AD/2.0
      DENK = DEL(KK)*AD/2.0
      RAT = DEL(KK)/DEL(KM)
      AMUL = DEL(KK)*DEL(KM)
      SUB = DEL(KK) - DEL(KM)
C
C     SETTING THE COEFFICIENT ARGUMENTS FOR THE FUNCTION ROUTINES.
```

```
C
      T1 = ZIJ(S,D)
      T2 = ZIJUP(SP,DP)
      T3 = ZIJDN(SF,DM)
      T4 = PPZIJ(SPP,DPP)
      T5 = DDZIJ(SMM,DMM)
C
      T1 = ZSSDN(SF,DM)*Y(K-3)/DENM
      T2 = ZSDDN(SF,DM)*Y(K-2)/DENM
      F1 = -DDZSE(SMM,DMM)*RAT/AD
      F2 = PPZSE(SPP,DPP)/(RAT*AD)
      F3 = ZSE(S,D)*SUB/AMUL
      T3 = -(F1 + F2 + F3)*Y(K+2)
      F1 = -1.0/DT
      F2 = -ZSSUP(SP,DP)/DENK
      F3 = -ZSSDN(SF,DM)/DENM
      T4 = (F1 + F2 + F3)*Y(K)
      F1 = -ZSDUP(SP,DP)/DENK
      F2 = -ZSDDN(SF,DM)/DENM
      F3 = ZSE(S,D)/EPS
      T5 = (F1 + F2 + F3)*Y(K+1)
      T6 = ZSSUP(SP,DP)*Y(K+3)/DENK
      T7 = ZSDUP(SP,DP)*Y(K+4)/DENK
C
C     VECTOR ELEMENTS FROM S EQUATION
C
      B(K) = T1 + T2 + T3 + T4 + T5 + T6 + T7
      T1 = ZDSDN(SF,DM)*Y(K-3)/DENM
      T2 = -ZDSDN(SF,DM)*Y(K)/DENM
      T3 = ZDDDN(SF,DM)*Y(K-2)/DENM
      T4 = -ZDDDN(SF,DM)*Y(K+1)/DENM
      T5 = ZDDUP(SP,DP)*Y(K+4)/DENK
      T6 = -ZDDUP(SP,DP)*Y(K+1)/DENK
      F1 = -1.0/DT
      F2 = ZDE(S,D)/EPS
      T7 = (F1 + F2)*Y(K+1)
      T8 = ZDSUP(SP,DP)*Y(K+3)/DENK
      T9 = -ZDSUP(SP,DP)*Y(K)/DENK
      F1 = -DDZDE(SMM,DMM)*RAT/AD
      F2 = PPZDE(SPP,DPP)/(RAT*AD)
      F3 = ZDE(S,D)*SUB/AMUL
      T10 = -(F1 + F2 + F3)*Y(K+2)
C
C     VECTOR ELEMENTS FROM D EQUATION
C
      B(K+1) = T1 + T2 + T3 + T4 + T5 + T6 + T7 + T8 + T9 + T10
      T1 = ZDS(S,D)*Y(K-3)*RAT/(EPS*AD)
      T2 = ZDD(S,D)*Y(K-2)*RAT/(EPS*AD)
      T3 = -ZDS(S,D)*Y(K)*SUB/(EPS*AMUL)
      T4 = -ZDD(S,D)*Y(K+1)*SUB/(EPS*AMUL)
      T5 = (-1.0/DT + ZDE(S,D)/EPS)*Y(K+2)
      T6 = -ZDS(S,D)*Y(K+3)/(EPS*RAT*AD)
      T7 = -ZDD(S,D)*Y(K+4)/(EPS*RAT*AD)
```

```
C
C       VECTOR ELEMENTS FROM E EQUATION
C
        B(K+2) = T1 + T2 + T3 + T4 + T5 + T6 + T7
 101    CONTINUE
C
C       VECTOR ELEMENTS ARISING FROM THE BOUNDARY CONDITIONS AT X=A
C
        D2 = DEL(R-1)/2.0
        D22 = DEL(R-1)*DEL(R-1)/2.0
        S = Y(RR-2)
        SF = Y(RR-5)
        D = Y(RR-1)
        DM = Y(RR-4)
C
C       SETTING THE COEFFICIENT ARGUMENTS FOR THE FUNCTION ROUTINES.
C
        T1 = ZIJ(S,D)
        T2 = ZIJDN(SF,DM)
C
        T1 = ZSS(S,D)*Y(RR-5)/D22
        T2 = ZSD(S,D)*Y(RR-4)/D22
        F1 = -1.0/DT
        F2 = -KSA/D2
        F3 = -ZSS(S,D)/D22
        T3 = (F1 + F2 + F3)*Y(RR-2)
        F1 = -KDA/D2
        F2 = -ZSD(S,D)/D22
        F3 = ZSE(S,D)/EPS
        T4 = (F1 + F2 + F3)*Y(RR-1)
        T5 = (ZSE(S,D)/(2.0*D2) + ZSEDN(SF,DM)/(2.0*D2))*Y(RR)
        B(RR-2) = T1 + T2 + T3 + T4 + T5
        T1 = ZDS(S,D)*Y(RR-5)/D22
        T2 = ZDD(S,D)*Y(RR-4)/D22
        T3 = (-KDA/D2 -ZDS(S,D)/D22)*Y(RR-2)
        F1 = -1.0/DT
        F2 = -KSA/D2
        F3 = -ZDD(S,D)/D22
        F4 = ZDE(S,D)/EPS
        T4 = (F1 + F2 + F3 + F4)*Y(RR-1)
        T5 = (ZDE(S,D)/(2.0*D2) + ZDEDN(SF,DM)/(2.0*D2))*Y(RR)
        B(RR-1) = T1 + T2 + T3 + T4 + T5
        T1 = (-1.0/DT)*Y(RR)
        T2 = KSA*Y(RR-1)/EPS
        T3 = KDA*Y(RR-2)/EPS
        B(RR) = T1 + T2 + T3
        RETURN
        END
```

```
      SUBROUTINE RHSVO (R,DEL,DT,Y,B,M,MMM)
C
C     SUBROUTINE RHSVO GENERATES THE PORTION  OF THE B VECTOR THAT DOES
C     NOT CHANGE WITH EACH ITERATION.
C
      INTEGER R,RR,RSTOP
      REAL KDL,KSL,KDO,KSO,KDA,KSA,KDR,KSR
      REAL I1,I2
      DOUBLE DEL
      DIMENSION DEL(100),Y(300),B(300)
      COMMON /ELEC/ EPS,ZI
      COMMON/UNITS/SM,DF,GDE,EPM,A,ZP,ZM,CON,TM,DIM,CREF,ZREF
      COMMON/RATES/KSL,KDL,KSO,KDO,KSA,KDA,KSR,KDR
      COMMON/CURRENT/I1,I2
      COMMON/BNDRY/SL,SR,DL,DR
     . RR = 3*R
      RSTOP=RR-3
      ZJD = -DIM*(I1+I2)/(2.0*ZP*ZM*96485.0*SM)
      T1=Y(1)/DT
      T2 = 2.0*(KSL*(SL+1.0) + KDL*(DL+(DF/SM)))/DEL(1)
      T3 = -2.0*(KSO + KDO*(DF/SM))/DEL(1)
      B(1)=T1+T2+T3
      T1=Y(2)/DT
      T2 = 2.0*(KSL*(DL+(DF/SM)) + KDL*(SL+1.0))/DEL(1)
      T3 = -2.0*(KSO*(DF/SM) + KDO)/DEL(1)
      B(2)=T1+T2+T3
      T1=Y(3)/DT + ZI/EPS
      T2 = ZJD/EPS
      T3 = (KSL*(DL+(DF/SM)) + KDL*(SL+1.0))/EPS
      T4 = -(KSO*(DF/SM))/EPS - (KDO/EPS)
      B(3)=T1+T2+T3+T4
      DO 100 I=4,RSTOP
      B(I) = Y(I)/DT
      L=MOD(I,3)
      IF (L .EQ. 0) B(I)=B(I)+ZI/EPS + ZJD/EPS
  100 CONTINUE
      T1=Y(RR-2)/DT
      T2 = 2.0*(KSR*(SR+1.0) + KDR*(DR+(DF/SM)))/DEL(R-1)
      T3 = -2.0*(KSA + KDA*(DF/SM))/DEL(R-1)
      B(RR-2)=T1+T2+T3
      T1=Y(RR-1)/DT
      T2 = 2.0*(KSR*(DR+(DF/SM)) + KDR*(SR+1.0))/DEL(R-1)
      T3 = -2.0*(KSA*(DF/SM) + KDA)/DEL(R-1)
      B(RR-1)=T1+T2+T3
      T1=Y(RR)/DT + ZI/EPS
      T2 = ZJD/EPS
      T3 = -(KSR*(DR+(DF/SM)) + KDR*(SR+1.0))/EPS
      T4 = (KSA*(DF/SM) + KDA)/EPS
      B(RR)=T1+T2+T3+T4
      IF (M .NE. MMM)GO TO 110
      DO 109 I=1,RR
      WRITE (61,1) B(I),I
  109  CONTINUE
```

```
 110   CONTINUE
 1     FORMAT (2X,E14.6,I5)
       RETURN
       END




       SUBROUTINE CMPR (Y,YY,TOL,R,KFLAG)
C
C      SUBROUTINE CMPR COMPARES THE CURRENT ITERATION VECTOR, Y, TO THE
C      CURRENT SOLUTION VECTOR, YY+Y. (YY+Y IS RENAMED YY DESTROYING THE
C      OLD SOLUTION VECTOR)  THE CURRENT ITERATION VECTOR IS TESTED TO
C      DETERMINE IF IT IS SMALL ENOUGH FOR THE PROGRAM TO PROCEED TO THE
C      NEXT TIME STEP.  SINCE SOME OF THE SOLUTION VECTOR COMPONENTS ARE
C      MUCH SMALLER AND HENCE LESS ACCURATE THEN OTHERS, THEY ARE NOT
C      INCLUDED IN THE TESTING.  EACH OF THE 3 COMPONENTS MAKING UP THE
C      SOLUTION VECTOR, S,D, AND E ARE CHECKED SEPARATELY.  KFLAG=0 MEANS
C      THE PRESENT ITERATION VECTOR IS SMALL ENOUGH FOR THE PROGRAM TO
C      PROCEED TO THE NEXT TIME STEP.  KFLAG=1 MEANS THE PROGRAM WILL
C      ITERATE AGAIN WITH THE DERIVATIVES EVALUATED AT YY+Y.  TOL IS THE
C      RELATIVE CHANGE TOLERANCE ALLOWED.
C
       DIMENSION Y(300),YY(300)
       INTEGER R,RR
       KFLAG=0
       RR=3*R
C
C      FORMING THE NEW SOLUTION VECTOR
C
       DO 100 I=1,RR
       YY(I)=YY(I)+Y(I)
 100   CONTINUE
C
C      M=1 STRIPS OUT THE S COMPONENTS, M=2 THE D COMPONENTS, M=3 THE E
C      COMPONENTS.
       DO 103 M=1,3
C
       YMAX=ABS(YY(M))
C
C      FINDING THE MAXIMUM VALUE OF S (IF M=1),D (IF M=2), OR E (IF M=3)
C
       DO 101 I=M,RR,3
       YMAX=AMAX1(ABS(YY(I)),YMAX)
 101   CONTINUE
C
C      FINDING THE MINIMUM VALUE THAT WILL BE CHECKED
C
       YMIN = YMAX/1.0E+09
       DO 102 J=M,RR,3
C
C      TESTING TO DETERMINE IF A VALUE SHOULD BE CHECKED
```

```
C
      IF (ABS(YY(J)) .LT. YMIN) GO TO 102
C
C     CHECKING TO DETERMINE IF THE CHANGE IN THE SOLUTION VECTOR IS
C     SMALL ENOUGH AT A GIVEN J
C
C     THE FOLLOWING 2 STATEMENTS PREVENT DIVISION BY ZERO
      AY=ABS(YY(J))
      IF (AY .LT. 1.0E-99) GO TO 102
      RATIO=Y(J)/YY(J) .
      TEST=ABS(RATIO)
      IF (TEST .GT. TOL) GO TO 104
  102 CONTINUE
  103 CONTINUE
      RETURN
  104 KFLAG=1
      RETURN
      END
```

```
      FUNCTION AVINT (X,Y,N,XLO,XUP,IND)
C
C     AVINT IS USED TO INTEGRATE THE NONUNIFORM SPACE MESH
C     FOR COMPUTATION OF THE POTENTIAL DIFFERENCE, TOTAL CHARGE
C     IN THE SYSTEM, AND TOTAL MOLES IN THE SYSTEM
C     IF IND IS RETURNED AS -1 XUP IS LESS THAT XLO
C     AND THE COMPUTATION WILL NOT PROCEED
C
      DIMENSION X(N),Y(N)
      DOUBLE X,XLO,XUP,SYL,A,B,C,CA,CB,CC,TERM1,TERM2,TERM3
      DOUBLE X1,X2,X3,SUM,DIFF
      IND=0
      IF (N .LT. 3) RETURN
      DO 10 I=2,N
      IF (X(I) .LE. X(I-1)) RETURN
  10  CONTINUE
      SUM=0.0
      IF (XLO .LE. XUP) GO TO 5
      SYL=XUP
      XUP=XLO
      XLO=SYL
      IND=-1
      GO TO 6
  5   IND=1
      SYL=XLO
  6   IB=1
      J=N
      DO 1 I=1,N
      IF (X(I) .GE. XLO) GO TO 7
  1   IB=IB+1
```

```
7     IB=MAXO(2,IB)
      IB=MINO(IB,N-1)
      DO 2 I=1,N
      IF (XUP .GE. X(J)) GO TO 8
2     J=J-1
8     J=MINO(J,N-1)
      J=MAXO(IB,J-1)
      DO 3 JM=IB,J
      X1=X(JM-1)
      X2=X(JM)
      X3 = X(JM+1)
      TERM1=Y(JM-1)/((X1-X2)*(X1-X3))
      TERM2=Y(JM)/((X2-X1)*(X2-X3))
      TERM3=Y(JM+1)/((X3-X1)*(X3-X2))
      A=TERM1+TERM2+TERM3
      B=-(X2+X3)*TERM1-(X1+X3)*TERM2-(X1+X2)*TERM3
      C=X2*X3*TERM1+X1*X3*TERM2+X1*X2*TERM3
      IF (JM .GT. IB)GO TO 14
      CA=A
      CB=B
      CC=C
      GO TO 15
14    CA=0.5*(A+CA)
      CB=0.5*(B+CB)
      CC=0.5*(C+CC)
15     DIFF = X2-SYL
      SUM = SUM + CA*((SYL**2.0)*DIFF + SYL*(DIFF**2.0)
     + + (DIFF**3.0)/3.0)
     + + CB*(SYL*DIFF + (DIFF**2.0)/2.0) + CC*DIFF
      CA=A
      CB=B
      CC=C
3     SYL=X2
      DIFF = XUP-SYL
      AVINT = SUM + CA*((SYL**2.0)*DIFF + SYL*(DIFF**2.0)
     + + (DIFF**3.0)/3.0)
     + + CB*(SYL*DIFF + (DIFF**2.0)/2.0) + CC*DIFF
      AVINT=AVINT
      IF (IND .EQ. 1) RETURN
      IND=1
      SYL=XUP
      XUP=XLO
      XLO=SYL
      AVINT=-AVINT
      RETURN
      END




      SUBROUTINE IC (KEY,Y,R)
C
```

```
      DIMENSION Y(300)
      INTEGER R,RR,RRR,RSTOP,RSTART
      COMMON/ICOND/SO,DO,EO
      L = MOD(R,2)
      RR=3*R
      RSTOP = (RR/2)-2
      RSTART = RSTOP + 3
      IF (L .NE. 0)RSTART = RSTOP + 2
      RRR=RR-2
      DO 160 I=1,RSTOP,3
      Y(I)=SO
      Y(I+1)=DO
      Y(I+2)=EO
160    CONTINUE
      DO 170 I=RSTART,RRR,3
      Y(I)=-SO
      Y(I+1)=DO
      Y(I+2)=EO
170    CONTINUE
      IF (L .EQ. 0)RETURN
      M = (RR+1)/2
      Y(M-1) = 0.0
      Y(M) = 0.0
      Y(M+1) = 0.0
      RETURN
      END




      FUNCTION ZIJ(S,D)
      COMMON/UNITS/SM,DF,GDE,EPM,A,ZP,ZM,CON,TM,DIM,CREF,ZREF
      COMMON/GREEK/C(24)
      REAL IC,M,ICP,MP,ICD,MD
      IC=(ZP*ZM/2.0)*(((ZP+ZM)*(D+(DF/SM))) + (ZM-ZP)*(S+1.0)
     + + ((ZREF*ZREF*CREF)/(ZP*ZM*SM)))
      IF (IC.LE.0.0) IC=1.0E-10
      Y=D+(DF/SM)-S-1.0
      Z= D + S + 1.0 + (DF/SM)
      IF (Y.GE.0.0) Y=-1.0E-10
      IF (Z.LE.0.0) Z=1.0E-10
      SUM=((ZM*ZM)*Y - (ZP*ZP)*Z)/(ZM-ZP)
      ZPP=C(1)*(ZM*(Y)) + C(2)*(ZM*(Y))**1.5
      ZMM=C(3)*(ZP*(Z)) + C(4)*(ZP*(Z))**1.5
      ZPM=C(5)*(SUM**1.5) + C(6)*(SUM**2.0)
      M=C(7) - C(8)/((IC)**0.5)
      B=C(9) + C(10)*IC
      CA=((ZP*ZPP) - (ZM*ZPM))/(Y)
      CB=((ZP*ZPM) - (ZM*ZMM))/(Z)
      CE=1.0 - ((0.25)*(ZP/ZM)*((ZP-ZM)**2.0)*ZM*(Y)*(M+B))
      CG=1.0 - ((0.25)*(ZM/ZP)*((ZP-ZM)**2.0)*ZP*(Z)*(M-B))
      CF=1.0 - ((0.25)*(ZP/ZM)*((ZP*ZP)-(ZM*ZM))*ZM*(Y)*(M+B))
```

```
      CH=1.0 + ((0.25)*(ZM/ZP)*((ZP*ZP)-(ZM*ZM))*ZP*(Z)*(M-B))
      CC=((ZP*ZPP) + (ZM*ZPM))/(Y)
      CD=((ZP*ZPM) + (ZM*ZMM))/(Z)
      SUMP=(ZP-ZM)/2.0
      ICP=ZP*ZM*(ZM-ZP)/2.0
      ZPPP=-(C(1)*ZM) - (1.5*ZM*C(2)*(ZM*(Y))**0.5)
      ZMMP=+(C(3)*ZP) + (1.5*ZP*C(4)*(ZP*(Z))**0.5)
      ZPMP=1.5*C(5)*(SUM**0.5)*SUMP + 2.0*C(6)*(SUM)*SUMP
      MP=(C(8)/(IC**1.5))*ICP
      BP=C(10)*ICP
      CCP=((ZP*ZPPP) + (ZM*ZPMP))/(Y)
     + +((ZP*ZPP) + (ZM*ZPM))/((Y)**2.0)
      CDP=((ZP*ZPMP) + (ZM*ZMMP))/(Z)
     + -((ZP*ZPM) + (ZM*ZMM))/((Z)**2.0)
      CFP=-((0.25)*(ZP/ZM)*((ZP*ZP)-(ZM*ZM))*ZM*(Y)*(MP+BP))
     + +((0.25)*(ZP/ZM)*((ZP*ZP)-(ZM*ZM))*ZM*(M+B))
      CHP=+((0.25)*(ZM/ZP)*((ZP*ZP)-(ZM*ZM))*ZP*(Z)*(MP-BP))
     + +((0.25)*(ZM/ZP)*((ZP*ZP)-(ZM*ZM))*ZP*(M-B))
      CAP=((ZP*ZPPP) - (ZM*ZPMP))/(Y)
     + +((ZP*ZPP) - (ZM*ZPM))/((Y)**2.0)
      CBP=((ZP*ZPMP) - (ZM*ZMMP))/(Z)
     + -((ZP*ZPM) - (ZM*ZMM))/((Z)**2.0)
      CEP=-((0.25)*(ZP/ZM)*((ZP-ZM)**2.0)*ZM*(Y)*(MP+BP))
     + +((0.25)*(ZP/ZM)*((ZP-ZM)**2.0)*ZM*(M+B))
      CGP=-((0.25)*(ZM/ZP)*((ZP-ZM)**2.0)*ZP*(Z)*(MP-BP))
     + -((0.25)*(ZM/ZP)*((ZP-ZM)**2.0)*ZP*(M-B))
      DCL=((ZP*ZP*ZPP) + (2.0*ZM*ZP*ZPM) + (ZM*ZM*ZMM))
      SCL=((ZP*ZP*ZPP) - (ZM*ZM*ZMM))
      SCLP=(ZP*ZP*ZPPP) - (ZM*ZM*ZMMP)
      DCLP=((ZP*ZP*ZPPP) + (2.0*ZP*ZM*ZPMP) + (ZM*ZM*ZMMP))
      SUMD=-(ZP+ZM)*0.5
      ICD=ZP*ZM*(ZP+ZM)/2.0
      ZPPD=(C(1)*ZM) + (1.5*ZM*C(2)*(ZM*(Y))**0.5)
      ZMMD=(C(3)*ZP) + (1.5*ZP*C(4)*(ZP*(Z))**0.5)
      ZPMD=1.5*C(5)*(SUM**0.5)*SUMD + 2.0*C(6)*(SUM)*SUMD
      MD=(0.5*C(8)/(IC**1.5))*ICD
      BD=C(10)*ICD
      CAD=((ZP*ZPPD)/(Y)) - ((ZM*ZPMD)/(Y))
     + -(((ZP*ZPP) - (ZM*ZPM))/((Y)**2.0))
      CBD=((ZP*ZPMD)/(Z)) - ((ZM*ZMMD)/(Z))
     + -(((ZP*ZPM) - (ZM*ZMM))/((Z)**2.0))
      CED=-(0.25)*(ZP/ZM)*((ZP-ZM)**2.0)*ZM*(M+B)
     + - ((0.25)*(ZP/ZM)*((ZP-ZM)**2.0)*ZM*(Y)*(MD+BD))
      CGD=-(0.25)*(ZM/ZP)*((ZP-ZM)**2.0)*ZP*(M-B)
     + - ((0.25)*(ZM/ZP)*((ZP-ZM)**2.0)*ZP*(Z)*(MD-BD))
      CCD=((ZP*ZPPD)/(Y)) + ((ZM*ZPMD)/(Y))
     + -(((ZP*ZPP) + (ZM*ZPM))/((Y)**2.0))
      CDD=((ZP*ZPMD)/(Z)) + ((ZM*ZMMD)/(Z))
     + -(((ZP*ZPM) + (ZM*ZMM))/((Z)**2.0))
      CFD=-(0.25)*(ZP/ZM)*((ZP*ZP)-(ZM*ZM))*ZM*(M+B)
     + - ((0.25)*(ZP/ZM)*((ZP*ZP)-(ZM*ZM))*ZM*(Y)*(MD+BD))
      CHD=-(0.25)*(ZM/ZP)*((ZP*ZP)-(ZM*ZM))*ZP*(M-B)
     + + ((0.25)*(ZM/ZP)*((ZP*ZP)-(ZM*ZM))*ZP*(Z)*(MD-BD))
```

```
      SCLD=(ZP*ZP*ZPPD) - (ZM*ZM*ZMMD)
      DCLD=((ZP*ZP*ZPPD) + (2.0*ZP*ZM*ZPMD) + (ZM*ZM*ZMMD))
      DO 222 I=4,10
      TEST = 0.0
      IF (C(I) .NE. 0.0)TEST = 1.0
222    CONTINUE
      ZIJ=((CA*CE) - (CB*CG))/(ZP*ZM)
      RETURN
      ENTRY ZSS
      ZIJ=((CA*CE) - (CB*CG))/(ZP*ZM)
      RETURN
      ENTRY ZDD
      ZIJ=((CF*CC) + (CD*CH))/(ZP*ZM)
      RETURN
      ENTRY ZSD
      ZIJ=((-CA*CF) - (CB*CH))/(ZM*ZP)
      RETURN
      ENTRY ZDS
      ZIJ=((-CC*CE) + (CD*CG))/(ZM*ZP)
      RETURN
      ENTRY ZDE
      ZIJ=-(96485.0*SM*A*A*DCL)/(ZP*ZM*CON*(8.314E7)*TM)
      RETURN
      ENTRY ZSE
      ZIJ=(96485.0*SM*A*A*SCL)/(CON*(8.314E7)*TM*ZP*ZM)
      RETURN
      ENTRY ZSSP
      ZIJ=((CAP*CE) + (CEP*CA))/(ZP*ZM)
     + -((CB*CGP) + (CG*CBP))/(ZP*ZM)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJ = 0.0
      RETURN
      ENTRY ZDDP
      ZIJ=((CF*CCP) + (CC*CFP))/(ZP*ZM)
     + + ((CD*CHP) + (CH*CDP))/(ZP*ZM)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJ = 0.0
      RETURN
      ENTRY ZSDP
      ZIJ=-((CA*CFP) + (CF*CAP))/(ZP*ZM)
     + - ((CB*CHP) + (CBP*CH))/(ZP*ZM)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJ = 0.0
      RETURN
      ENTRY ZDSP
      ZIJ=((CD*CGP) + (CG*CDP))/(ZP*ZM)
     + -((CE*CCP) + (CEP*CC))/(ZP*ZM)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJ = 0.0
      RETURN
      ENTRY ZSEP
      ZIJ=(96485.0*SM*A*A*SCLP)/(CON*(8.314E7)*TM*ZP*ZM)
      RETURN
      ENTRY ZDEP
      ZIJ=-(96485.0*SM*A*A*DCLP)/(CON*(8.314E7)*TM*ZP*ZM)
      RETURN
      ENTRY ZSSD
```

```
      ZIJ=((CA*CED) + (CE*CAD))/(ZM*ZP)
     + -((CB*CGD) + (CG*CBD))/(ZM*ZP)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJ = 0.0
      RETURN
      ENTRY ZDDD
      ZIJ=((CF*CCD) + (CC*CFD))/(ZM*ZP)
     + + ((CD*CHD) + (CH*CDD))/(ZM*ZP)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJ = 0.0
      RETURN
      ENTRY ZSDD
      ZIJ=-((CA*CFD) + (CF*CAD))/(ZM*ZP)
     + -((CB*CHD) + (CBD*CH))/(ZM*ZP)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJ = 0.0
      RETURN
      ENTRY ZDSD
      ZIJ=((CD*CGD) + (CDD*CG))/(ZM*ZP)
     + -((CC*CED) + (CE*CCD))/(ZM*ZP)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJ = 0.0
      RETURN
      ENTRY ZSED
      ZIJ=(96485.0*SM*A*A*SCLD)/(CON*(8.314E7)*TM*ZP*ZM)
      RETURN
      ENTRY ZDED
      ZIJ=-(96485.0*SM*A*A*DCLD)/(CON*(8.314E7)*TM*ZP*ZM)
      RETURN
      END




      FUNCTION ZIJDN(S,D)
      COMMON/UNITS/SM,DF,GDE,EPM,A,ZP,ZM,CON,TM,DIM,CREF,ZREF
      COMMON/GREEK/C(24)
      REAL IC,M,ICP,MP,ICD,MD
      IC=(ZP*ZM/2.0)*(((ZP+ZM)*(D+(DF/SM))) + (ZM-ZP)*(S+1.0)
     + + ((ZREF*ZREF*CREF)/(ZP*ZM*SM)))
      IF (IC.LE.0.0) IC=1.0E-10
      Y=D+(DF/SM)-S-1.0
      Z= D + S + 1.0 + (DF/SM)
      IF (Y.GE.0.0) Y=-1.0E-10
      IF (Z.LE.0.0) Z=1.0E-10
      SUM=((ZM*ZM)*Y - (ZP*ZP)*Z)/(ZM-ZP)
      ZPP=C(1)*(ZM*(Y)) + C(2)*(ZM*(Y))**1.5
      ZMM=C(3)*(ZP*(Z)) + C(4)*(ZP*(Z))**1.5
      ZPM=C(5)*(SUM**1.5) + C(6)*(SUM**2.0)
      M=C(7) - C(8)/((IC)**0.5)
      B=C(9) + C(10)*IC
      CA=((ZP*ZPP) - (ZM*ZPM))/(Y)
      CB=((ZP*ZPM) - (ZM*ZMM))/(Z)
      CE=1.0 - ((0.25)*(ZP/ZM)*((ZP-ZM)**2.0)*ZM*(Y)*(M+B))
      CG=1.0 - ((0.25)*(ZM/ZP)*((ZP-ZM)**2.0)*ZP*(Z)*(M-B))
      CF=1.0 - ((0.25)*(ZP/ZM)*((ZP*ZP)-(ZM*ZM))*ZM*(Y)*(M+B))
```

```
      CH=1.0 + ((0.25)*(ZM/ZP)*((ZP*ZP)-(ZM*ZM))*ZP*(Z)*(M-B))
      CC=((ZP*ZPP) + (ZM*ZPM))/(Y)
      CD=((ZP*ZPM) + (ZM*ZMM))/(Z)
      SUMP=(ZP-ZM)/2.0
      ICP=ZP*ZM*(ZM-ZP)/2.0
      ZPPP=-(C(1)*ZM) - (1.5*ZM*C(2)*(ZM*(Y))**0.5)
      ZMMP=+(C(3)*ZP) + (1.5*ZP*C(4)*(ZP*(Z))**0.5)
      ZPMP=1.5*C(5)*(SUM**0.5)*SUMP + 2.0*C(6)*(SUM)*SUMP
      MP=(C(8)/(ICP**1.5))*ICP
      BP=C(10)*ICP
      CCP=((ZP*ZPPP) + (ZM*ZPMP))/(Y)
     + +((ZP*ZPP) + (ZM*ZPM))/((Y)**2.0)
      CDP=((ZP*ZPMP) + (ZM*ZMMP))/(Z)
     + -((ZP*ZPM) + (ZM*ZMM))/((Z)**2.0)
      CFP=-((0.25)*(ZP/ZM)*((ZP*ZP)-(ZM*ZM))*ZM*(Y)*(MP+BP))
     + +((0.25)*(ZP/ZM)*((ZP*ZP)-(ZM*ZM))*ZM*(M+B))
      CHP=+((0.25)*(ZM/ZP)*((ZP*ZP)-(ZM*ZM))*ZP*(Z)*(MP-BP))
     + +((0.25)*(ZM/ZP)*((ZP*ZP)-(ZM*ZM))*ZP*(M-B))
      CAP=((ZP*ZPPP) - (ZM*ZPMP))/(Y)
     + +((ZP*ZPP) - (ZM*ZPM))/((Y)**2.0)
      CBP=((ZP*ZPMP) - (ZM*ZMMP))/(Z)
     + -((ZP*ZPM) - (ZM*ZMM))/((Z)**2.0)
      CEP=-((0.25)*(ZP/ZM)*((ZP-ZM)**2.0)*ZM*(Y)*(MP+BP))
     + +((0.25)*(ZP/ZM)*((ZP-ZM)**2.0)*ZM*(M+B))
      CGP=-((0.25)*(ZM/ZP)*((ZP-ZM)**2.0)*ZP*(Z)*(MP-BP))
     + -((0.25)*(ZM/ZP)*((ZP-ZM)**2.0)*ZP*(M-B))
      DCL=((ZP*ZP*ZPP) + (2.0*ZM*ZP*ZPM) + (ZM*ZM*ZMM))
      SCL=((ZP*ZP*ZPP) - (ZM*ZM*ZMM))
      SCLP=(ZP*ZP*ZPPP) - (ZM*ZM*ZMMP)
      DCLP=((ZP*ZP*ZPPP) + (2.0*ZP*ZM*ZPMP) + (ZM*ZM*ZMMP))
      SUMD=-(ZP+ZM)*0.5
      ICD=ZP*ZM*(ZP+ZM)/2.0
      ZPPD=(C(1)*ZM) + (1.5*ZM*C(2)*(ZM*(Y))**0.5)
      ZMMD=(C(3)*ZP) + (1.5*ZP*C(4)*(ZP*(Z))**0.5)
      ZPMD=1.5*C(5)*(SUM**0.5)*SUMD + 2.0*C(6)*(SUM)*SUMD
      MD=(0.5*C(8)/(ICP**1.5))*ICD
      BD=C(10)*ICD
      CAD=((ZP*ZPPD)/(Y)) - ((ZM*ZPMD)/(Y))
     + -(((ZP*ZPP) - (ZM*ZPM))/((Y)**2.0))
      CBD=((ZP*ZPMD)/(Z)) - ((ZM*ZMMD)/(Z))
     + -(((ZP*ZPM) - (ZM*ZMM))/((Z)**2.0))
      CED=-(0.25)*(ZP/ZM)*((ZP-ZM)**2.0)*ZM*(M+B)
     + -((0.25)*(ZP/ZM)*((ZP-ZM)**2.0)*ZM*(Y)*(MD+BD))
      CGD=-(0.25)*(ZM/ZP)*((ZP-ZM)**2.0)*ZP*(M-B)
     + -((0.25)*(ZM/ZP)*((ZP-ZM)**2.0)*ZP*(Z)*(MD-BD))
      CCD=((ZP*ZPPD)/(Y)) + ((ZM*ZPMD)/(Y))
     + -(((ZP*ZPP) + (ZM*ZPM))/((Y)**2.0))
      CDD=((ZP*ZPMD)/(Z)) + ((ZM*ZMMD)/(Z))
     + -(((ZP*ZPM) + (ZM*ZMM))/((Z)**2.0))
      CFD=-(0.25)*(ZP/ZM)*((ZP*ZP)-(ZM*ZM))*ZM*(M+B)
     + -((0.25)*(ZP/ZM)*((ZP*ZP)-(ZM*ZM))*ZM*(Y)*(MD+BD))
      CHD=-(0.25)*(ZM/ZP)*((ZP*ZP)-(ZM*ZM))*ZP*(M-B)
     + +((0.25)*(ZM/ZP)*((ZP*ZP)-(ZM*ZM))*ZP*(Z)*(MD-BD))
```

```
      SCLD=(ZP*ZP*ZPPD) - (ZM*ZM*ZMMD)
      DCLD=((ZP*ZP*ZPPD) + (2.0*ZP*ZM*ZPMD) + (ZM*ZM*ZMMD))
      DO 222 I=4,10
      TEST = 0.0
      IF (C(I) .NE. 0.0)TEST = 1.0
  222  CONTINUE
      ZIJDN=((CA*CE) - (CB*CG))/(ZP*ZM)
      RETURN
      ENTRY ZSSDN
      ZIJDN=((CA*CE) - (CB*CG))/(ZP*ZM)
      RETURN
      ENTRY ZDDDN
      ZIJDN=((CF*CC) + (CD*CH))/(ZP*ZM)
      RETURN
      ENTRY ZSDDN
      ZIJDN=((-CA*CF) - (CB*CH))/(ZM*ZP)
      RETURN
      ENTRY ZDSDN
      ZIJDN=((-CC*CE) + (CD*CG))/(ZM*ZP)
      RETURN
      ENTRY ZDEDN
      ZIJDN=-(96485.0*SM*A*A*DCL)/(ZP*ZM*CON*(8.314E7)*TM)
      RETURN
      ENTRY ZSEDN
      ZIJDN=(96485.0*SM*A*A*SCL)/(CON*(8.314E7)*TM*ZP*ZM)
      RETURN
      ENTRY ZSSPDN
      ZIJDN=((CAP*CE) + (CEP*CA))/(ZP*ZM)
     + -((CB*CGP) + (CG*CBP))/(ZP*ZM)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJDN = 0.0
      RETURN
      ENTRY ZDDPDN
      ZIJDN=((CF*CCP) + (CC*CFP))/(ZP*ZM)
     + + ((CD*CHP) + (CH*CDP))/(ZP*ZM)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJDN = 0.0
      RETURN
      ENTRY ZSDPDN
      ZIJDN=-((CA*CFP) + (CF*CAP))/(ZP*ZM)
     + - ((CB*CHP) + (CBP*CH))/(ZP*ZM)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJDN = 0.0
      RETURN
      ENTRY ZDSPDN
      ZIJDN=((CD*CGP) + (CG*CDP))/(ZP*ZM)
     + -((CE*CCP) + (CEP*CC))/(ZP*ZM)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJDN = 0.0
      RETURN
      ENTRY ZSEPDN
      ZIJDN=(96485.0*SM*A*A*SCLP)/(CON*(8.314E7)*TM*ZP*ZM)
      RETURN
      ENTRY ZDEPDN
      ZIJDN=-(96485.0*SM*A*A*DCLP)/(CON*(8.314E7)*TM*ZP*ZM)
      RETURN
      ENTRY ZSSDDN
```

```
      ZIJDN=((CA*CED) + (CE*CAD))/(ZM*ZP)
     + -((CB*CGD) + (CG*CBD))/(ZM*ZP)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJDN = 0.0
      RETURN
      ENTRY ZDDDDN
      ZIJDN=((CF*CCD) + (CC*CFD))/(ZM*ZP)
     + + ((CD*CHD) + (CH*CDD))/(ZM*ZP)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJDN = 0.0
      RETURN
      ENTRY ZSDDDN
      ZIJDN=-((CA*CFD) + (CF*CAD))/(ZM*ZP)
     + -((CB*CHD) + (CBD*CH))/(ZM*ZP)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJDN = 0.0
      RETURN
      ENTRY ZDSDDN
      ZIJDN=((CD*CGD) + (CDD*CG))/(ZM*ZP)
     + -((CC*CED) + (CE*CCD))/(ZM*ZP)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJDN = 0.0
      RETURN
      ENTRY ZSEDDN
      ZIJDN=(96485.0*SM*A*A*SCLD)/(CON*(8.314E7)*TM*ZP*ZM)
      RETURN
      ENTRY ZDEDDN
      ZIJDN=-(96485.0*SM*A*A*DCLD)/(CON*(8.314E7)*TM*ZP*ZM)
      RETURN
      END



      FUNCTION ZIJUP(S,D)
      COMMON/UNITS/SM,DF,GDE,EPM,A,ZP,ZM,CON,TM,DIM,CREF,ZREF
      COMMON/GREEK/C(24)
      REAL IC,M,ICP,MP,ICD,MD
      IC=(ZP*ZM/2.0)*(((ZP+ZM)*(D+(DF/SM))) + (ZM-ZP)*(S+1.0)
     + + ((ZREF*ZREF*CREF)/(ZP*ZM*SM)))
      IF (IC.LE.0.0) IC=1.0E-10
      Y=D+(DF/SM)-S-1.0
      Z= D + S + 1.0 + (DF/SM)
      IF (Y.GE.0.0) Y=-1.0E-10
      IF (Z.LE.0.0) Z=1.0E-10
      SUM=((ZM*ZM)*Y - (ZP*ZP)*Z)/(ZM-ZP)
      ZPP=C(1)*(ZM*(Y)) + C(2)*(ZM*(Y))**1.5
      ZMM=C(3)*(ZP*(Z)) + C(4)*(ZP*(Z))**1.5
      ZPM=C(5)*(SUM**1.5) + C(6)*(SUM**2.0)
      M=C(7) - C(8)/((IC)**0.5)
      B=C(9) + C(10)*IC
      CA=((ZP*ZPP) - (ZM*ZPM))/(Y)
      CB=((ZP*ZPM) - (ZM*ZMM))/(Z)
      CE=1.0 - ((0.25)*(ZP/ZM)*((ZP-ZM)**2.0)*ZM*(Y)*(M+B))
      CG=1.0 - ((0.25)*(ZM/ZP)*((ZP-ZM)**2.0)*ZP*(Z)*(M-B))
      CF=1.0 - ((0.25)*(ZP/ZM)*((ZP*ZP)-(ZM*ZM))*ZM*(Y)*(M+B))
```

```
      CH=1.0 + ((0.25)*(ZM/ZP)*((ZP*ZP)-(ZM*ZM))*ZP*(Z)*(M-B))
      CC=((ZP*ZPP) + (ZM*ZPM))/(Y)
      CD=((ZP*ZPM) + (ZM*ZMM))/(Z)
      SUMP=(ZP-ZM)/2.0
      ICP=ZP*ZM*(ZM-ZP)/2.0
      ZPPP=-(C(1)*ZM) - (1.5*ZM*C(2)*(ZM*(Y))**0.5)
      ZMMP=+(C(3)*ZP) + (1.5*ZP*C(4)*(ZP*(Z))**0.5)
      ZPMP=1.5*C(5)*(SUM**0.5)*SUMP + 2.0*C(6)*(SUM)*SUMP
      MP=(C(8)/(IC**1.5))*ICP
      BP=C(10)*ICP
      CCP=((ZP*ZPPP) + (ZM*ZPMP))/(Y)
     + +((ZP*ZPP) + (ZM*ZPM))/((Y)**2.0)
      CDP=((ZP*ZPMP) + (ZM*ZMMP))/(Z)
     + -((ZP*ZPM) + (ZM*ZMM))/((Z)**2.0)
      CFP=-((0.25)*(ZP/ZM)*((ZP*ZP)-(ZM*ZM))*ZM*(Y)*(MP+BP))
     + +((0.25)*(ZP/ZM)*((ZP*ZP)-(ZM*ZM))*ZM*(M+B))
      CHP=+((0.25)*(ZM/ZP)*((ZP*ZP)-(ZM*ZM))*ZP*(Z)*(MP-BP))
     + +((0.25)*(ZM/ZP)*((ZP*ZP)-(ZM*ZM))*ZP*(M-B))
      CAP=((ZP*ZPPP) - (ZM*ZPMP))/(Y)
     + +((ZP*ZPP) - (ZM*ZPM))/((Y)**2.0)
      CBP=((ZP*ZPMP) - (ZM*ZMMP))/(Z)
     + -((ZP*ZPM) - (ZM*ZMM))/((Z)**2.0)
      CEP=-((0.25)*(ZP/ZM)*((ZP-ZM)**2.0)*ZM*(Y)*(MP+BP))
     + +((0.25)*(ZP/ZM)*((ZP-ZM)**2.0)*ZM*(M+B))
      CGP=-((0.25)*(ZM/ZP)*((ZP-ZM)**2.0)*ZP*(Z)*(MP-BP))
     + -((0.25)*(ZM/ZP)*((ZP-ZM)**2.0)*ZP*(M-B))
      DCL=((ZP*ZP*ZPP) + (2.0*ZM*ZP*ZPM) + (ZM*ZM*ZMM))
      SCL=((ZP*ZP*ZPP) - (ZM*ZM*ZMM))
      SCLP=(ZP*ZP*ZPPP) - (ZM*ZM*ZMMP)
      DCLP=((ZP*ZP*ZPPP) + (2.0*ZP*ZM*ZPMP) + (ZM*ZM*ZMMP))
      SUMD=-(ZP+ZM)*0.5
      ICD=ZP*ZM*(ZP+ZM)/2.0
      ZPPD=(C(1)*ZM) + (1.5*ZM*C(2)*(ZM*(Y))**0.5)
      ZMMD=(C(3)*ZP) + (1.5*ZP*C(4)*(ZP*(Z))**0.5)
      ZPMD=1.5*C(5)*(SUM**0.5)*SUMD + 2.0*C(6)*(SUM)*SUMD
      MD=(0.5*C(8)/(IC**1.5))*ICD
      BD=C(10)*ICD
      CAD=((ZP*ZPPD)/(Y)) - ((ZM*ZPMD)/(Y))
     + -(((ZP*ZPP) - (ZM*ZPM))/((Y)**2.0))
      CBD=((ZP*ZPMD)/(Z)) - ((ZM*ZMMD)/(Z))
     + -(((ZP*ZPM) - (ZM*ZMM))/((Z)**2.0))
      CED=-(0.25)*(ZP/ZM)*((ZP-ZM)**2.0)*ZM*(M+B)
     + -((0.25)*(ZP/ZM)*((ZP-ZM)**2.0)*ZM*(Y)*(MD+BD))
      CGD=-(0.25)*(ZM/ZP)*((ZP-ZM)**2.0)*ZP*(M-B)
     + -((0.25)*(ZM/ZP)*((ZP-ZM)**2.0)*ZP*(Z)*(MD-BD))
      CCD=((ZP*ZPPD)/(Y)) + ((ZM*ZPMD)/(Y))
     + -(((ZP*ZPP) + (ZM*ZPM))/((Y)**2.0))
      CDD=((ZP*ZPMD)/(Z)) + ((ZM*ZMMD)/(Z))
     + -(((ZP*ZPM) + (ZM*ZMM))/((Z)**2.0))
      CFD=-(0.25)*(ZP/ZM)*((ZP*ZP)-(ZM*ZM))*ZM*(M+B)
     + -((0.25)*(ZP/ZM)*((ZP*ZP)-(ZM*ZM))*ZM*(Y)*(MD+BD))
      CHD=-(0.25)*(ZM/ZP)*((ZP*ZP)-(ZM*ZM))*ZP*(M-B)
     + +((0.25)*(ZM/ZP)*((ZP*ZP)-(ZM*ZM))*ZP*(Z)*(MD-BD))
```

```
      SCLD=(ZP*ZP*ZPPD) - (ZM*ZM*ZMMD)
      DCLD=((ZP*ZP*ZPPD) + (2.0*ZP*ZM*ZPMD) + (ZM*ZM*ZMMD))
      DO 222 I=4,10
      TEST = 0.0
      IF (C(I) .NE. 0.0)TEST = 1.0
  222  CONTINUE
      ZIJUP=(96485.0*SM*A*A*SCL)/(CON*(8.314E7)*TM*ZP*ZM)
      RETURN
      ENTRY ZSSUP
      ZIJUP=((CA*CE) - (CB*CG))/(ZP*ZM)
      RETURN
      ENTRY ZDDUP
      ZIJUP=((CF*CC) + (CD*CH))/(ZP*ZM)
      RETURN
      ENTRY ZSDUP
      ZIJUP=((-CA*CF) - (CB*CH))/(ZM*ZP)
      RETURN
      ENTRY ZDSUP
      ZIJUP=((-CC*CE) + (CD*CG))/(ZM*ZP)
      RETURN
      ENTRY ZDEUP
      ZIJUP=-(96485.0*SM*A*A*DCL)/(ZP*ZM*CON*(8.314E7)*TM)
      RETURN
      ENTRY ZSEUP
      ZIJUP=(96485.0*SM*A*A*SCL)/(CON*(8.314E7)*TM*ZP*ZM)
      RETURN
      ENTRY ZSSPUP
      ZIJUP=((CAP*CE) + (CEP*CA))/(ZP*ZM)
     + -((CB*CGP) + (CG*CBP))/(ZP*ZM)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJUP = 0.0
      RETURN
      ENTRY ZDDPUP
      ZIJUP=((CF*CCP) + (CC*CFP))/(ZP*ZM)
     + + ((CD*CHP) + (CH*CDP))/(ZP*ZM)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJUP = 0.0
      RETURN
      ENTRY ZSDPUP
      ZIJUP=-((CA*CFP) + (CF*CAP))/(ZP*ZM)
     + - ((CB*CHP) + (CBP*CH))/(ZP*ZM)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJUP = 0.0
      RETURN
      ENTRY ZDSPUP
      ZIJUP=((CD*CGP) + (CG*CDP))/(ZP*ZM)
     + -((CE*CCP) + (CEP*CC))/(ZP*ZM)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJUP = 0.0
      RETURN
      ENTRY ZSEPUP
      ZIJUP=(96485.0*SM*A*A*SCLP)/(CON*(8.314E7)*TM*ZP*ZM)
      RETURN
      ENTRY ZDEPUP
      ZIJUP=-(96485.0*SM*A*A*DCLP)/(CON*(8.314E7)*TM*ZP*ZM)
      RETURN
      ENTRY ZSSDUP
```

```
      ZIJUP=((CA*CED) + (CE*CAD))/(ZM*ZP)
     + -((CB*CGD) + (CG*CBD))/(ZM*ZP)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJUP = 0.0
      RETURN
      ENTRY ZDDDUP
      ZIJUP=((CF*CCD) + (CC*CFD))/(ZM*ZP)
     + + ((CD*CHD) + (CH*CDD))/(ZM*ZP)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJUP = 0.0
      RETURN
      ENTRY ZSDDUP
      ZIJUP=-((CA*CFD) + (CF*CAD))/(ZM*ZP)
     + -((CB*CHD) + (CBD*CH))/(ZM*ZP)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJUP = 0.0
      RETURN
      ENTRY ZDSDUP
      ZIJUP=((CD*CGD) + (CDD*CG))/(ZM*ZP)
     + -((CC*CED) + (CE*CCD))/(ZM*ZP)
      IF (C(2) .EQ. 0.0 .A. TEST .EQ. 0.0)ZIJUP = 0.0
      RETURN
      ENTRY ZSEDUP
      ZIJUP=(96485.0*SM*A*A*SCLD)/(CON*(8.314E7)*TM*ZP*ZM)
      RETURN
      ENTRY ZDEDUP
      ZIJUP=-(96485.0*SM*A*A*DCLD)/(CON*(8.314E7)*TM*ZP*ZM)
      RETURN
      END



      FUNCTION DDZIJ(S,D)
      COMMON/UNITS/SM,DF,GDE,EPM,A,ZP,ZM,CON,TM,DIM,CREF,ZREF
      COMMON/GREEK/C(24)
      Y=D+(DF/SM)-S-1.0
      Z= D + S + 1.0 + (DF/SM)
      IF (Y.GE.0.0) Y=-1.0E-10
      IF (Z.LE.0.0) Z=1.0E-10
      SUM=((ZM*ZM)*Y - (ZP*ZP)*Z)/(ZM-ZP)
      ZPP=C(1)*(ZM*(Y)) + C(2)*(ZM*(Y))**1.5
      ZMM=C(3)*(ZP*(Z)) + C(4)*(ZP*(Z))**1.5
      ZPM=C(5)*(SUM**1.5) + C(6)*(SUM**2.0)
      DCL=((ZP*ZP*ZPP) + (2.0*ZM*ZP*ZPM) + (ZM*ZM*ZMM))
      SCL=((ZP*ZP*ZPP) - (ZM*ZM*ZMM))
      SUMP=(ZP-ZM)/2.0
      ZPPP=-(C(1)*ZM) - (1.5*ZM*C(2)*(ZM*(Y))**0.5)
      ZMMP=+(C(3)*ZP) + (1.5*ZP*C(4)*(ZP*(Z))**0.5)
      ZPMP=1.5*C(5)*(SUM**0.5)*SUMP + 2.0*C(6)*(SUM)*SUMP
      DCLP=((ZP*ZP*ZPPP) + (2.0*ZP*ZM*ZPMP) + (ZM*ZM*ZMMP))
      SCLP=(ZP*ZP*ZPPP) - (ZM*ZM*ZMMP)
      SUMD=-(ZP+ZM)*0.5
      ZPPD=(C(1)*ZM) + (1.5*ZM*C(2)*(ZM*(Y))**0.5)
      ZMMD=(C(3)*ZP) + (1.5*ZP*C(4)*(ZP*(Z))**0.5)
```

```
ZPMD=1.5*C(5)*(SUM**0.5)*SUMD + 2.0*C(6)*(SUM)*SUMD
DCLD=((ZP*ZP*ZPPD) + (2.0*ZP*ZM*ZPMD) + (ZM*ZM*ZMMD))
SCLD=(ZP*ZP*ZPPD) - (ZM*ZM*ZMMD)
DDZIJ=(96485.0*SM*A*A*SCLP)/(CON*(8.314E7)*TM*ZP*ZM)
RETURN
ENTRY DDZDE
DDZIJ=-(96485.0*SM*A*A*DCL)/(ZP*ZM*CON*(8.314E7)*TM)
RETURN
ENTRY DDZSE
DDZIJ=(96485.0*SM*A*A*SCL)/(CON*(8.314E7)*TM*ZP*ZM)
RETURN
ENTRY DDZSED
DDZIJ=(96485.0*SM*A*A*SCLD)/(CON*(8.314E7)*TM*ZP*ZM)
RETURN
ENTRY DDZDED
DDZIJ=-(96485.0*SM*A*A*DCLD)/(CON*(8.314E7)*TM*ZP*ZM)
RETURN
ENTRY DDZSEP
DDZIJ=(96485.0*SM*A*A*SCLP)/(CON*(8.314E7)*TM*ZP*ZM)
RETURN
ENTRY DDZDEP
DDZIJ=-(96485.0*SM*A*A*DCLP)/(CON*(8.314E7)*TM*ZP*ZM)
RETURN
END
```

```
FUNCTION PPZIJ(S,D)
COMMON/UNITS/SM,DF,GDE,EPM,A,ZP,ZM,CON,TM,DIM,CREF,ZREF
COMMON/GREEK/C(24)
Y=D+(DF/SM)-S-1.0
Z= D + S + 1.0 + (DF/SM)
IF (Y.GE.0.0) Y=-1.0E-10
IF (Z.LE.0.0) Z=1.0E-10
SUM=((ZM*ZM)*Y - (ZP*ZP)*Z)/(ZM-ZP)
ZPP=C(1)*(ZM*(Y)) + C(2)*(ZM*(Y))**1.5
ZMM=C(3)*(ZP*(Z)) + C(4)*(ZP*(Z))**1.5
ZPM=C(5)*(SUM**1.5) + C(6)*(SUM**2.0)
DCL=((ZP*ZP*ZPP) + (2.0*ZM*ZP*ZPM) + (ZM*ZM*ZMM))
SCL=((ZP*ZP*ZPP) - (ZM*ZM*ZMM))
SUMP=(ZP-ZM)/2.0
ZPPP=-(C(1)*ZM) - (1.5*ZM*C(2)*(ZM*(Y))**0.5)
ZMMP=+(C(3)*ZP) + (1.5*ZP*C(4)*(ZP*(Z))**0.5)
ZPMP=1.5*C(5)*(SUM**0.5)*SUMP + 2.0*C(6)*(SUM)*SUMP
DCLP=((ZP*ZP*ZPPP) + (2.0*ZP*ZM*ZPMP) + (ZM*ZM*ZMMP))
SCLP=(ZP*ZP*ZPPP) - (ZM*ZM*ZMMP)
SUMD=-(ZP+ZM)*0.5
ZPPD=(C(1)*ZM) + (1.5*ZM*C(2)*(ZM*(Y))**0.5)
ZMMD=(C(3)*ZP) + (1.5*ZP*C(4)*(ZP*(Z))**0.5)
ZPMD=1.5*C(5)*(SUM**0.5)*SUMD + 2.0*C(6)*(SUM)*SUMD
DCLD=((ZP*ZP*ZPPD) + (2.0*ZP*ZM*ZPMD) + (ZM*ZM*ZMMD))
```

```
SCLD=(ZP*ZP*ZPPD)  -  (ZM*ZM*ZMMD)
PPZIJ=(96485.0*SM*A*A*SCL)/(CON*(8.314E7)*TM*ZP*ZM)
RETURN
ENTRY PPZDE
PPZIJ=-(96485.0*SM*A*A*DCL)/(ZP*ZM*CON*(8.314E7)*TM)
RETURN
ENTRY PPZSE
PPZIJ=(96485.0*SM*A*A*SCL)/(CON*(8.314E7)*TM*ZP*ZM)
RETURN
ENTRY PPZSED
PPZIJ=(96485.0*SM*A*A*SCLD)/(CON*(8.314E7)*TM*ZP*ZM)
RETURN
ENTRY PPZDED
PPZIJ=-(96485.0*SM*A*A*DCLD)/(CON*(8.314E7)*TM*ZP*ZM)
RETURN
ENTRY PPZSEP
PPZIJ=(96485.0*SM*A*A*SCLP)/(CON*(8.314E7)*TM*ZP*ZM)
RETURN
ENTRY PPZDEP
PPZIJ=-(96485.0*SM*A*A*DCLP)/(CON*(8.314E7)*TM*ZP*ZM)
RETURN
END.
```

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