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## MODELING AND REACTOR SIMULATION

**Electrochemical reactors differ from chemical reactors by the importance of the distribution of electrical potential and the effect of electric potential variations on mass transfer and heterogeneous reaction rates. Basic principles and examples for including these effects in reactor design will be considered.**

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There are four scientific areas which form the basis for most chemical engineering modeling and reactor simulations: thermodynamics, transport phenomena, chemical kinetics, and system analysis. In the field of electrochemical reactor simulation the same principles apply with the addition of electrical potential as a thermodynamic variable and its gradient as a transport driving force. Electrochemistry typically involves an electron transfer step at an interface between an electronically conducting phase and an ionically conducting phase. Electrons must not occur in a free or independently transportable condition in the ionically conducting phase.

Electronically conducting phases are typically solid metals or semiconductors. Ionically conducting phases are typically liquids called electrolytes or electrolytic solutions. Notable exceptions exist. Considering the more typical cases, solid-liquid reacting interfaces suggest a comparison to heterogeneous catalysis. There is considerable similarity. A major difference is the requirement for all the solid, electronic phase surface area which is active to have a continuous connection to an outside electrical circuit or to another operating electrode in the case of series connected cells. The potential distribution limits the useful size or thickness of extended surface area electrodes. If electrodes are too large and/or incorrectly

shaped, there will be large nonproductive regions. These complexities make the typical overall reaction rate per unit volume of electrochemical reactors orders of magnitude below typical heterogeneous, catalytic reactors. Consequently, electrochemical processing is often limited due to high capital cost.

A primary objective of electrochemical reactor design is to increase the reaction rate per unit volume while keeping operating costs at a minimum, that is, achieving high current densities with low electrical potential losses. The losses are divided into three categories: resistance or IR losses, potential losses associated with concentration variations, and potential losses associated with driving the surface reaction at finite rates.

Minimizing surface potential losses is largely a matter of heterogeneous catalysis which is a rather specialized field not yet well established or described by fundamental laws. The designer is often caught between raising temperatures to increase chemical reaction rate constants while fighting corrosion problems associated with higher temperatures. If adequate catalysts are not available, an alternative is to increase the specific area of the electrode. Getting adequate mass transfer to and from the extended surface area is often the critical problem over which the designer has control.

Catalyst research is generally long term, costly, and uncertain. The use of high surface area electrodes with emphasis on designing for optimum mass transfer is usually the short term objective for an electrochemical design engineer.

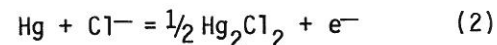
#### THERMODYNAMICS

The electrical state of a phase is defined by its electrical potential. Electrical potentials are always relative to some reference potential. There is no working definition which can define an absolute potential. Thus, it is always necessary to refer to differences in potential between phases. Voltage measuring devices measure the difference in electrical potential between two identical, electronically conducting phases, typically copper. The electronic potential is related to the chemical potential of the electrons in the respective phases by the expression

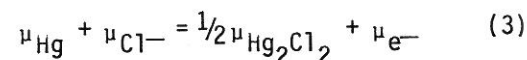
$$\phi_1 - \phi_2 = \frac{\mu_e^{(2)} - \mu_e^{(1)}}{F} \quad (1)$$

where  $\phi_1$  and  $\phi_2$  are the electrical potentials of phase 1 and 2 respectively,  $\mu_e^{(2)}$  is the chemical potential of electrons in phase 2,  $\mu_e^{(1)}$  is the chemical potential of electrons in phase 1, and  $F$  is Faraday's constant 96487 coulombs per equivalent.

There is no known method for measuring directly the electrical potential in an electrolyte. All that can be done is to place electronic conductors, a metal or semiconductor, into the solution and measure the potential difference between the electronic conductors. Such devices are called reference electrodes. No current or at least a negligibly small current must be allowed to pass across the interface between the electronic conductor of the reference electrode and the electrolyte. Newman (1973a), following Guggenheim to whom Newman refers, has discussed the principle of local equilibrium which relates the reference electrode electronic potential to the chemical potential of ions in the solution. The result is a working definition of the electrical state of the electrolyte phase. The reference electrode must "be reversible" to some ion in the solution. A calomel cell in a chloride solution is the classic example. It is reversible to the chloride ion.



The principle of local equilibrium means the following relation exists:



By inserting two reference electrodes in an electrolyte, the potential difference between the two reference electrodes relates the chemical potential between the chloride ions at the two locations.

$$\begin{aligned} \mu_{\text{Cl}^-}^{(1)} - \mu_{\text{Cl}^-}^{(2)} &= \mu_{e^-}^{(1)} - \mu_{e^-}^{(2)} - \mu_{\text{Hg}}^{(1)} + \mu_{\text{Hg}}^{(2)} \\ &+ \mu_{\text{Hg}_2\text{Cl}_2}^{(1)} - \mu_{\text{Hg}_2\text{Cl}_2}^{(2)} \end{aligned} \quad (4)$$

Since the chemical potential of Hg and  $\text{Hg}_2\text{Cl}_2$  will normally be the same at the two locations, Equation (4) can be written:

$$\mu_{\text{Cl}^-}^{(1)} - \mu_{\text{Cl}^-}^{(2)} = F(\phi^{(2)} - \phi^{(1)}) \quad (5)$$

The measured potential difference,  $\phi^{(2)} - \phi^{(1)}$ , reflects changes in the electrical state between the two locations plus changes in concentration or other aspects of the local environment. Concentration and electrical contributions can not be uniquely separated and it is not necessary to do so. It is often useful, however, to separate the potential difference into a potential difference identified primarily with the change in electrical state or flow of electrical current  $\Delta\phi_{IR}$ , and the difference arising primarily from the variation in concentration,  $\eta_c$ .

$$\phi^{(2)} - \phi^{(1)} = \Delta\phi_{IR} + \eta_c \quad (6)$$

The potential difference identified with current flow or resistance overpotential is defined as the line integral between the two reference electrodes of the current density,  $i$ , divided by an average conductivity between the two electrodes,  $K_\infty$ .

$$\Delta\phi_{IR} = \int_{\ell} \frac{i}{K_\infty} d\ell \quad (7)$$

The concentration overpotential is what is left over.

$$\eta_c = \phi^{(2)} - \phi^{(1)} - \Delta\phi_{IR} \quad (8)$$

Newman (1973b) has shown a general form for  $\eta_c$  which is rather complex. For many cases the expression reduces to the simpler Nernst equation which, as applied to the calomel reference electrodes in a chloride media, becomes

$$\eta_c = \frac{RT}{F} \ln \frac{C_{\text{Cl}^-}^{(1)}}{C_{\text{Cl}^-}^{(2)}} \quad (9)$$

#### ELECTROCHEMICAL KINETICS

As an example, consider a hydrogen oxygen fuel cell. Let  $\phi_A$  be the hydrogen electrode potential and  $\phi_C$  be the oxygen electrode potential, see Figure 1 for a schematic sketch of the cell. The cell potential,  $U$ , is  $\phi_A - \phi_C$ . A reference electrode is placed just outside the double layer of each working electrode. The reference electrode adjacent to the hydrogen electrode,  $\phi_{RA}$ , is a reversible hydrogen electrode across which no current passes. It is bathed in the same electrolyte as the surface of the working hydrogen electrode. Current is passing across the surface of working electrodes. The reference electrode adjacent to the oxygen electrode,  $\phi_{CA}$ , is a reversible oxygen electrode. The potential difference between the two reference electrodes,  $\phi_{RA} - \phi_{RC}$ , is the sum of the hydrogen-oxygen open circuit potential,  $U^\circ$ , plus the resistance overpotential,  $\Delta\phi_{RA}$ , plus the concentration overpotential,  $\eta_c$ . Often  $\eta_c$  is separated into an anodic plus a cathodic contribution associated with concentration variations at each electrode. The surface overpotential at the hydrogen electrode,  $\eta_{SA}$ , is defined as  $\phi_A - \phi_{RA}$ . The surface overpotential at the oxygen electrode,  $\eta_{SC}$ , is defined as  $\phi_C - \phi_{RC}$ .

A required input for electrochemical reactor simulation modeling is a quantitative expression for the transfer current density,  $j$ , as a function of the appropriate surface overpotential and local electrolyte concentration. There is no unique functional form and there are no easy rules of getting the correct function. Unfortunately, the

electrochemists give us only some rough guidelines. Often, an expression of the following form is found to work.

$$j = i_0 \left\{ \frac{\alpha_a F \eta_s}{RT} e^{\frac{\alpha_a F \eta_s}{RT}} - \frac{\alpha_c F \eta_s}{RT} e^{-\frac{\alpha_c F \eta_s}{RT}} \right\} \quad (10)$$

Here  $i_0$ ,  $\alpha_a$ , and  $\alpha_c$  are kinetic parameters. The exchange current density,  $i_0$ , is a function of the local electrolyte concentration, often of the form

$$i_0 = i_0^0 (C_e/C_e^0)^\gamma \quad (11)$$

where  $i_0^0$  is the exchange current density at the reference concentration  $C_e^0$  and  $\gamma$  is some constant between 0 and 2. The kinetic parameter values can change markedly with changes in the surface condition of the electrode. The true functional form for Equation (10) and values for the governing parameters must normally be determined using extensive experimental tests of current voltage behavior under carefully controlled conditions of electrolyte composition and electrode surface conditions.

#### TRANSPORT

The basic equations to be solved for a typical electrochemical reactor are the species conservation equations.

$$\frac{\partial C_i}{\partial t} = \nabla_1 N_i + R_i \quad (12)$$

Here  $C_i$  is the concentration of species  $i$  in moles of species  $i$  per unit volume of the solution phase.  $N_i$  is the flux of species  $i$  in moles of  $i$  per unit area per unit time.  $R_i$  is the rate of production of species  $i$  in moles of  $i$  per unit volume. The fundamental laws of transport are used to express  $N_i$  as a function of appropriate driving forces. Newman (1973c) teaches us two forms for  $N_i$ . One is the dilute solution theory.

$$N_i = -D_i \nabla C_i - u_i C_i F z_i \nabla \phi + C_i v \quad (13)$$

This equation is well explained by Newman (1973c) and shows how flux depends on a diffusion contribution,  $D_i \nabla C_i$ , on a migration or electric field contribution,  $u_i C_i F z_i \nabla \phi$ , and on a convective flow

contribution,  $C_i v$ . This equation has been very useful over the years and is satisfactory for many purposes.

For situations involving several species at high concentration, Equation (13) does not contain sufficient cross terms such as the transport of A due to a movement of species B. For example, in membranes the transport of neutral water due to an electric field is caused by movement of hydrated ions. Such effects are better accounted for using the so called concentrated transport theory based on the Stefan Maxwell equations for transport.

$$\underline{d}_i = \sum_j K_{ij} (v_j - v_i) \quad (13)$$

A complete discussion of this equation is beyond the scope of this paper and readers are referred to Chapter 12 of the previously referenced text by Newman or to Hirschfelder et al. (1954) for a more complete discussion of this equation. A key aspect of Equation (13) is to recognize that for  $n$  species in a solution there will be  $n-1$  independent species flux equations,  $n-1$  independent driving forces, and  $n(n-1)/2$  independent diffusion type transport parameters.

#### THE SYSTEM

The basic design equations can be placed in six categories.

##### • Flux equations

$$N_i = -D_i \nabla C_i - z_i F u_i C_i \nabla \phi_2 + C_i v \quad (12)$$

or

$$\underline{d}_i = \sum_j K_{ij} (v_j - v_i) \quad \text{where } N_i = C_i v_i \quad (13)$$

##### • Electroneutrality equation

$$\sum_i z_i C_i = 0 \quad (14)$$

##### • Current equation

$$i = F \sum_j z_j N_j \quad (15)$$

##### • Species conservation equations

$$\frac{\partial C_i}{\partial t} = -\nabla_1 N_i + R_i \quad (11)$$

##### • Overall continuity equation

$$\nabla \cdot \underline{v} = 0 \quad (16)$$

##### • Equations of motion

$$\rho \frac{Dv}{Dt} = -\nabla P + \mu \nabla^2 v + \rho g \quad (17)$$

It must be remembered that these are classes of equations and often the equations as written must be replaced by alternate equations better suited for a particular situation. The various choices of flux equations has been mentioned. The electroneutrality equation is usually valid, but in the double layer, at the junction of two semiconductors, or in materials more like dielectrics than electrolytes it may be necessary to replace Equation (14) by Poisson's equation. The current equation is much like a definition and always true.

The most important of the equations are the species conservation equations. For most electrochemical engineering problems, these equations apply only to the solution phase. In a porous electrode, a correction must be made for volume occupied by the solid. An  $\epsilon$ , the volume fraction occupied by the liquid phase, is included in Equation (11) to account for the exclusion of liquid by the presence of the solid phase.

It is an important procedure in modeling to begin with the simplest model possible and build. A simple model often has analytic solutions which provide early, useful insight into the problem. A simple computer code can usually be easily written and comparison made between numerical and analytic solutions which is usually very instructive. As the model is made more complex, analytical solutions become impossible. The gradual adding of new physical processes and mathematical equations allows needed insight into both the physical interrelations of the various simultaneous processes and the mathematical structure of the problem. It also allows stepwise building and debugging of the code in an ordered manner.

If possible, a single conservation equation and one variable should be the beginning of a code. Consider the system  $H_2O - KOH - K_2Zn(OH)_4$  in a solid Zn plus ZnO matrix. If  $\epsilon$  is assumed constant,  $v$  zero, and no pressure variations, there are three independent conservation equations, that is, there are four species and the number of independent species conservation equations is  $n-1$ . The sum of the charged species conservation equations yields the charge conservation equation

$$\nabla \cdot i_2 = aj \quad (18)$$

If concentrations are uniform, Equation (18) is the only species conservation equation needed and solution potential,  $\phi_2$ , the only variable. The transfer current density,  $j$ , is related to the solution potential by an appropriate kinetic equation such as

$$j = i_0 \left\{ e^{\frac{\alpha_a F}{RT} (\phi_1 - \phi_2)} - e^{\frac{\alpha_c F}{RT} (\phi_1 - \phi_2)} \right\} \quad (9)$$

In the beginning let  $\phi_1$ , potential of the metal phase, be constant and zero. By combining Equations (12) and (15), one gets Ohm's law if concentrations are uniform.

$$i_2 = -K \frac{d\phi_2}{dx} \quad (19)$$

Combining Equations (18), (9) and (19) yields

$$-\frac{d}{dx} K \frac{d\phi_2}{dx} = ai_0 \left\{ e^{\frac{-\alpha_a F}{RT} \phi_2} - e^{\frac{\alpha_a F}{RT} \phi_2} \right\} \quad (20)$$

The solution to these equations gives  $\phi_2$ ,  $j$ , and  $i_2$  as functions of  $x$  for given applied potentials. One can then add a species conservation equation for  $OH^-$  and  $C_{OH^-}$  as a variable. Equation (18) must be modified to account for variations in  $C_{OH^-}$  along with  $C_{OH^-}$  dependence of  $i_0$ . A suitable expression must be realized for  $R_{OH^-}$ . An example might be from Faraday's Law

$$R_{OH^-} = \frac{-2aj}{F} \quad (21)$$

Once  $C_{OH^-}$  variations with  $x$  and applied potential are examined, the  $Zn(OH)_4^{2-}$  ion species conservation equation can be added and  $C_{Zn(OH)_4^{2-}}$  included as a variable. An expression for  $R_{Zn(OH)_4^{2-}}$  might include  $Zn(OH)_4^{2-}$  production based on Faraday's law,  $a_{1j}/2F$ , and its removal from solution based on laws which describe nucleation and precipitation,  $k_m a_2 (C_3 - C_3^{Sat})$ .

At this point one has  $\phi_2$ ,  $C_{OH^-}$ ,  $C_{Zn(OH)_4^{2-}}$ ,  $i_2$ , and  $j$  as functions of position and applied potential. Water concentration,  $C_0$ , is fixed once the ion concentrations are

known. When that level of the model is fully tested and understood, one can add  $\epsilon$  and  $v$  as variables.

The continuity equation is the sum of all four species continuity equations converted to their mass rather than molar forms. When one considers the liquid and solid phases as a superimposed continuum as taught by Newman and Tobias (1962), the continuity equation becomes two equations interrelating the continuity of liquid and solid phases.

$$\frac{\partial \epsilon}{\partial t} = \nabla \cdot v \quad (22)$$

and

$$\frac{\partial \epsilon}{\partial t} = \sum_j S_j \bar{V}_j \dot{R}_j \quad \text{solid} \quad (23)$$

In Equation (23) the summation is over all solid species;  $S_j$  is the stoichiometric coefficient which is negative if species  $j$  is produced. The  $\bar{V}_j$  is the partial molar volume of species  $j$  and  $\dot{R}_j$  is the same reaction rate per unit volume as defined for the regular solution species conservation equations. Although changes in  $\epsilon$  must give rise to changes in  $v$  as shown by Equation (22), it is mathematically possible to add Equation (23) and not Equation (22). The physical significance may be suspect, but adding the equations one at a time is highly recommended.

The addition of Equations (22) and (23) is a major step mathematically since it introduces time as a variable. As new variables are added, previous equations must be updated to include effects of new variables. It is important to recognize that these effects can be added one step at a time, and should be.

Once the one dimensional problem is satisfactorily understood, a second spatial dimension can be added to the model. Detailed math models in two spatial dimensions have not been common. The cost of computing has been high and the skills to do it not widely known. Improved numerical techniques and lower computing costs can be expected to make more complete and descriptive models popular and useful. Another useful addition to many models is a or possibly several competing, parasitic processes at one electrode. Hydrogen evolution plus zinc reactions at a negative

battery electrode or oxygen evolution at a nickel oxide electrode are examples. The surface overpotential driving forces are handled by multiple reference electrodes. For the nickel oxide electrode, a reversible nickel oxide reference electrode defines  $\eta_s$  for the nickel valence change reaction and a reversible oxygen reference defines  $\eta_s$  for the oxygen evolution reaction. Such models can then predict current efficiency for a given reaction as a function of time and/or position depending on the completeness of the equations.

The equations of motion are needed only if pressure variations and their effect on velocity are needed as is the case for forced convection, flow through or flow by electrodes. Often the flow patterns are determined experimentally or solved for independently of the previously discussed equations and velocity is simply inserted into the previous equations as a known function of position, independent of time. It is possible and reasonable to include some form of the equations of motion and add pressure as a variable and solve all of the equations together.

#### NUMERICAL METHODS

Many numerical techniques can be used to solve the equations. A technique with which the author has had considerable recent success will be briefly described. The procedure is based on Newman's (1973d) BAND(J) subroutine for matrix inversion. BAND(J) will invert any set of tridiagonal matrixes. As Newman has shown us, any set of linear ordinary differential equations can be put in the form of finite difference equations which form a set of tridiagonal matrixes. Since most equations are nonlinear, it is necessary to put the equations in linear form and iterate over the nonlinearities. Often the order is to linearize and then put in finite difference form. If the equations are put in finite difference form first, it is then possible to use a simple, general Fortran code to handle all of the linearization and details associated with calling BAND(J). Although linearization and setting up the logic for calling BAND(J) is straightforward, it can be time consuming and formidable to beginners. The standardized procedures used in the general code being described here causes some lack of optimization and resulting programs take somewhat longer to run than a code specifically written for a specific problem. For a one dimensional problem or

one dimension plus time, the increase in computer run time may be 10 to 50%. A modified form of the procedure can be used for two dimensional problems which are second order in both directions (elliptic problems), but the time penalty may be large compared to other methods. More efficient approaches which retain coding simplicity are still being worked on for the two dimensional elliptic problems which are faster in terms of computer run time.

Although computer run time may be somewhat longer to solve a particular set of equations, the time to write the code and debug the program is much less than for other approaches. Experiences with students and professors at BYU indicates that the coding, debugging, and revisions can be done in one fifth the time compared to more usual techniques. One now has the option of trading machine time for human labor. In the great tradition of the industrial revolution, the trade has usually been profitable. Students have named the subroutine DIFEQ. To use the technique all that one must do is write the differential equations in finite difference form and code them in a subroutine known as FUNCT(J). DIFEQ calls FUNCT(J) and does all the work of solving the equations by linearizing them and iterating on any nonlinearities.

Any differential equation can be put in finite difference form (see any text on numerical methods applied to differential equations). Newman outlines the procedure in the Appendix of his book. The result is an equation of the form

$$\sum_{K=1}^N A(I,K)*C(K,J-1) + \sum_{K=1}^N B(I,K)*C(K,J) + \sum_{K=1}^N D(I,K)*C(K,J+1) - G(I) = 0 \quad (24)$$

The subscript I refers to the number of the equation of which there are N. The subscript K refers to the particular dependent variable C(K,J-1). The subscript J refers to the mesh point number. If the equation is linear, the functions represented by A, B, D, and G are constants or functions only of the dependent variable such as position x and or time t. Thus, for a given J (that is location in space and/or time is fixed) A, B, D, and G are real numbers. Newman's BAND(J) works by feeding it the numerical values of A, B, D, and G for each value of J. Although it appears simple once the concept is fully

grasped, getting the concept and the time to set up the calculation procedures on a computer has been sufficiently formidable that, based on the author's experience, few students would try it. By using DIFEQ, the necessity of gaining a complete grasp of BAND(J) initially is eliminated and the labor of coding reduced. It is hoped that the principles behind BAND(J) may be learned and appreciated more easily through the use of DIFEQ while allowing a worker to more quickly actually begin to solve important problems.

If the equations are nonlinear, A, B, D, and G will be functions of one or more of the independent variables C(K,J). For simplicity, the function defined by Equation (24) will be called F(I).

$$F(I) = \sum_{K=1}^N \left\{ A(I,K)*C(K,J-1) + B(I,K)*C(K,J) + D(I,K)*C(K,J+1) \right\} - G(I). \quad (25)$$

If one estimates a set of C(K,J) as a trial solution, F(I) can be represented by a Taylor series keeping only the first order terms.

$$F(I) = F(I)^0 + \sum_{K=1}^N \sum_{M=J-1}^J \left( \frac{\partial F(I)}{\partial C(K,M)} \right)^0 * [C(K,M) - C^0(K,M)] \quad (26)$$

The index K goes from one to N, and M takes on the three values J-1, J, and J+1. By comparing Equations (26) and (25), it can be seen that

$$A(I,K) = \left( \frac{\partial F(I)}{\partial C(K,J-1)} \right)^0 \quad (27)$$

$$B(I,K) = \left( \frac{\partial F(I)}{\partial C(K,J)} \right)^0 \quad (28)$$

$$D(I,K) = \left( \frac{\partial F(I)}{\partial C(K,J+1)} \right)^0 \quad (29)$$

$$G(I) = -F(I)^0 + \sum_{K,M} \left( \frac{\partial F(I)}{\partial C(K,M)} \right)^0 * C(K,M)^0. \quad (30)$$

The program DIFEQ takes all the partial derivatives numerically by calling the subroutine FUNCT(J) for various values of the arguments.

The programmer must write a subroutine FUNCT(J) which contains the N equations in finite difference form for all interior points. Appropriate boundary condition equations must be supplied at the boundaries at J equal one and J equal NJ. Appropriate input and output subroutines must also be supplied. The simplest form of the porous electrode equations is the single equation

$$F(1) = a_j - v \cdot i_2 \quad (18)$$

A simple code using DIFEQ and solving this equation is given in the Appendix. The result yields the so called secondary current distribution applicable for a simple redox surface overpotential expression and no concentration variations. Other equations can easily be added.

#### CLOSURE

What can a model of an electrochemical system do for the design engineer? Probably the greatest help is being able to understand what is going on and how various processes interrelate allowing one to gain insight into a system and interpret behavior with a minimum of practical, expensive hands-on experience. It can provide a picture of concentration, potential, porosity, current density, reaction rate, velocity, and temperature as functions of position and time for various design configurations and operating conditions. By using a complete model, it may be possible to predict costs and then use the model to optimize design configurations and operating conditions. Such a model might also be used as part of an automatic control loop to allow computers and automatic control equipment to improve the response and optimization of the control function.

Unfortunately, the state of the art in math modeling of electrochemical systems has rarely reached to the lofty objectives just described. Hopefully we are moving toward the ideal. In the meantime, the model can be a partial aid to design and operating engineers in accomplishing their respective assignments.

## LITERATURE CITED

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3. Ibid., Chapter 20 (1973b).
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5. Ibid., Appendix C (1973d).
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## APPENDIX

The first routine listed is the main program nicknamed DIFEQ. It takes all the partial derivatives necessary for any problem, defines A, B, D, and G's for each value of J and calls BAND(J). It tests each iteration and continues iterating until convergence to one part in 10,000 at all points is achieved. The procedure has been tested on about 30 problems by about 15 different students. It generally works well. Occasionally the internal value of CU must be changed from 1.0001 to 1.001 or 1.00001 for a particular variable. If a function is highly sensitive to a particular variable then CU equal 1.00001 may work better. If a function is very insensitive to a variable, then CU equal 1.001 may be selected. Values of CU can be specifically adjusted for each function F(I) and each variable C(K,J). Such tailor making adds considerable complexity, however, and so far CU equal 1.0001 has worked well for many cases. There is a procedure to prevent dividing by zero when the variable is zero. It probably needs improvement. The subroutine DIFEQ is listed at the end of this Appendix.

The subroutine DIFEQ is general and can be used for solving up to 10 simultaneous equations with an equal number of unknowns. All that is needed is to write the equations in finite difference form in a subroutine FUNCT(J). More equations can be solved if the dimensions in the common statement are increased.

An example of a single equation for FUNCT(J) is given right after the subroutine

DIFEQ. The subroutine is for Equation (18) using Equations (9) and (19) to relate  $i_2$  and  $j$  to the potential  $\phi_2$ . The dependent variable is  $\phi_2$ .

The boundary conditions applied at  $J = 1$  and  $J = NJ$  set  $i_2$  equal zero at  $J = 1$  and  $\phi_2$  equal some given value, CNJ, at  $J = NJ$ . In addition, the boundary conditions include reaction rate  $a_j$  between  $x = 0$  and  $x = H/2$  at  $J = 1$  and between  $x = H^*x - h/2$  and  $x = H^*x$  at  $J = NJ$ .

Besides the subroutine FUNCT(J), the programmer must provide a main or calling routine to provide parameters needed by FUNCT(J) and to print out the answer. Such parameters must be included in the COMMON statement. The calling routine normally includes an initialization procedure which provides the initial estimates for the variable C(K,J). An example calling routine is listed just behind FUNCT(J). A sample output is listed just after the calling routine. For the simple problem given, an analytic solution is possible if a linear form of the redox expression is used. At low applied potential (the linear region), the two solutions agree to within %. Better agreement is achieved by using more mesh points. To these routines must be added the subroutine BAND(J) and MATINV(N,M,DETERM) which were written by Newman (1973d).

As presented so far, the procedure is good only for ordinary differential equations. If a second dimension involves only first derivatives with respect to the second independent variable such as time, only prior problem solutions are needed. The programmer can code to simply march forward in the second independent variable. The DIFEQ-BAND(J) procedure has been extensively tested for this application and works well. Programming labor is much less than alternate procedures and run time increases only modestly, 10 to 50%.

If the second dimension is second order in the independent variable, some sort of relaxation procedure is needed. The ADI (alternating direction implicit) method has been tested in a very preliminary way. The coding time seems greatly reduced compared to alternate techniques. But the computer run time may be too long compared to other techniques to justify its use. Further tests of the technique are under way.

C GENERALIZED CALLING SUBROUTINE FOR BAND(J) TO SOLVE DIFFERENTIAL EQUATIONS TAKING PARTIAL DERIVATIVES NUMERICALLY

C ITS SHORT NAME IS DIFEQ

SUBROUTINE DIFEQ

IMPLICIT REAL\*8(A-H, O-Z)

DIMENSION AA(10, 10), SUM(10), COLD(10, 101)

COMMON A(10, 10), B(10, 10), C(10, 101), D(10, 21), G(10), X(10, 10),

1Y(10, 10), N, NJ, ITPRT, F(10), ITCNT,

2H, THICK, CNJ, EXCUR, ALPHA, ALPHC, APUV, EFORT, CAPPA

CU=1.0001

CD=2.0-CU

ITCNT=0

10 CONTINUE

DO 15 K=1, N

DO 15 J=1, NJ

COLD(K, J)=C(K, J)

15 CONTINUE

J=0

IF(ITCNT.GT.20)GO TO 50

ITCNT=ITCNT+1

20 CONTINUE

J=J+1

L=J-3

DO 25 I=1, N

SUM(I)=0.0

25 CONTINUE

IF(J.EQ.1) MM=3

IF(J.GT.1.AND.J.LT.NJ) MM=2

IF(J.EQ.NJ) MM=1

DO 35 M=MM, MM+2

DO 35 K=1, N

SAVEC=C(K, L+M)

IF(DABS(SAVEC).LT.1.0D-14) C(K, L+M)=1.0D-14

C(K, L+M)=C(K, L+M)\*CU

CALL FUNCT(J)

DO 30 I=1, N

AA(I, K)=F(I)

30

CONTINUE

C(K, L+M)=SAVEC

IF(DABS(SAVEC).LT.1.0D-14) C(K, L+M)=1.0D-14

C(K, L+M)=C(K, L+M)\*CD

CALL FUNCT(J)

C(K, L+M)=SAVEC

IF(DABS(SAVEC).LT.1.0D-14) C(K, L+M)=1.0D-14

DO 35 I=1, N

AA(I, K)=(AA(I, K)-F(I))/((CU-CD)\*C(K, L+M))

C(K, L+M)=SAVEC

SUM(I)=SUM(I)+AA(I, K)\*C(K, L+M)

IF(L+M.EQ.J-2) Y(I, K)=AA(I, K)

IF(L+M.EQ.J-1) A(I, K)=AA(I, K)

IF(L+M.EQ.J) B(I, K)=AA(I, K)

IF(L+M.EQ.J+1) D(I, K)=AA(I, K)

IF(L+M.EQ.J+2) X(I, K)=AA(I, K)

```

35 CONTINUE
  CALL FUNCT(J)
  DO 40 I=1,N
    G(I)=-F(I)+SUM(I)
40 CONTINUE
  CALL BAND(J)
  IF (J.LT.NJ) GO TO 20
  DO 45 K=1,N
    DO 45 J=1,NJ
      IF (DABS(C(K,J)).LT.1.0D-14)GO TO 45
      IF (DABS((C(K,J)-COLD(K,J))/C(K,J)).GT.1.0D-4) GO TO 10
45 CONTINUE
50 RETURN
  END

  SUBROUTINE FUNCT(J)
  IMPLICIT REAL*8(A-H, O-Z)
  COMMON A(10,10), B(10,10), C(10,101), D(10,21), G(10), X(10,10),
  1Y(10,10), N, NJ, ITPRT, F(10), ITCNT,
  2H, THICK, CNJ, EXCUR, ALPHA, ALPHC, APUV, EFORT, CAPPA
  IF (J.EQ.1) THEN
    CUR2UP=-CAPPA*(C(1,2)-C(1,1))/H
    CGTR=(5.0*C(1,1)+4.0*C(1,2)-C(1,3))/B.0
    TRCUR=EXCUR*(DEXP(-EFORT*ALPHA*CGTR)-DEXP(EFORT*ALPHC*CGTR))
    F(1)=APUV*TRCUR-CUR2UP*2.0/H
  ELSEIF (J.EQ.NJ) THEN
    CUR2UP=-CAPPA*(3.0*CNJ-4.0*C(1,NJ-1)+C(1,NJ-2))/2.0/H
    CUR2DN=-CAPPA*(CNJ-C(1,NJ-1))/H
    CGTR=(5.0*CNJ+4.0*C(1,NJ-1)-C(1,NJ-2))/B.0
    TRCUR=EXCUR*(DEXP(-EFORT*ALPHA*CGTR)-DEXP(EFORT*ALPHC*CGTR))
    F(1)=APUV*TRCUR-(CUR2UP-CUR2DN)*2.0/H
  ELSE
    CUR2UP=-CAPPA*(C(1,J+1)-C(1,J))/H
    CUR2DN=-CAPPA*(C(1,J)-C(1,J-1))/H
    TRCUR=EXCUR*(DEXP(-EFORT*ALPHA*C(1,J))-DEXP(EFORT*ALPHC*C(1,J)))
    F(1)=APUV*TRCUR-(CUR2UP-CUR2DN)/H
  ENDIF
  RETURN
  END

```

C  
C

```

  MAIN PROGRAM

  IMPLICIT REAL*8(A-H, O-Z)
  DIMENSION CUR(101), TRCUR(101)
  COMMON A(10,10), B(10,10), C(10,101), D(10,21),
  1G(10), X(10,10), Y(10,10), N, NJ, ITPRT, F(10), ITCNT,
  2H, THICK, CNJ, EXCUR, ALPHA, ALPHC, APUV, EFORT, CAPPA
  OPEN (UNIT=18, FILE='input', STATUS='old')
  OPEN (UNIT=19, FILE='output', STATUS='new')
  REWIND 18
  REWIND 19
  5 READ(18,*, END=999)N, NJ, ITPRT, THICK, CNJ, EXCUR,
  1ALPHA, ALPHC, APUV, CAPPA
  EFORT=38.944
  H=THICK/FLOAT(NJ-1)
  DO 10 J=1,NJ
    C(1,J)=CNJ*DFLOAT(J-1)/DFLOAT(NJ-1)

```

```

10 CONTINUE
  CALL DIFEG,
  DO 20 J=1,NJ-1
    CUR(J)=-CAPPA*(C(1,J+1)-C(1,J))/H
    TRCUR(J)=EXCUR*(DEXP(-EFORT*ALPHA*C(1,J))
  1-DEXP(EFORT*ALPHC*C(1,J)))
20 CONTINUE
  CUR(NJ)=-CAPPA*(3.0*C(1,NJ)-4.0*C(1,NJ-1)+C(1,NJ-2))/2/H
  TRCUR(NJ)=EXCUR*(DEXP(-EFORT*ALPHA*C(1,NJ))
  1-DEXP(EFORT*ALPHC*C(1,NJ)))
  WRITE(19,200)N, NJ, ITPRT, THICK, H, CNJ, EXCUR,
  1ALPHA, ALPHC, APUV, CAPPA
  WRITE (19,201) ITCNT
  WRITE (19,202) (J, C(1, J), CUR(J), TRCUR(J), J=1, NJ)
  GO TO 5
200 FORMAT('\n', 'N=', I3, 16X, 'NJ=' I3, 12X, 'ITPRT=', I3, 10X, 'ITCNT=' I3/
  1'THICK=', G12.5, 3X, 'H=', G12.5, 4X, 'CNJ=', G12.5, 3X, 'EXCUR=', G12.5/
  2'ALPHA=', G12.5, 3X, 'ALPHC=', G12.5, 'APUV=', G12.5, 2X, 'CAPPA=', G12.5)
201 FORMAT('\n', 'ITCNT=', I3/'\n', T10, 'J', T19, 'POTENTIAL', T35,
  1'CURRENT AT J+1/2', T58, 'TRANSFER CURRENT'/)
202 FORMAT(' ', 5X, I3, 5X, G12.5, 9X, G12.5, 13X, G12.5)
999 STOP
  END

```

N= 1	NJ= 21	ITPRT= 1	ITCNT= 3
THICK= .10000e-02	H= .50000e-04	CNJ= .10000e-01	EXCUR= 60.000
ALPHA= 1.5000	ALPHC= .50000	APUV= 5000.0	CAPPA= 30.000

ITCNT= 3

J	POTENTIAL	CURRENT AT J+1/2	TRANSFER CURRENT
1	.73560e-02	-3.7748	-30.198
2	.73623e-02	-11.330	-30.221
3	.73812e-02	-18.902	-30.290
4	.74127e-02	-26.503	-30.404
5	.74569e-02	-34.144	-30.564
6	.75138e-02	-41.837	-30.770
7	.75835e-02	-49.592	-31.021
8	.76662e-02	-57.422	-31.319
9	.77619e-02	-65.337	-31.662
10	.78708e-02	-73.350	-32.052
11	.79930e-02	-81.473	-32.489
12	.81288e-02	-89.715	-32.971
13	.82783e-02	-98.091	-33.501
14	.84418e-02	-106.61	-34.077
15	.86195e-02	-115.29	-34.701
16	.88117e-02	-124.13	-35.371
17	.90185e-02	-133.15	-36.090
18	.92404e-02	-142.36	-36.856
19	.94777e-02	-151.78	-37.670
20	.97307e-02	-161.41	-38.532
21	.99997e-02	-166.23	-39.443

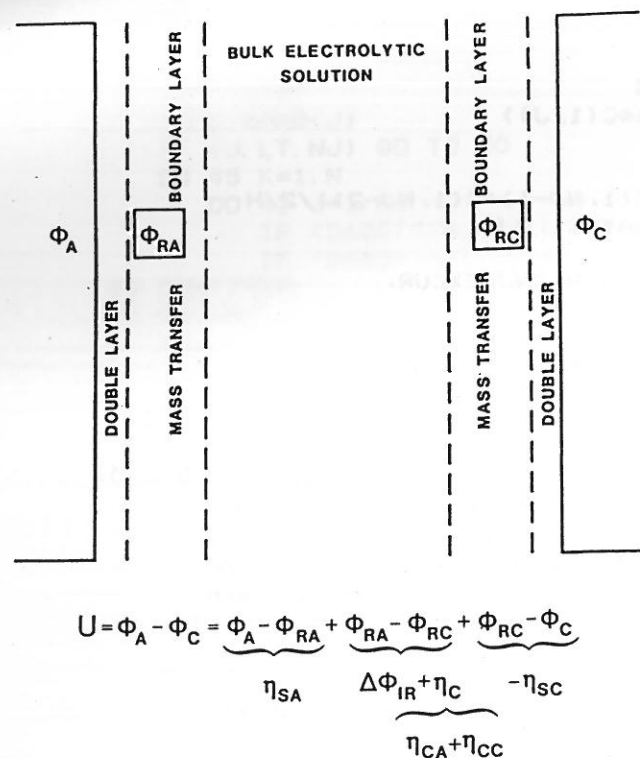


Figure 1. Schematic representation illustrating how potential drop across an electrolytic cell is subdivided into categories.

It is hardly necessary in this day of economic emphasis, encountered in every walk of life and highlighted in nearly every news journal, to define the importance of the economic aspects of electrochemical processes for the scientist, engineer, or process operator. Nevertheless, several points should be emphasized since conceding in general that "the economics are of primary importance" does not equate to application of the principle that ultimately economics will determine whether the process plant is built (or changed), as well as when, where, by what amount and in what ways. First, one key factor, is the principle that there is always an alternate to the specific proposal under consideration; there are frequently numerous alternates, and selection of the proper alternate as the base case for economic comparison is quite necessary to a correct economic decision making process.

Second, a useful economic analysis study is not trivial. It requires starting with a scope. The completeness, accuracy, and detail present in the scope define the maximum accuracy of the economic estimate. A good economic estimate demands that one spend a significant fraction of his effort toward reducing the un-addressed items and elements to the irreducible minimum, consistent with the time available to make the economic analysis.

## ECONOMIC EVALUATION OF AN ELECTROCHEMICAL PROCESS

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It is extremely helpful to define the purpose of the economic projection at the outset. Economic analyses may be undertaken for a variety of reasons. Examples of some reasons are:

1. Justify necessary approvals to construct a facility.
2. Support requests for funds to do project engineering.
3. Obtain approvals/funds to do advance materials procurement.
4. Select between alternate equipment.
5. Select between alternate processes.
6. Direct research program planning.
7. Direct process development planning.
8. Justify preliminary exploratory work.
9. Compare competitive equipment/processes.
10. Make decisions to implement minor profit improvement programs.
11. Support task force work.

The first three to five of these examples depending on the size of the organization will ordinarily be handled by professional cost estimators and economic analysts. Anyone of the latter examples frequently falls as an assignment to any company engineer or scientist.

Having identified the purpose of the work we can determine whether reasonable accuracy is needed in the total figures or