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A STUDY ON THE ELECTROCHEMICAL IMPREGNATION PROCESS IN THE MANUFACTURING OF CADMIUM ELECTRODE

FINAL REPORT

by

Yung-Chung Lin
Yuen-Koh Kao, Principal Investigator

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The electrochemical reactions, involved in the electro-chemical impregnation process for the fabrication of the cadmium electrode, contain a very complicated sequence of reactions. In this work, the electrochemical impregnation process was examined both experimentally and theoretically.

Experimentally, two sets of potentiostatic transients were obtained for a nickel microelectrode in two different electrolytes. The first set of data was obtained in an electrolyte which contained no cadmium ion; the second set of data was obtained in an electrolyte which contained cadmium ions. The

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) higher current density obtained in the second data set was due to the occurrence of the co-precipitation reaction between cadmium ions and hydroxy ions which were generated by the electrochemical reaction.

Two models, which described the transport process and reactions under two different experimental conditions were developed. The model for a cadmium-ion-free electrolyte was used to identify the rate of the heterogeneous electrode reaction by matching the model prediction with the experimental results. The heterogeneous reaction rate constants so obtained were then used to identify the rate of the homogeneous precipitation reaction by again matching its model prediction with the experimental results.

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NOMENCLATURE

A,B	discretization coefficient matrices
C_i	concentration of species i, moles/cm^3
C_i^*	dimensionless concentration of species i
C_0	concentration of substance 0, moles/cm^3
D_i	diffusion coefficient of species i, cm^2/sec
D_0	diffusion coefficient of substance 0, cm^2/sec
F	Faraday's constant, 96487 Coulomb/equiv.
I_1, I_2	cathodic current densities of reactions (24) and (25), respectively, Amper/cm^2
I	overall current density, Amper/cm^2
$J_{i,j}$	Jacobian matrix
k	homogeneous reaction rate constant, sec^{-1}
K	dimensionless homogeneous reaction rate constant, $K=k\delta^2/D_2$
K_1	cathodic rate constant of reaction (23), cm/sec
K_2	anodic rate constant of reaction (23), cm^7/moles^2-sec
K_{a1},K_{a2}	anodic rate constants of reactions (24) and (25), respectively, cm^4/moles-sec
K_{c1}	cathodic rate constant of reaction (24), cm^4/moles-sec
K_{c2}	cathodic rate constant of reaction (25), cm/sec
Ksp	solubility product of $Cd(OH)_2$, 2×10^{-23} moles^3/cm^9
n	number of electrons transferred in electrode reaction
N	number of interior collocation points
N_i	flux of species i, moles/cm^2-sec

N_0	flux of substance O, moles/cm^2-sec
r_1, r_2	reaction rates of reactions (24) and (25), respectively, moles/cm^2-sec
r	overall reaction rate of reaction (23), moles/cm^2-sec
R	universal gas constant, 8.3143 Joule/mole-deg
R_i	rate of production of species i, moles/cm^3-sec
T	absolute temperature, deg K
t	time, sec
V	applied potential, Volt
x	spatial direction
z_i	collocation point, $z_i = \xi_i / \xi_s$

Greek Letters

β_1, β_2	symmetry factors
δ	diffusion thickness, cm
ξ	spatial variable, $\xi = x/\delta$
ξ_i	collocation point
ξ_s	spline collocation point
τ	dimensionless time, $\tau = D_2 t/\delta^2$

Subscripts

i	i=1,2,3 corresponding to NO_3^-, OH^- and Cd^{+2} ions i=1,...N+2 corresponding to collocation-point number
0	reduction substance on the electrode surface

s	spline collocation point

Superscripts

b	bulk condition
o	surface condition

CHAPTER 1

INTRODUCTION

Nickel-cadmium storage batteries have been in use for more than fifty years; since World War II, new design principles have been introduced which have greatly extended their usefulness. Many theories and investigations have been put forward concerning the reaction mechanisms of both cadmium and nickel electrodes. Because the activity of the nickel electrode has been more fully characterized than that of the cadmium electrode, we will focus our attention on the behavior of the cadmium electrode.

There are a number of methods used for the fabrication of cadmium electrodes. These methods are usually classified into three categories: (a) pressed powder or pasted type(1,2,3), (b) impregnated nickel sinter type(4,5,6,7,8) and (c) electrochemical impregnation(9,10,11,12). The last method, however, is simple in operation and can, in theory, achieve high loading of active material in a single impregnation cycle at the lowest cost.

In the electrochemical impregnation process, electrochemically active material is introduced into the porous nickel plaqe by electrochemical precipitation. The plaque, which serves as a cathode, is submerged into an electrolysis cell containing an aqueous solution of cadmium nitrate at a temperature near the boiling point of the solution. The initial pH value of the impregnation solution is adjusted to around 3 by titration with nitric acid. (As the pH value of the bath increases, i.e., becomes more basic, cadmium hydroxide begins to precipitate in regions other than within the pores of the plaque, and active material is lost in the bath, which is not what we want.)

The electrochemical reaction at the cathode during impregnation could either be the liberation of hydrogen,

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- , \tag{1}$$

or the reduction of nitrate ion,

$$\begin{array}{lllll} H_2O & + NO_3^- & + 2e^- \longrightarrow & NO_2^- & +2OH^- \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 2H_2O & + NO_3^- & + 2e^- \dashrightarrow & HNO_2 & +3OH^- \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 6H_2O & + NO_3^- & + 8e^- \longrightarrow & NH_3 & +9OH^- \end{array} \; . \tag{2}$$

Both reactions produce hydroxy ions which then either diffuse away from the electrode porous surface or react with the cadmium ions present in the pores to form cadmium hydroxide. The cadmium hydroxide then deposits within the pores of the porous plaque.

The precipitation reaction is:

$$Cd^{+2} + 2OH^- \longrightarrow Cd(OH)_2. \qquad (3)$$

There is the possibility of forming cadmium according to the reduction reaction:

$$Cd(OH)_2 + 2e^- \longrightarrow Cd + 2OH^-. \qquad (4)$$

This reaction is presumably prevented from taking place by hydroxy ion generated on the electrode surface by reaction (1) or (2), so that there is no chance for cadmium ions to diffuse through the solution onto the surface and be reduced to cadmium metal.

Following impregnation, the electrode is cathodically polarized in a 25 % potassium hydroxide solution with the impregnated plate connected as the cathode and subjected to low direct anodic current (0.25 to 0.75 amp/in^2). The solution is maintained at about 100°C for a period of from 15 to 45 minutes to convert cadmium hydroxide to cadmium in the pores of the plaque by reaction (4) or to remove any nitrate ion or other undesirable reduction products. The active material of the electrode is presumed to be both cadmium hydroxide and cadmium.

In this work, the electrochemical impregnation process for the fabrication of the cadmium electrode was examined both experimentally and theoretically.

Experimentally, a set of current-density-vs.-time transients at constant applied potential were obtained for a nickel microelectrode. The current density was due to the occurrence of the electrode reaction (2) and precipitation reaction (3) presented earlier. For the purpose of identifying the electrochemical reactions, another set of current-density-vs.-time transients were obtained using an electrolyte which contained no cadmium ion. In this case, the precipitation reaction (3) no longer took place. The reactions at the electrode were the only reactions taking place.

The transient current responsed in an electrolyte which contained cadmium ions differed significantly from that in an electrolyte which did not contain the cadmium ions. This difference is presumed to be due to the precipitation reaction. The current obtained in the presence of cadmium ions in the electrolyte at any time was higher than that obtained at the same applied potential in the absence of cadmium ions. This result is explainable by the fact that the cadmium ions in the solution consumed the hydroxy ions which were produced by the heterogeneous reaction (2) and, as a result, promoted the heterogeneous electrode reactions.

The experimental current-density-vs.-time curves obtained in the potential-step experiment were used to identify both the heterogeneous electrochemical and the homogeneous precipitation reaction rate expressions. The heterogeneous rate was identified first from the experimental results in which there was no cadmium ion in the electrolyte. The precipitation rate was then identified from the experimental results in which the cadmium ions were present in the electrolyte.

A set of differential equations which described the transport process in the cadmium-ion-free solution was solved in terms of two unknown constants. The unknown constants, related to the heterogeneous electrode reactions, were identified by matching the theoretical results with the results of the experiment. The precipitation reaction rate constant was then obtained by a similar procedure.

CHAPTER 2

LITERATURE REVIEW

Impregnation of nickel sinters with cadmium hydroxide, followed by electrochemical reduction to cadmium, is the most economical method by which to fabricate cadmium electrodes. Almost all of the research works concerning this subject may be divided into three types: (a) manufacturing techniques development, (b) impregnation process study and (c) charge-discharge study.

During recent years, manufacturing techniques, especially those involving electrochemical impregnation, have employed widely varying operating conditions(13,14,15,16). There are several parameters that affect the electrochemical impregnation process such as:

1) Temperature: Beauchamp (14) emphasized the fact that high impregnation bath temperature keeps the size of cadmium hydroxide crystals small, and thereby obtaining a more active electrode.
2) pH value: In Beauchamp's process (14), the pH value was closely controlled by buffering the cadmium nitrate solution with sodium nitrite. Pickett (16) in a similar process, maintained the pH value of the cadmium nitrate bath between 3-5 by titrating the solution with proper amount of nitric acid.

3) Current density: The current density, based on apparent electrode surface, is another important variable. Beauchamp(14) used D. C. current of 4-8 amps/in^2 while Bulan (15) used alternating current of 1.2-1.6 amps/in^2 and claims that the electrode impregnated by alterning current technique retained more of its capacity after cycling as compared to electrodes fabricated by other methods. Pickett(16) presents another technique similar to the above and claims that his technique yields higher loading cadmium electrodes and achieves about 85% utilization of the active material.

The electrochemistry of the $Cd/Cd(OH)_2$ electrode in concentrated alkaline solution, typically KOH as in the Ni-Cd battery, has been studied extensively both theoretically and experimentally(17,18,19,20). Bennion, et al.(17) in their theoretical development, present two models, the solution-diffusion model and film model, in considering the failure mechanism in the performance of secondary batteries using metal/metal salt couples. They conclude that one mode of failure of the metal/metal oxide porous electrode is the blocking of the pore or the complete covering of surface by product crystallities. Falk(18) obtained X-ray diffraction patterns from electrodes submerged in electrolyte during charge and discharge by means of a special test cell. He claims that, during charge, $Cd(CH)_2$ is successfully transformed into Cd metal in the cadmium electrode, but even after a strong overcharge, this transformation is not complete, as indicated by the X-ray pattern at this stage. Furthermore, $Cd(OH)_2$ is the end product during discharge and there is no evidence of the presence of a CdO film which is believed to be responsible for the passivation of the electrode. Gross and Glocking(19) summarized the results of recent research by characterizing the negative cadmium electrode in a nickel-cadmium cell and evaluating some of the published results about which researchers still disagree among themselves, such as the mechanism for passivation, which is an important phenomena that affects the capacity of the nickel-cadmium cell.

In comparison to the extensive studies on the electrochemistry of the $Cd/Cd(OH)_2$ electrode in KOH solution, there is little information available concerning the electrochemical reactions taking place during the electrochemical impregnation process which uses cadmium nitrate solution as electrolyte. The only research works known to the author are the electrochemical impregnation studies using cycling voltammetry(21,22). They used a 0.013 cm^2 nickel microelectrode and a 0.064 cm^2 cadmium microelectrode. Some important conclusions of their studies are summarized below:

(1) There was a large reduction wave at -0.63V vs SCE(Saturated Calomel Electrode) which appeared only during the initial negative scan. This is believed to be the reduction of a solution species to liberate OH^- ion in the presence of Cd^{+2} to precipitate cadmium hydroxide on the electrode surface.

(2) A second reduction process was observed at -0.62V vs SCE during the reverse positive scan. This is due to the reductive formation of metallic cadmium from cadmium oxide or hydroxide that was deposited on the electrode surface during the previous forward scan.

(3) Some processes (or one of the processes) during the first cycle effectively passivated the electrode to further electroactivity. The formation of the gray material at -0.63V vs SCE, discussed in (1), was the most probable reason for the passivation of the electrode.

CHAPTER 3

THEORETICAL APPROACH

3.1 General

In voltammetry at constant voltage, the current through the electrolytic cell is measured as a function of time while the potential of the polarized electrode is held at a constant value. The current is affected by both the transfer process and the electrochemical and/or chemical reactions.

A plane electrode is immersed in a solution which contains a substance O. At the imposed potential, O is reduced to another substance R at the electrode surface, according to the following electrochemical reaction:

$$O + ne^- \longrightarrow R \qquad (5)$$

The current-density-vs.-time curve obtained at a constant voltage depends on both the kinetics of the electrochemical reaction and the rate of mass transfer.

Under our experimental conditions, diffusion is the only mode of mass transfer. The other two modes of mass transfer, namely, migration and convection, are insignificant. Migration is eliminated by the presence of a large excess of supporting electrolyte which reduces the potential field. Convection is avoided due to the conditions that (1) the solution is not stirred and (2) the duration of electrolysis is short, so that the density change has not yet become a significant factor and natural convection has not taken place.

The dimension of the cell, as compared to the microelectrode used, is so large that the solution may be regarded as extending to infinity; i.e., the diffusion process is semi-infinite. According to Fick's first law, the flux of the substance O at a distance x from the electrode and in the direction perpendicular to the electrode is:

$$N_O\,(x,t) = -\,D_O \frac{\partial C_O(x,t)}{\partial x} \quad . \qquad (6)$$

Conservation of the species O leads to the following differential equation:

$$\frac{\partial C_O(x,t)}{\partial t} = D_O \frac{\partial^2 C_O(x,t)}{\partial x^2} \quad , \qquad (7)$$

where C_O is the concentration of substance O, which is a function of x and t. D_O is the diffusion coefficient of substance O, and is assumed to be a constant.

When the substance 0 is reduced at a very high rate, by imposing a sufficiently large potential step, such that the concentration of this substance at the electrode surface is reduced to zero soon after the start of electrolysis, the boundary condition at the electrode/electrolyte interface for equation (7) is $C_0(0,t)=0$ for $t>0$. Initially before the electrolysis, the solution is homogeneous, and the concentration C_0 at $t=0$ is uniform with the bulk value. The other boundary condition is that C_0 approaches its bulk value when x is sufficiently large.

The electrolysis current is equal to the product of the charge involved in the reduction of one mole of substance 0 by the flux of this substance at the electrode surface. Thus the current density (current per unit electrode surface area) is:

$$I= nFN_0(0,t), \tag{8}$$

where n is the number of electrons involved in the reduction reaction of substance 0, F is the Faraday constant, and $N_0(0,t)$ is the flux of substance 0 for x=0.

The solution of the above problem is$^{(23)}$:

$$I= nFD_0^{\frac{1}{2}} C_0^b \frac{1}{\pi^{\frac{1}{2}} t^{\frac{1}{2}}}, \tag{9}$$

where C_0^b is the bulk value of substance 0.

The current density represented by equation (9) is called the limiting current density of electrochemical reaction (5). This is the maximum current density which can be achieved by this reaction. It was found that if nitrate ion is the only reducible substance, the current density predicted by equation (9) is considerably lower than the experimental value. This contradition is resolved if one realizes that under the experimental conditions water is also reduced.

At any other less-negative potential the current will depend on the electrode kinetics. Now the condition that the reducible substance concentration becomes zero after the application of the potential step has to be replaced by a kinetics equation, which is a function of potential and the concentrations of surface reactant and product. No general solution is available except for the case when the reaction rate is linearly dependent on the concentrations of the surface reactant and product(23).

3.2 Description of the Model

The real porous electrode is formed by sintering nickel powder on a nickel grid to form a plaque. The plaque serves as the cathode, which is positioned in a cadmium nitrate solution with a pH value between 3 to 5. The passage of the current produces hydroxy ions which cause the cadmium to be deposited into the porous pores. The transport phenomena associated with electrochemical reactions in a porous medium is very complicated. The approach here is to study the intrinsic reactions which take place inside the pores in a simple flat electrode. The plate electrode is submerged in a semi-infinite pool of electrolyte so that the mass transfer problem can be treated as a one-dimensional problem in the x-direction (perpendicular to the electrode surface). In the solution side, there is a thin double-charge layer near the electrode. The thickness of the double layer is on the order of 10 to 100 Å. It is too thin to be probed adequately, and the theory of the diffuse layer is a microscopic, rather than a macroscopic, phenomena. The mass transfer region to be considered here is thus located outside of this double layer.

The electrodeposition process operates on the principle that the hydroxy ion, which is generated by the reduction process, coprecipitates with the cadmium ion in the solution to form cadmium hydroxide crystalloid. The approach taken here to unravel the complicated sequence of reactions is to form a model which describes the transport processes and reactions. The model will first be used to analyze the experimental results obtained under the condition of no pricipitation reaction, by using an electrolytic solution which is free of cadmium ions. The heterogeneous reduction reaction will be determined. The transport and reaction problems will then be examined in the case when the solution contains cadmium ions. The rate of the precipitation reaction will then be determined by matching the model's prediction and the experimental results.

3.3 Formulation of Transport Process Equations

Three ionic species to be considered in the electrochemical system are NO_3^-, OH^- and Cd^{+2} ions. In the absence of migration and convection, the flux of each species is expressed as(24):

$$N_i = - D_i \frac{\partial C_i}{\partial x} \quad , \; i=1,2,3 \; , \qquad (10)$$

where N_i is the flux of species i (moles/cm^2-sec),
D_i is the diffusion coefficient of species i (cm^2/sec),
C_i is the concentration of species i (moles/cm^3), which is a function of both x and t, and i=1,2,3 corresponding to NO_3^-, OH^- and Cd^{+2} ions.

The equation of continuity of each species is(24):

$$\frac{\partial C_i}{\partial t} = - \frac{d\,N_i}{d\,t} + R_i \; , \quad i=1,2,3 \; , \qquad (11)$$

where R_i is the rate of production of species i (moles/cm^3-sec) by precipitation reaction, which occurs only in the presence of cadmium ions.

Substitution of equation (10) into (11) gives

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} + R_i \;, \quad i=1,2,3 \tag{12}$$

It is assumed that the precipitation reaction (3) can be treated as a homogeneous reaction and is linearly proportional to the degree of supersaturation. Therefore, the consumption rate of cadmium ion due to this reaction is :

$$R_3 = -k\left[C_3 - \frac{Ksp}{(C_2)^2}\right] \;, \tag{13}$$

where k is the homogeneous reaction rate constant (sec^{-1}),

Ksp is the solubility constant of Cd(OH)$_2$

and has the value of 2x10^{-23} (moles^3/cm^9)$^{(25)}$.

By the stoichiometric relation of equation (3), the consumption rate of hydroxy ion due to the same reaction is :

$$R_2 = 2\,R_3 = -2\,k\left[C_3 - \frac{Ksp}{(C_2)^2}\right] . \tag{14}$$

Substitution of equations (13) and (14) into equation (12) leads to the following two differential equations :

$$\frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial x^2} - 2\,k\left[C_3 - \frac{Ksp}{(C_2)^2}\right] , \tag{15}$$

$$\frac{\partial C_3}{\partial t} = D_3\frac{\partial^2 C_3}{\partial x^2} - k\left[C_3 - \frac{Ksp}{(C_2)^2}\right] \qquad (16)$$

For NO_3^- ion,

$R_1 = 0.$

Equation (12) for NO_3^- ion may be reduced to :

$$\frac{\partial C_1}{\partial t} = D_1\frac{\partial^2 C_1}{\partial x^2} \quad . \qquad (17)$$

Only two of the three differential equations need to be solved for the concentration profiles, due to the electroneutrality condition$^{(24)}$:

$$2C_3-C_1-C_2=0 \quad . \qquad (18)$$

Substitution of equation (18) into equation (15) gives:

$$\frac{\partial C_2}{\partial t} = D_2\frac{\partial^2 C_2}{\partial x^2} - 2k\left[\frac{1}{2}(C_1+C_2)-\frac{K_{sp}}{(C_2)^2}\right] \quad . \qquad (19)$$

Equations (17) and (19) are solved simultaneously to obtain the concentration profiles of C_1 and C_2, i.e., NO_3^- and OH^- ions. The C_d^{+2} profile can then be obtained by equation (18) from the known profiles of C_1 and C_2.

A set of differential equations, which are simpler than equations (17) and (19), are obtained when the electrolyte contains no cadmium ion. In the absence of cadmium ion, the precipitation reaction (3) can not occur; thus, R_i terms are all equal to zero. Equation (12) is then reduced to:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2}, \quad i=1,2 \ , \tag{20}$$

in which i=1,2 corresponds to NO_3^- and OH^- ions.

Equation (20) is written for C_1 and C_2:

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2} \quad , \tag{21}$$

$$\frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial x^2} \quad . \tag{22}$$

The other condition, the concentrations of various ions at the electrode/electrolyte interface after the start of the current flow, has to be described by the electrode kinetics of the reduction reaction of NO_3^- ions.

3.4 Electrode Kinetics

The possible reduction reactions are numerous, as shown in equation (2). Since in each reaction, OH^- ion is generated, we will represent the production of OH^-

ions as the following electrochemical reaction:

$$2H_2O + NO_3 + 2e^- \longrightarrow HNO_2 + 3OH^-. \qquad (23)$$

Because there are two electrons involved in the reaction, it is likely not an elementary step. Let's assume the reaction comprises two elementary steps, each step involving the transfer of one electron, and a dissociation reaction:

$$NO_3^- + H_2O + e^- \underset{K_{a1}}{\overset{K_{c1}}{\rightleftharpoons}} NO_2^- + (OH)_2^- \qquad \text{(slow)}, \qquad (24a)$$

$$(OH)_2^- + e^- \underset{K_{a2}}{\overset{K_{c2}}{\rightleftharpoons}} 2OH^- \qquad \text{(fast)}, \qquad (24b)$$

$$NO_2^- + H_2O \overset{K_d}{\rightleftharpoons} HNO_2 + OH^- \qquad \text{(fast)}, \qquad (25)$$

where K_{c1} and K_{c2} are cathodic reaction constants, and K_{a1} and K_{a2} are anodic reaction constants, respectively. K_d is the dissociation reaction constant. $(OH)_2^-$ ion is an unstable intermediate ion which immediately enters the next reaction (24b). The rates of these elementary steps should always be proportional to each other. For the elementary steps listed above, reaction (24b) should occur once every time reaction (24a) occurs.

Let I_1 and I_2 denote the cathodic current densities of reactions (24a) and (24b), and r_1 and r_2 denote the reaction rates of reactions (24a) and (24b), respectively.

Then, the relationship between r_1, I_1 and surface ion concentrations of NO_3^-, $(OH)_2^-$, which appear in elementary step (24a), may be written as$^{(26)}$:

$$r_1 = \frac{I_1}{nF} = \frac{I_1}{F} \qquad (n=1)$$

$$= K_{a1}\left[C^o_{NO_2^-}\right]\left[C^o_{(OH)_2^-}\right] \exp\left[\frac{(1-\beta_1)F}{RT} V\right]$$

$$-K_{c1}\left[C^o_{NO_3^-}\right]\left[C^o_{H_2O}\right] \exp\left[-\frac{\beta_1 F}{RT} V\right] . \qquad (26)$$

Similarly, for reaction (24b), one has:

$$r_2 = \frac{I_2}{nF} = \frac{I_2}{F} \qquad (n=1)$$

$$= K_{a2}\left[C^o_{OH^-}\right]^2 \exp\left[\frac{(1-\beta_2)F}{RT} V\right]$$

$$-K_{c2}\left[C^o_{(OH)_2^-}\right] \exp\left[-\frac{\beta_2 F}{RT} V\right], \qquad (27)$$

where β_1 and β_2 are symmetry factors representing the fractions of applied potential V, which promotes the cathodic reaction. $C^o_{NO_3^-}$, $C^o_{(OH)_2^-}$ and $C^o_{OH^-}$ are the surface ion concentrations of NO_3^-, $(OH)_2^-$ and OH^- on the electrode surface.

Since reactions (24a) and (24b) occur at the same rate, we have:

$$I = I_1 + I_2 = 2I_2 = 2I_1 ,$$

where I is overall current density. It is further assumed that reaction (24b) is fast, and is essentially in equilibrium. From equation (27),

$$C^o_{(OH)_2^-} = \frac{K_{a2}\left[C^o_{OH^-}\right]^2 \exp\left[\frac{(1-\beta_2)F}{RT}V\right]}{K_{c2}\exp\left[-\frac{\beta_2 F}{RT}V\right]} \qquad (28)$$

and $\frac{I_1}{F} = \frac{I}{2F}$ =r = overall reaction rate. (29)

Substituting equation (28) into equation (26) and combining equation (29) gives:

$$\frac{I}{2F} = r = \frac{K_{a1}K_{a2}}{K_{c2}}\left[C^o_{NO_2^-}\right]\left[C^o_{OH^-}\right]^2 \exp\left[\frac{(2-\beta_1)F}{RT}V\right]$$

$$- K_{c1}\left[C^o_{NO_3^-}\right]\left[C^o_{H_2O}\right]\exp\left[-\frac{\beta_1 F}{RT}V\right] \quad . \qquad (30)$$

From reaction (25) one may write

$$K_d = \frac{\left[C^o_{HNO_2}\right]\left[C^o_{OH^-}\right]}{\left[C^o_{NO_2^-}\right]\left[C^o_{H_2O}\right]} \quad .$$

Substitution of the above expression into equation (30) leads to:

$$\frac{I}{2F} = r = \frac{K_{a1}K_{a2}}{K_{c2}K_d} \frac{\left[C^o_{HNO_2}\right]\left[C^o_{OH^-}\right]^3}{\left[C^o_{H_2O}\right]} \exp\left[\frac{(2-\beta_1)F}{RT} V\right]$$

$$- K_{c1}\left[C^o_{NO_3^-}\right]\left[C^o_{H_2O}\right] \exp\left[-\frac{\beta_1 F}{RT} V\right] . \qquad (31)$$

This is an overall expression of the relationship among the current density, surface concentrations of ions involved in the reaction (23) and applied potential. When the applied potential is kept constant and the surface concentrations of H_2O and HNO_2 are almost constant, equation (31) is simplified to:

$$\frac{I}{2F} = r = K_2\left[C^o_{OH^-}\right]^3 - K_1\left[C^o_{NO_3^-}\right], \qquad (31a)$$

where $K_2 = \frac{K_{a1}K_{a2}}{K_{c2}K_d} \frac{\left[C^o_{HNO_2}\right]}{\left[C^o_{H_2O}\right]} \exp\left[\frac{(2-\beta_1)F}{RT} V\right]$,

$$K_1 = K_{c1}\left[C^o_{H_2O}\right] \exp\left[-\frac{\beta_1 F}{RT} V\right] .$$

One can see from equation (31a) that the reaction is third order with respect to OH^- ion and first order with respect to NO_3^- ion. Equation (31a) will be used as one of our boundary conditions to be discussed in the next section.

3.5 Initial and Boundary Conditions

For both cases, i.e., electrolyte containing cadmium ions and electrolyte containing no cadmium ions, two initial and four boundary conditions are needed to solve the differential equations (17) and (19) or (21) and (22).

At t=0, the concentration of each ion is equal to its bulk value at each point along the x-direction. The initial conditions are as follows:

1. at t=0, $C_1 = C_1^b$ for all x,
2. at t=0, $C_2 = C_2^b$ for all x,

where the superscript "b" denotes the bulk condition.

The first boundary condition is the consequence of the fact that the flux at the interface has to be equal to the rate of heterogeneous electrode reaction, i.e.:

$$\left[-D_1 \frac{\partial C_1}{\partial x}\right]_{x=0} = K_2 \left[C_2^o\right]^3 - K_1 \left[C_1^o\right], \qquad (32)$$

where superscript "o" denotes the surface condition. To satisfy the stoichiometric relation of equation (23), one has, at x=0:

$$3\left[-D_1 \frac{\partial C_1}{\partial x}\right]_{x=0} = \left[D_2 \frac{\partial C_2}{\partial x}\right]_{x=0} . \qquad (33)$$

This is the second boundary condition. The other two boundary conditions are:

3. at $x=\infty$, $C_1 = C_1^b$,
4. at $x=\infty$, $C_2 = C_2^b$.

That is, the concentrations far away from the electrode/electrolyte interface do not change.

The flux in equation (32) is proportional to the current density as a function of time:

$$I = -2FD_1\left[\frac{\partial C_1}{\partial x}\right]_{x=0} \tag{34}$$

CHAPTER 4

EXPERIMENTAL WORKS

A potential-step was generated from a function generator and was applied to the working electrode/electrolyte interface in the electrochemical cell. The cathodic current was thus sampled and stored in memory at a constant time interval by a microcomputer. The resulting current/time transient was then plotted by a x-y recorder or printed out by a line printer by recalling these current data from the memory of the microcomputer.

4.1 The Electrochemical Cell

The current transient under a potential step condition was obtained in a three-electrode cell. The cell and electrodes configuration is shown in Figure 1. The working electrode was a nickel microelectrode. It was made of a nickel wire which was pressure-fitted into a teflon cylinder. The flat, exposed surface was 0.013 cm^2. A saturated calomel electrode (SCE) and a cadmium bar were used as the reference and the counter electrodes, respectively.

The cell was filled with electrolyte of either

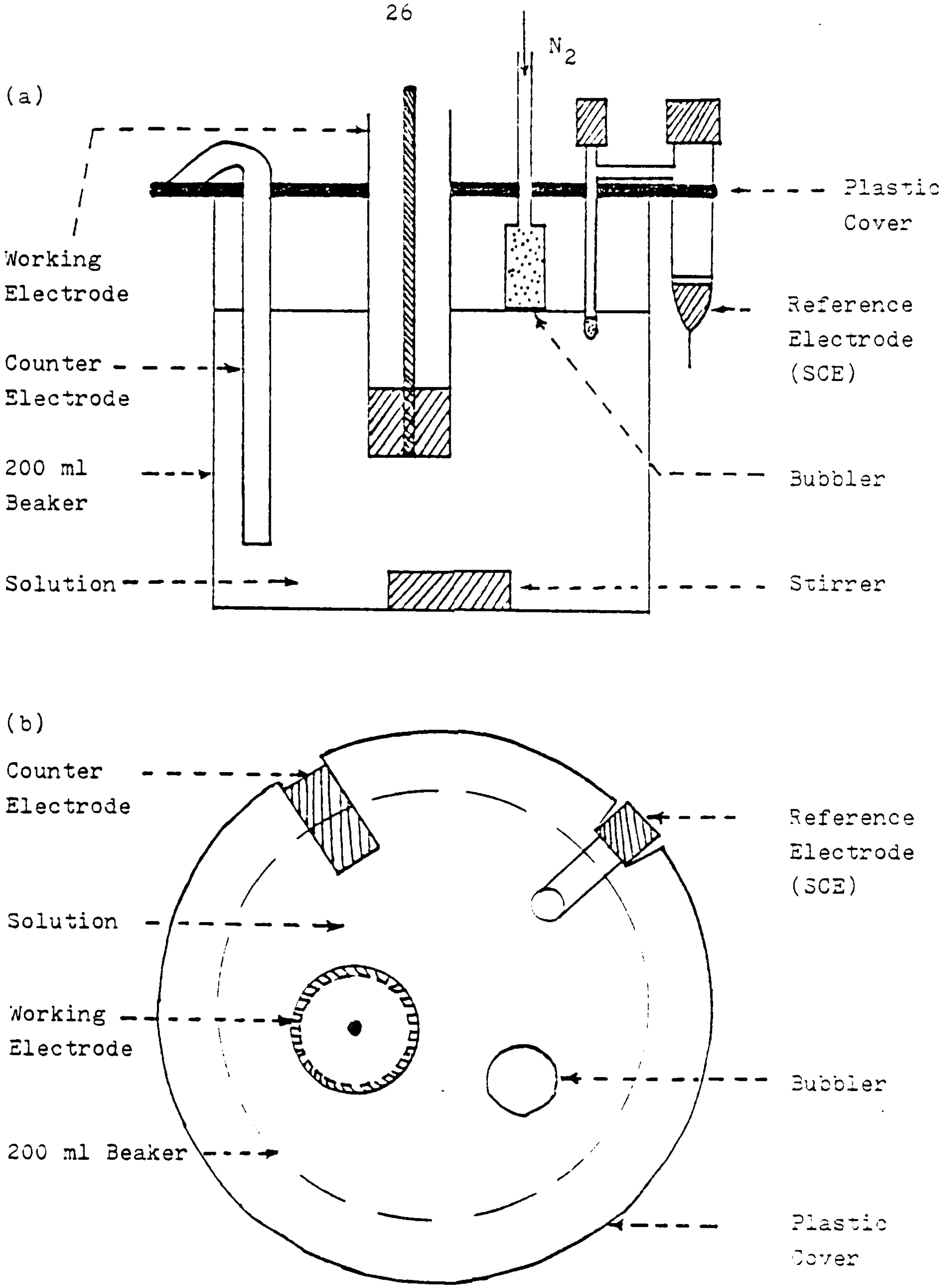


Figure 1. The Electrochemical Cell: (a) Side View, (b) Top View.

cadmium nitrate solution or potassium nitrate solution. The pH value of the solution was controlled. Potassium chloride was used as the supporting electrolyte. The electrolytic solution was not stirred during the experiment, so that the conditions of semi-infinite linear diffusion were maintained.

Two experimental parameters were varied:

1) the ion concentration of the solutions and
2) the magnitude of the potential-step applied to the interface.

4.2 The Instruments and Electrical Setup

The block diagram for the experiment setup is shown in Figure 2. The instruments shown in Figure 2 contain the following equipment:

a) A Princeton Applied Research (PAR) Model 173 Potentiostat/Galvanostat: In the experiment, the operating mode was set at CONTROL E., which means that the instrument functioned as a potentiostat. The current was measured while keeping the potential of the working electrode constant. This was accomplished by setting the counter electrode to the required level so that the working electrode potential was at a programmed potential with respect to the reference electrode. The instrument is provided with a Model 176 Current-to-Voltage Converter which is the "basic" plug-in

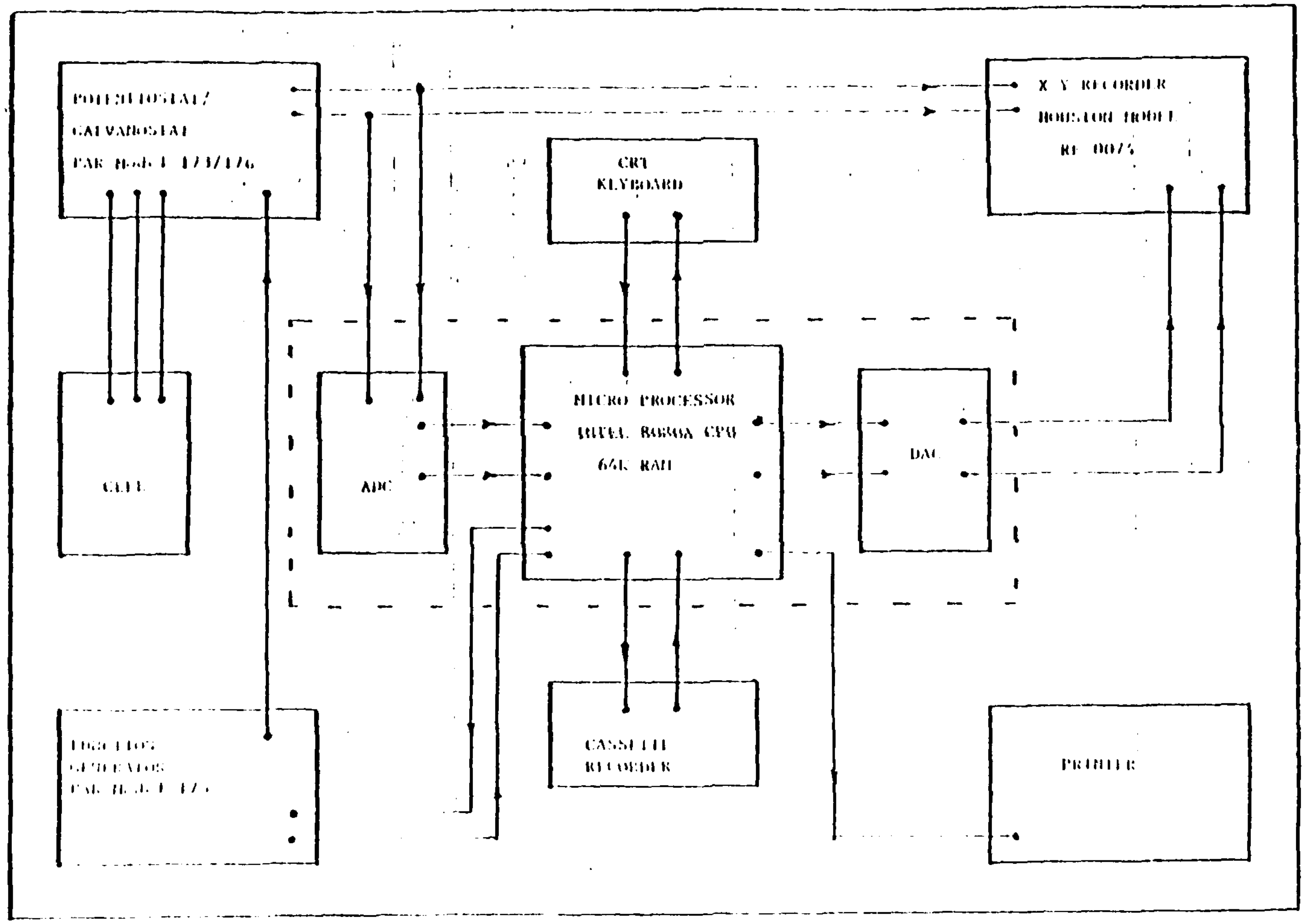


Figure [illegible]. Block Diagram for the Determination of the Current vs Time Relation.

module. The M 176 provides a dc voltage output which is proportional to the current. The cell current can be either displayed on the panel, by a x-y recorder, or monitored by the microcomputer. Connection to the cell was made through the external cable. The counter electrode was connected to the red clip, the working electrode to the green clip and the reference electrode to the Electrometer Probe which has a very high impedance, thereby insuring us that the current was flowing to the reference electrode.

b) A PAR Model 175 Function Generator: This is a programmable waveform generator which has two operating modes, SWEEP and PULSE. The former generates a sequence of triangular waves, while the latter generates a sequence of step function. For the potential step experiment, the operating mode was set at PULSE mode and the pulse width selector at STEP position. The magnitude of the step function was set by the setting of the B potential (upper limit) in the POTENTIAL section on the front panel of this instrument.

c) An Intel CPU 8080A Bases Microcomputer (64K RAM): The microcomputer was the central part of the experimental setup. The functions of the microcomputer in the experiment were:

(1) to trigger the Function Generator which activated the potential step presented earlier.

(2) to sample the current outputs from the M 176 Converter and store them in the memory.

(3) to convert these digital data back into analog signals

and then plot them on the x-y recorder.

(4) to print the digital data on the line printer.

(5) to store these digital data in the tapes.

The peripheral equipment of the microcomputer include a CRT (TV screen), the keyboard, a cassette recorder and a line printer.

d) A Houston Model RE 0074 x-y Recorder: The Recorder receives the analog outputs from the DAC (Digital-Analog Converter) and plots them on the graph paper.

4.3 The Computer Program

A computer program written in BASIC language was used to carry out the experiment. The program consists of a main program and a machine-language subroutine called "MUG". This subroutine includes an execution statement which generates a trigger signal to activate the Function Generator. A potential step was then immediately applied to the working electrode, and thereafter the computer started to sample and store the current output at a fixed time interval. The analog signal was converted into a digital datum by a 12 bits ADC (Analog-Digital Converter) and then stored in the memory. When the number of samples reached a preset value, the sampling routine was terminated. The digital signals stored in the memory were binary numbers. These data were converted into decimal numbers and then converted into analog signals, and finally plotted on the x-y recorder and printed on the line printer. This was executed by the main program. The main program and the "MUG" subroutine are presented fully in Appendix A1 and A2.

4.4 Experimental Conditions and Procedures

In the experiment, the initial pH value of the electrolyte was maintained at 3.0, which was the condition used in the actual electrochemical impregnation process. This was accomplished by titrating the electrolytic solution with a concentrated HCl solution. The concentrations of nitrate ion used were 0.005M, 0.0025M and 0.00125M prepared from either the KNO_3 or $Cd(NO_3)$ solution. The cadmium ion concentrations were 0.0025M, 0.00125M and 0.000625M. All the electrolytic solutions contained 0.5M KCl as the supporting electrolyte.

It was found later that the electrolysis of water made significant contribution to the total current, because the current obtained was significantly higher than the limiting current. In order to obtain the current due only to the reduction of nitrate ions, several runs with solutions which contained no nitrate ion were conducted. The solutions used for this purpose were either water or 0.0025M $CdCl_2$ solution. Both solutions contained 0.5M KCl as the supporting electrolyte. This current was subtracted from the current obtained in the presence of nitrate ions in the solution. The resulting current is the faradic current of the reduction of nitrate ions.

The magnitudes of the potential-step used in this study were -0.40V, -0.60V and -0.80V versus the equilibrium potential which was at approximately -0.354V vs SCE.

The experimental procedures are listed blow:

(1) The electrical circuit was set up as shown in Figure 2, except that the cell was disconnected from the Potentiostat/ Galvanostat by setting the cell selector on the instrument to the OFF position. A proper current range was then chosen from the Current Range Switch to make sure that the current output would not be overloaded. The Function Generator was initialized by depressing the INITIAL control pushbuttom. The initial potential was set at zero volts.

(2) A known volume of electrolytic solution and an equal volume of supporting electrolyte, KCl, were added to the cell and titrated with HCl solution to a pH value of 3.0. The solution was then deaerated by bubbling purified nitrogen through the stirred solution for about ten minutes. The gas continued to pass above the solution during the experiment.

(3) After the working electrode surface was polished by a 3/0 alumina paper, it was rinsed thoroughly with distilled

and deionized water, and then was positioned in the cell. The electrodes (the working electrode, counter electrode and reference electrode) were then connected to the Potentiostat/Galvanostat as described in section 4.3. After the electrodes were correctly connected, the cell selector was switched to the EXTERNAL CELL position. The rest potential of the solution could be determined by turning the knob in the APPLIED POTENTIAL/CURRENT section of the front-panel of the Potentiostat/Galvanostat so that the current reading displyed on the front panel meter was zero. The applied potential was then the rest potential.

(4) The upper limit (B potential) on the Function Generator was set. The value of the B potential plus the rest potential was the total potential applied to the electrochemical cell.

(5) The experiment was initiated by running the computer program. The current/time data were stored in the computer's memory and then the results were converted to line printer output.

4.5 Experimental Results

Two sets, a total of twenty-two runs, were made. The first set of runs was conducted in solutions which contained no cadmium ion. The second set of runs was made in solutions which contained cadmium ions. For each set of runs, blank runs were made in the solutions without the presence of nitrate ion for the purpose of determining the background current due to the water decomposition reaction. The solution for blank runs for the first set was water, while the solution for blank runs for the second set was made by using the 0.0025M $CdCl_2$ solution.

The current-density-vs.-time data printed by the H 14 Line Printer are shown in Table B.1 through Table B.22 in appendix B. The measured current was converted to the current density which appears in those tables. This is calculated by dividing the current by the electrode surface area $0.013cm^2$.

Tables B.1 through B.9 are the first data set which used potassium nitrate as the electrolytic solution, while Tables B.10 through B.12 are the background currents of water used to subtract from the first data set.

Tables B.13 through B.21 are the second data set which used cadmium nitrate as the electrolytic solution, while Table B.22 is the background current of water in the presence of cadmium ions.

A series of current-density-vs.-time curves with various electrolytic solution concentrations and applied overpotentials are shown in Figures 3 through 6. In these figures, the current due to the electrolysis of water has been eliminited by using the routine tabulated in Table 1.

Figures 3 through 5 are the current-density-vs.-time curves obtained in the solutions which did not contain cadmium ion. Figure 3 shows the current-density-vs.-time curves obtained in a solution containing 0.005M nitrate ion and at potentials -0.40V, -0.60V and -0.80V from the equilibrium potential. Figure 4 shows the current-density-vs.-time curves obtained in a solution containing 0.0025M nitrate ion, and at potentials -0.40V, -0.60V and -0.80V from the equilibrium potential. Figure 5 shows the current-density-vs.-time curves obtained in a solution containing 0.00125M nitrate ion at -0.40V, -0.60V and -0.80V from the equilibrium potential. Due to the lack of blank runs with 0.00125M and 0.000625M cadmium ion concentrations and -0.60V and -0.80V from the equilibrium potential, only one current-density-vs.-time curve was obtained with 0.005M nitrate ion and 0.0025M cadmium ion concentration at the potential of -0.40V from the equilibrium potential. This is shown in Figure 6.

4.6 Discussion of Experimental Results

Some characteristics can be seen from the curves shown in Figures 3 through 6.

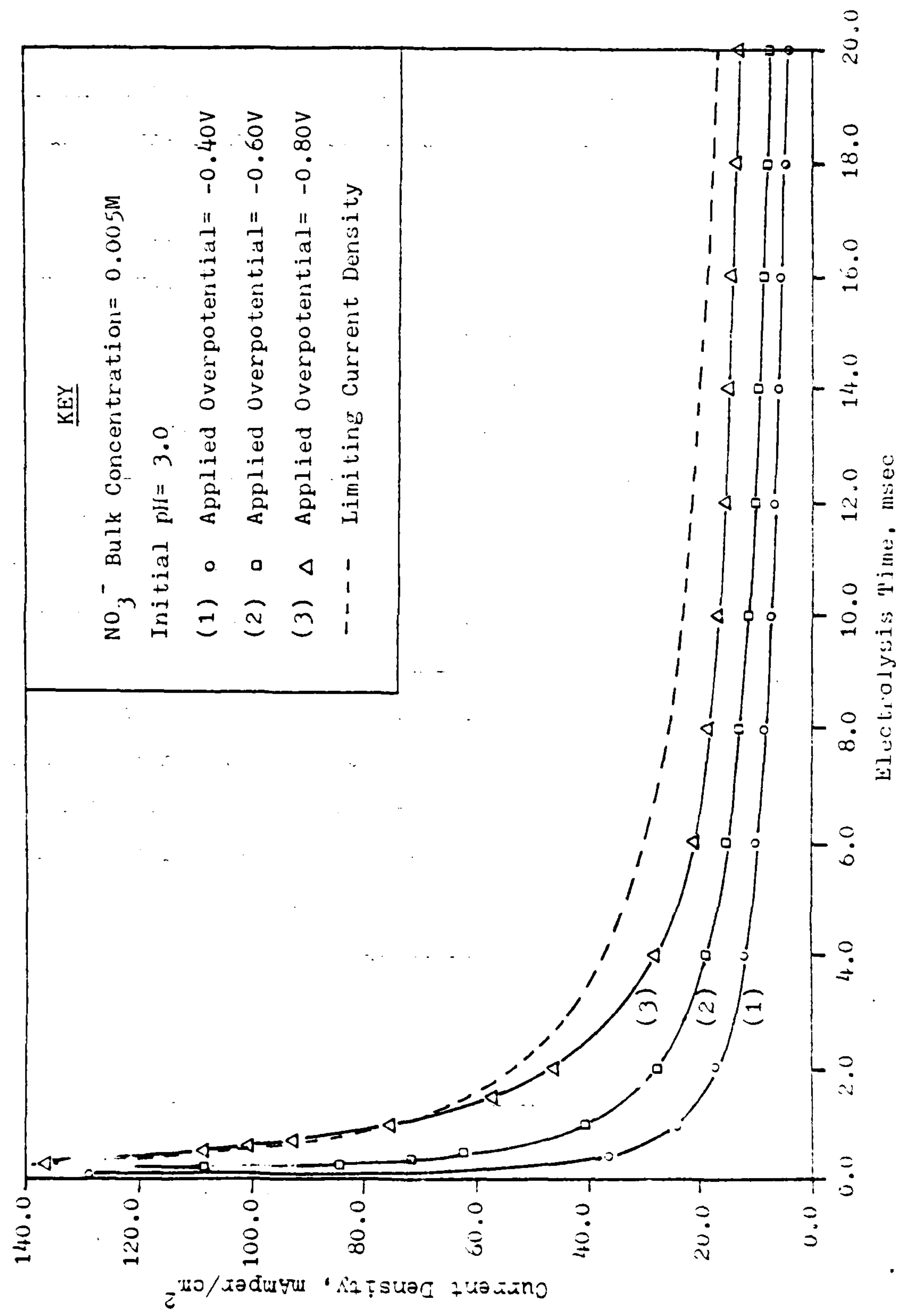


Figure 3: Current-Density-vs.-Time Curves in the Case of Electrolyte Containing No Cadmium Ion.

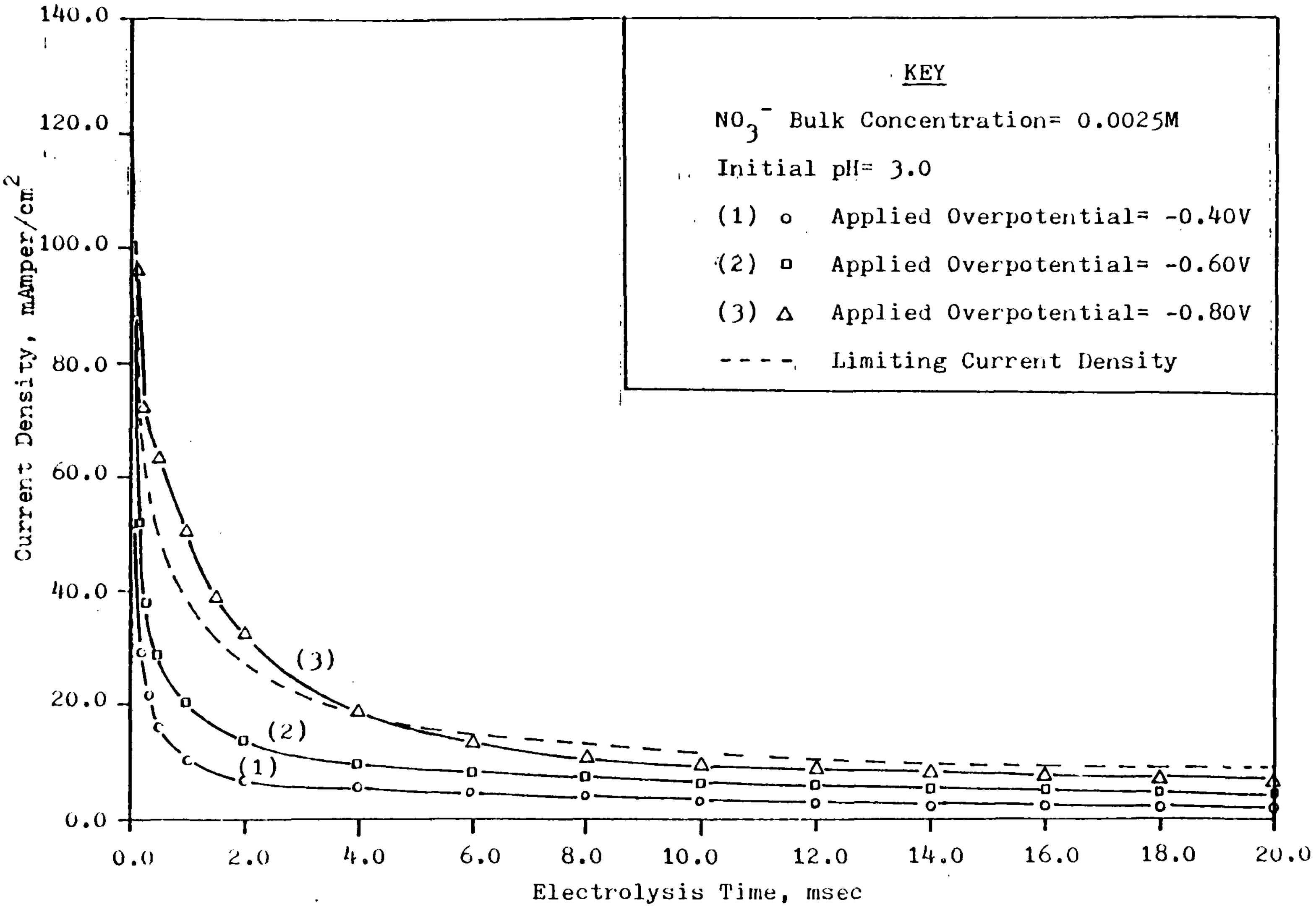


Figure 4: Current-Density-vs.-Time Curves in the Case of Electrolyte Containing No Cadmium Ion.

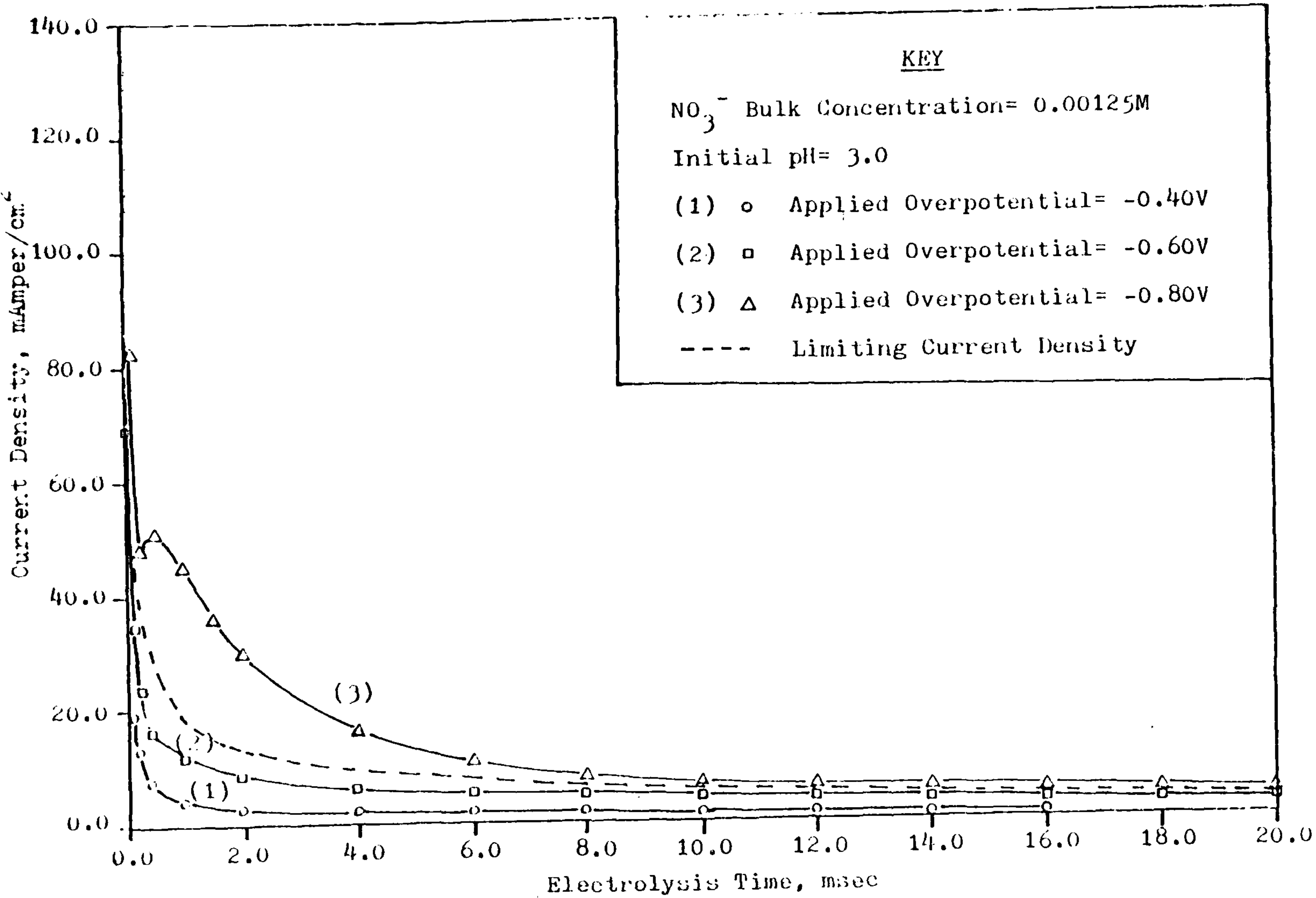


Figure 5: Current-Density-vs.-Time Curves in the Case of Electrolyte Containing No Cadmium Ion.

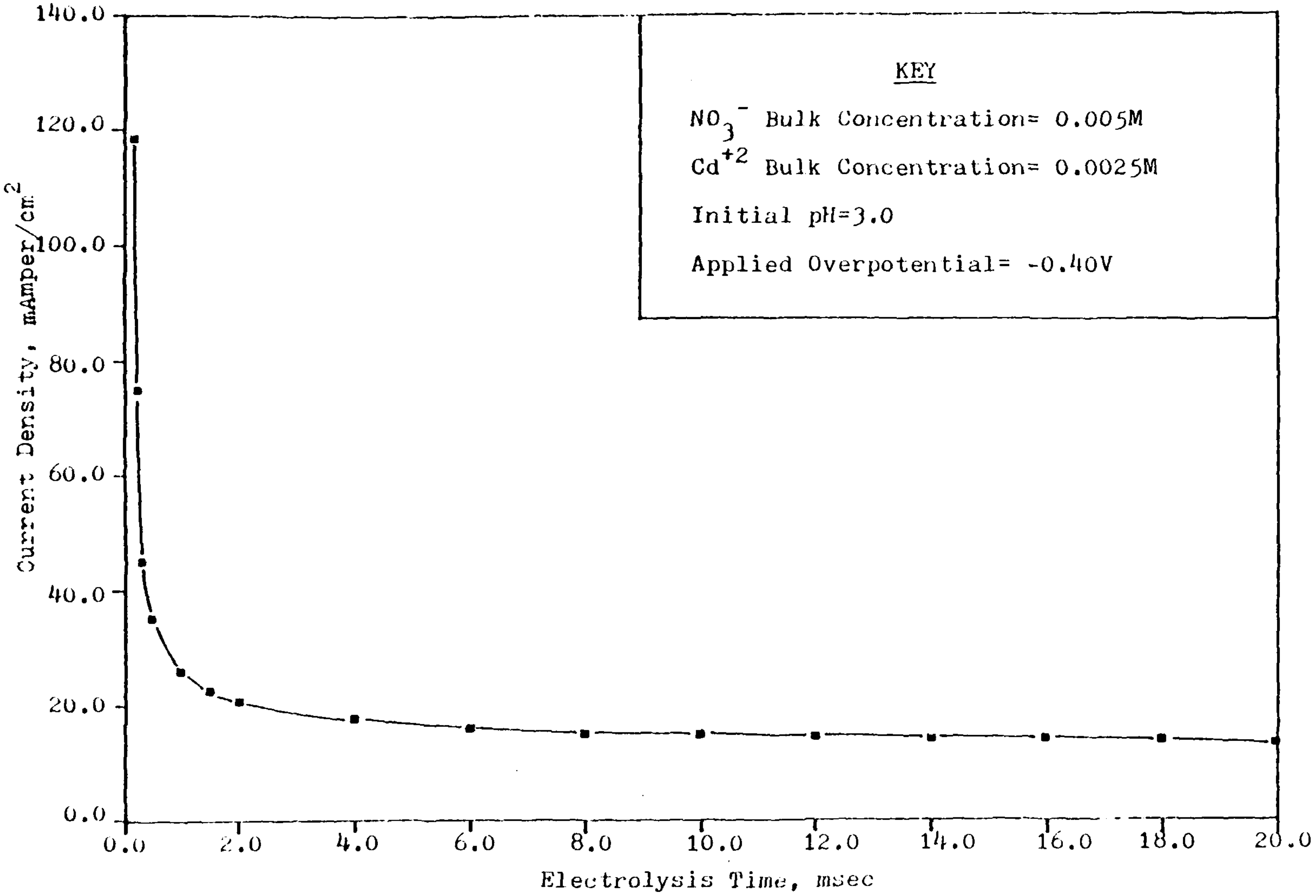


Figure 6: Current-Density-vs.-Time Curve in the Case of Electrolyte Containing 0.0025M Cadmium Ion.

Table 1: Evaluation of Current-Density-vs.-Time Data Plotted in Figures 3 Through 6.

Figure is plotted		by subtracting the corresponding current density at each time point in	from that of in
Figure 3	(1)	Table B.1	Table B.10
	(2)	Table B.2	Table B.11
	(3)	Table B.3	Table B.12
Figure 4	(1)	Table B.4	Table B.10
	(2)	Table B.5	Table B.11
	(3)	Table B.6	Table B.12
Figure 5	(1)	Table B.7	Table B.10
	(2)	Table B.8	Table B.11
	(3)	Table B.9	Table B.12
Figure 6		Table B.13	Table B.22

Firstly, the current density decays with time in a hyperbolic fashion. This is the result of depletion of the NO_3^- ions near the electrode surface. Theoretically, there is an initial sharp rise of current associated with double-layer charging(27), due to the application of a potential-step. This was not observed in the experiment, however, because the time for charging is usually very short as compared to the electrolysis time.

Secondly, the sharp current drops in the beginning indicate that very sharp concentration gradients are established for the nitrate ions and the hydroxy ions as soon as the surface reaction (23) takes place. The concentration gradients are gradually decreased due to the diffusion layer extending in the direction of decreasing concentration gradients. The result is that the decay of the current density is not as fast as in the beginning.

The curves for the case of potential at -0.80V from the equilibrium potential and solutions containing 0.0025M and 0.00125M nitrate ion, as shown in the upper-most curves in Figures 4 and 5, respectively, are somewhat different from the others. These two curves do not follow the same trends as their lower potential counterparts. It is suggested that the reactant, nitrate ion, near the electrode surface, is used up in a very short time and another reaction must be taking place. This behavior is the most pronounced as shown in the upper-most curve in Figure 5. A maximum current is observed at time equal to about 0.5 msec. This curve thus strongly supports our explanation that some other reaction is taking place at that time. On the other hand, the absence of this behavior in the curve for the case of 0.005M nitrate ion shown in the upper-most curve in Figure 3 suggests that the nitrate ion concentration near the electrode surface is not zero.

Two parameters were varied in the experiment, i.e., the concentration of the electrolyte solutions and the value of the potential from the equilibrium potential (rest potential). The changing of either the bulk concentration of the electrolyte solutions or the overpotential that is applied to the working electrode will change the value of the current density. For a given bulk concentration, the increase in the applied overpotential increases the electrochemical reaction rate on the electrode surface. The effect of the applied overpotential on the current density can also be observed in Figures 3 through 5. In each of these figures, a plot of the limiting current-density-vs.-time curve is also shown. The limiting current density is calculated by equation (9) with the corresponding bulk concentration of the nitrate ion. Recall that the limiting current is defined as maximum current one can obtain as the applied overpotential is increased. The surface concentration of the reactant for the case of limiting current is, in fact, zero at any time. After examining Figures 3 through 5, we find that, for the case of -0.80V, some of the values of current density exceed the limiting current density. This phenomenon becomes more significant when the bulk concentration of potassium nitrate is decreased. The reason for this phenomenon probably is that at the high applied overpotential, many reactions can subsequently be expected to take place. The maximum current appearing in the curve for the case of -0.80V is a result of this behavior.

When the applied overpotential is fixed, the heterogeneous reaction rate constants in both the cathodic and anodic directions, K_1 and K_2, are fixed. The supply of the nitrate ions on the electrode surface comes only in the way of diffusion of the nitrate ions from the bulk solution. Increasing the bulk concentration will increase the rate of nitrate ion supply to the electrode surface, thusly increasing the current density. Figures 7 through 9 show the effect of the bulk concentration of the electrolytic solution on the current density with fixed applied overpotential. From the three figures, we can see that the current density is approximately proportional to the bulk concentration of potassium nitrate, except for the case of -0.80V.

When electrolytic solution contains cadmium ions, a different set of results was obtained. The experimental current-density-vs.-time curve obtained in a 0.0025M

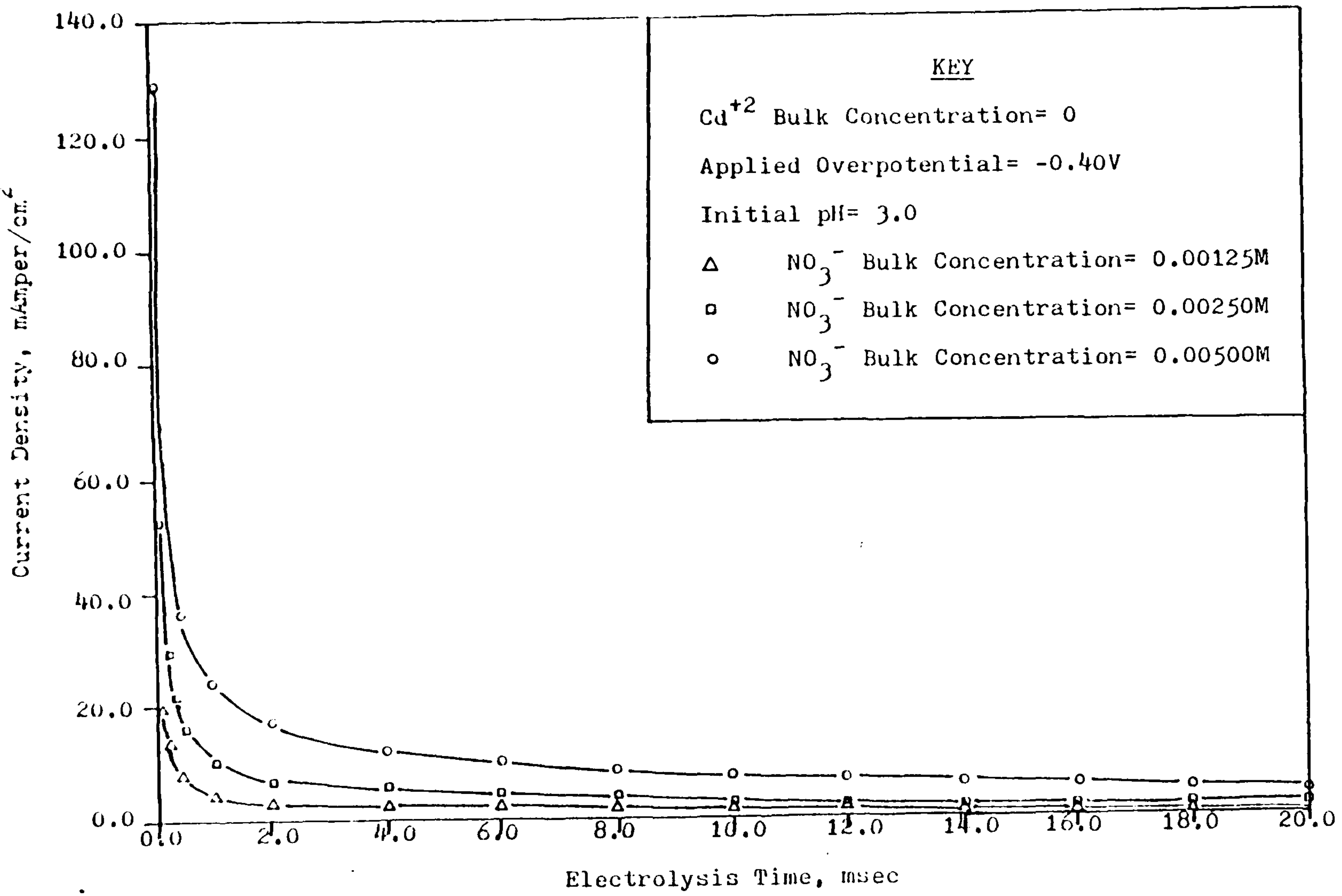


Figure 7: Effect of the Bulk Concentration of the Electrolytic Solution on the Current Density with Fixed Applied Overpotential.

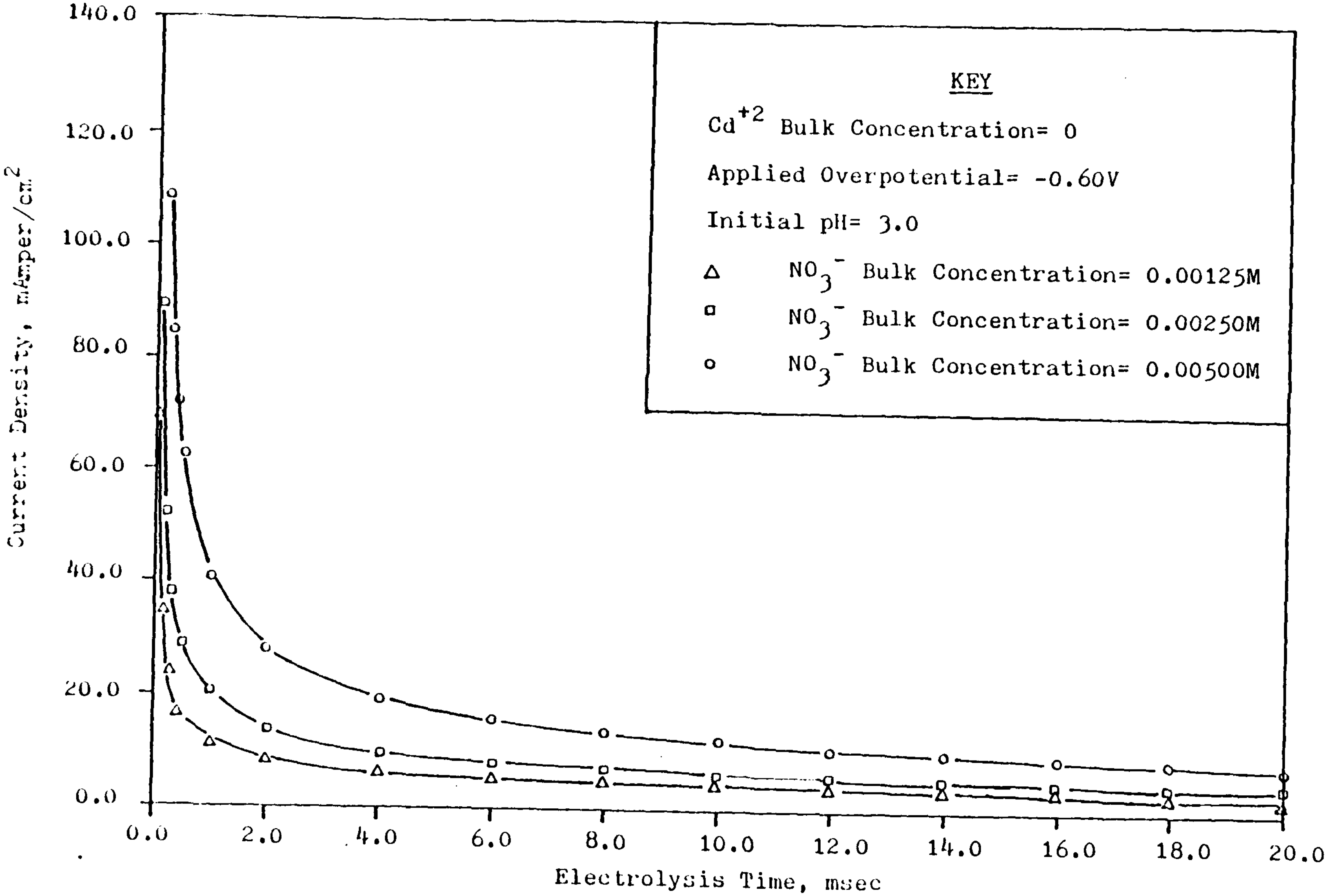


Figure 8: Effect of the Bulk Concentration of the Electrolytic Solution on the Current Density with Fixed Applied Overpotential

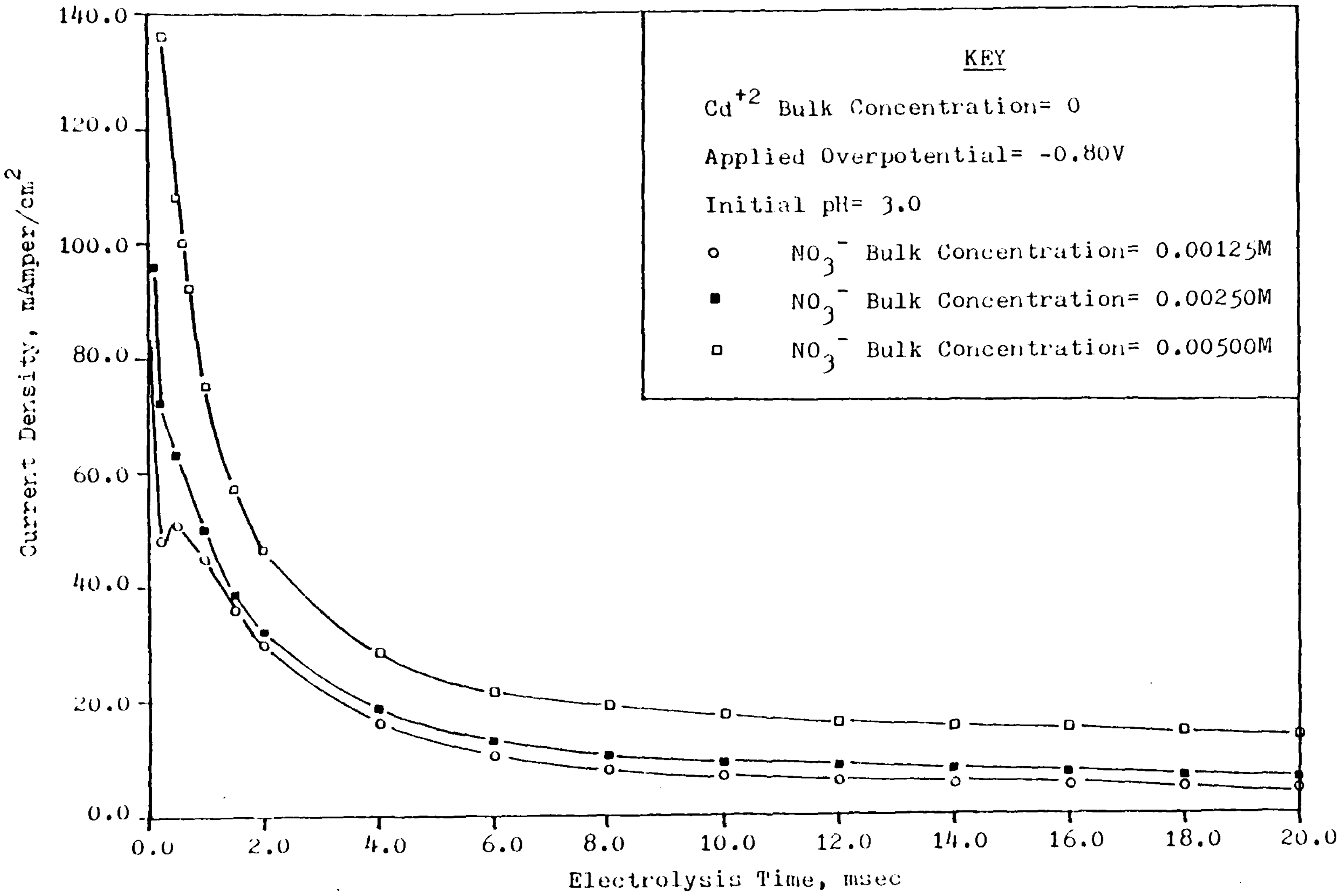


Figure 9: Effect of the Bulk Concentration of the Electrolytic Solution on the Current Density with Fixed Applied Overpotential.

$Cd(NO_3)_2$ solution and at -0.40V applied overpotential is shown in Figure 6. In addition to the electrochemical reduction of the nitrate ions on the electrode surface, a precipitation reaction also takes place in the solution because the cadmium ions in the electrolytic solution can coprecipitate with the hydroxy ions produced by the electrochemical reaction on the electrode surface. The current density is expected to be greater than that when the cadmium ion is absent from the electrolytic solution. Figure 10 shows the current-density-vs.-time curves obtained in a 0.005M KNO_3 solution and in a 0.0025M $Cd(NO_3)_2$ solution. The applied overpotential is -0.40V for both cases. From the curves, one can see that the current density obtained in the 0.0025M $Cd(NO_3)_2$ solution is larger than that obtained in a 0.005M KNO_3 solution. The reason for this is that the consumption of the hydroxy ions due to the precipitation reaction establishes a driving force to produce more hydroxy ions and thus promote the electrochemical reaction. Some interesting facts may be seen from the figure. Firstly, the difference between two current densities increases as time increases, finally reaching a constant difference; secondly, the rate of decrease of the current density with time is slower for the case of using $Cd(NO_3)_2$ as the electrolytic solution. One may thus obtain a larger steady state current density using $Cd(NO_3)_2$ as the electrolytic solution.

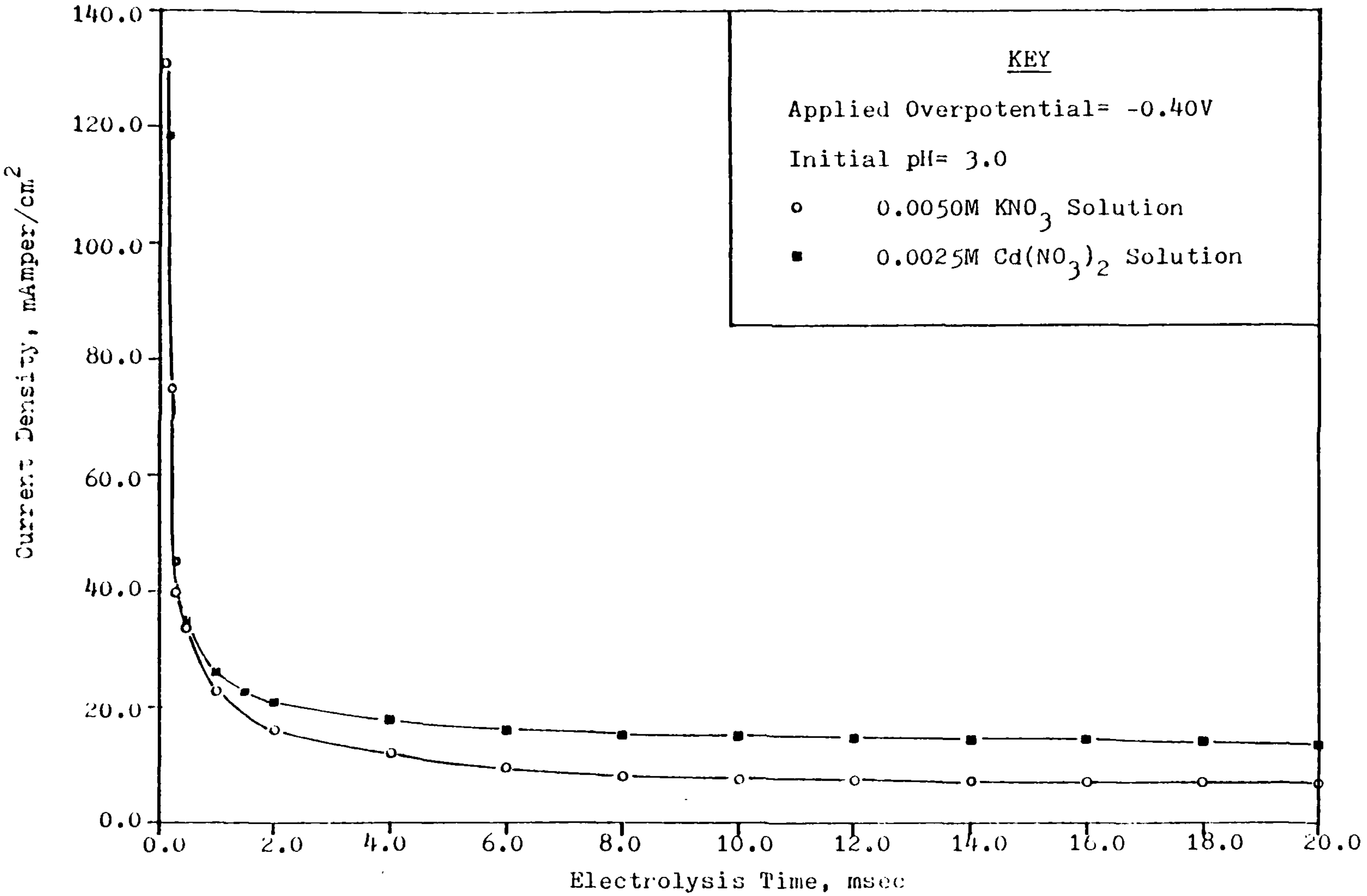


Figure 10: Current-Density-vs.-Time Curves Using Various Electrolytic Solutions.

CHAPTER 5

NUMERICAL SOLUTIONS
OF THE THEORETICAL MODEL

5.1 Orthogonal Collocation Method

There are many numerical techniques which can be used to solve the differential equations of the theoretical model presented earlier in Chapter 3.

Orthogonal collocation method was selected as the method of solution. The orthogonal collocation method requires very little implicit mathematics and results in a large savings in computer time over the common finite difference scheme such as the Crank-Nicholson method. A brief description of the orthogonal collocation method is presented in Appendix C.

5.2 Working Equations

5.2.1 Dimensionless Form of the Differential Equations

The orthogonal collocation method requires the region of solution to be restricted to the interval $[0,1]$. This is accomplished by normalizing the spatial variable by the parameter, δ, the diffusion thickness, $\xi = x/\delta$.

The concentration variables are also reduced to the dimensionless forms:

$$C_1^* = \frac{C_1}{C_1^b} \quad ; \quad C_2^* = \frac{C_2}{C_1^b} ,$$

the dimensionless time is defined as:

$$\tau = \frac{D_2 t}{\delta^2} .$$

Substituting the above dimensionless variables into equations (17) and (19) and rearranging leads to the following dimensionless equations:

$$\frac{\partial C_1^*}{\partial \tau} = \left(\frac{D_1}{D_2}\right)\frac{\partial^2 C_1^*}{\partial \xi^2} \tag{35}$$

$$\frac{\partial C_2^*}{\partial \tau} = \frac{\partial^2 C_2^*}{\partial \xi^2} - 2K\left[\tfrac{1}{2}(C_1^* + C_2^*) - \frac{DKsp}{(C_2^*)^2}\right] \tag{36}$$

where $K = \frac{k\delta^2}{D_2}$ and $DKsp = \frac{Ksp}{(C_1^b)^3}$

are the dimensionless homogeneous reaction rate constant and solubility product, respectively. Similarly, equations (21) and (22) become:

$$\frac{\partial C_1^*}{\partial \tau} = \left(\frac{D_1}{D_2}\right)\frac{\partial^2 C_1^*}{\partial \xi^2} \tag{37}$$

$$\frac{\partial C_2^*}{\partial \tau} = \frac{\partial^2 C_2^*}{\partial \xi^2} \tag{38}$$

The initial conditions are:

1. at $\tau=0$, $C_1^*=1$, for all $0 \leq \xi \leq 1$,
2. at $\tau=0$, $C_2^* = C_2^b/C_1^b$, for all $0 \leq \xi \leq 1$.

The first two boundary conditions come from the dimensionless form of equations (32) and (33):

$$1. \quad \left(\frac{D_1\ C_1^b}{\delta}\right) \left[\frac{\partial C_1^*}{\partial \xi}\right]_{\xi=0} + \left[K_2\ (C_1^b)^3\ (C_2^{o*})^3 - (K_1 C_1^b)\ C_1^{o*}\right] = 0\ ,$$

$$2. \quad 3\left(\frac{D_1}{D_2}\right) \left[\frac{\partial C_1^*}{\partial \xi}\right]_{\xi=0} + \left[\frac{\partial C_2^*}{\partial \xi}\right]_{\xi=0} = 0\ .$$

The other two boundary conditions are:

3. at $\xi=1$, $C_1^*=1$, for $\tau > 0$,
4. at $\xi=1$, $C_2^*=C_2^b/C_1^b$, for $\tau > 0$.

5.2.2 Discretized Equations

The solution is approximated by a (N+2)th-order Legendre polynomial which satisfies the differential equations and boundary conditions exactly at N+2 points. Those points are chosen to be zeros of the Legendre polynomial of degree N over the interval (0,1) and with the boundary points 0 and 1. Discretizing the spatial derivatives at those points leads to the following set of first-order ordinary differential equations:

$$\left.\frac{dC_1^*}{d\tau}\right|_{\xi_i} = \left(\frac{D_1}{D_2}\right)\left[\sum_{j=1}^{N+2} B_{i,j}\, C_1^*(\xi_j,\tau)\right]$$

$$i= 2,\ldots\ldots N+1, \qquad (39)$$

$$\left.\frac{dC_2^*}{d\tau}\right|_{\xi_i} = \sum_{j=1}^{N+2} B_{i,j}\, C_2^*(\xi_j,\tau) - 2K\left[\tfrac{1}{2}(C_1^*(\xi_i,\tau) + C_2^*(\xi_i,\tau) - \frac{DKsp}{C_2^*(\xi_i,\tau)^{2}}\right]$$

$$i= 2,\ldots.\ N+1, \qquad (40)$$

where ξ_i, $i=2,\ldots N+1$ are the N interior collocation points while ξ_1 and ξ_{N+2} are exterior collocation points which correspond to the boundary points at $\xi=0$ and $\xi=1$, respectively, and $0=\xi_1<\xi_i<\xi_{N+2}=1$, $i=2,\ldots N+1$. $B_{i,j}$ is a (N+2) by (N+2) coefficient matrix which comes from the discretization of the second derivative ($\partial^2C_1^*/\partial\xi^2$ or $\partial^2C_2^*/\partial\xi^2$) at each collocation point. A detailed explanation of matrix B is shown in Appendix C. $C_1^*(\xi_j,\tau)$ and $C_2^*(\xi_j,\tau)$ are the concentrations of species 1 and 2, respectively, at time τ and position ξ_j.

The discretized equations from equations (37) and (38) are:

$$\left.\frac{dC_1^*}{d\tau}\right|_{\xi_i} = \left(\frac{D_1}{D_2}\right)\left[\sum_{j=1}^{N+2} B_{i,j}\, C_1^*(\xi_j,\tau)\right], \quad i = 2,\ldots N+1, \qquad (41)$$

and

$$\left.\frac{dC_2^*}{d\tau}\right|_{\xi_i} = \sum_{j=1}^{N+2} B_{i,j}\, C_2^*(\xi_j,\tau), \quad i=2,\ldots N+1. \qquad (42)$$

The other four equations are obtained by requiring that the approximation polynomial satisfies the boundary conditions:

$$\left(\frac{D_1 C_1^b}{\delta}\right)\left[\sum_{j=1}^{N+2} A_{1,j} C_1^*(\xi_j,\tau)\right] + \left[K_2 (C_1^b)^3 C_2^*(\xi_1,\tau)^3 - (K_1 C_1^b) C_1^*(\xi_1,\tau)\right] = 0, \quad \text{for all } \tau > 0, \qquad (43)$$

$$3\left(\frac{D_1}{D_2}\right)\left[\sum_{j=1}^{N+2} A_{1,j} C_1^*(\xi_j,\tau)\right] + \left[\sum_{j=1}^{N+2} A_{1,j} C_2^*(\xi_j,\tau)\right] = 0, \quad \text{for all } \tau > 0, \qquad (44)$$

$$C_1^*(\xi_{N+2},\tau) = 1, \quad \text{for all } \tau > 0, \qquad (45)$$

$$C_2^*(\xi_{N+2},\tau) = C_2^b / C_1^b, \quad \text{for all } \tau > 0, \qquad (46)$$

where $A_{i,j}$ is an element of another (N+2) by (N+2) coefficient matrix which comes from the discretization of the first-order derivative ($\partial C_1^*/\partial\xi$ or $\partial C_2^*/\partial\xi$) at each collocation points. Since only boundary conditions 1 and 2 (equations (43) and (44)) require the evaluation of the first-order derivative at $\xi_1=0$, only the first row of the matrix A, i.e., $A_{1,j}$, is used here.

The initial conditions for both cases are the same:

I.C.'s

1. at $\tau=0$, $C_1^*(\xi_i,\tau)= 1$, $i=1,\ldots N+2$,
2. at $\tau=0$, $C_2^*(\xi_i,\tau)= C_2^b/C_1^b$, $i=1,\ldots,N+2$.

5.2.3 Calculation of Current Density

The current density is related to the flux of the nitrate ion at the electrode surface by equation (34). The discretized and dimensionless form of equation (34) is:

$$I= -\left[\frac{2FD_1C_1^b}{\delta}\right]\left[\frac{\partial C_1^*}{\partial\xi}\right]_{\xi=0}$$

$$= -\left[\frac{2FD_1C_1^b}{\delta}\right]\left[\sum_{j=1}^{N+2} A_{1,j}\, C_1^*(\xi_j,\tau)\right] . \qquad (47)$$

5.3 The Introduction of a Spline Point to the Discretized Equations

The diffusion thickness introduced in the derivation of the dimensionless form in the previous section can be justified by selecting the total electrolysis time such that diffusion effects are negligible at $x=\delta$ during that period. At the beginning of the electrolysis, the diffusion thickness selected according to the total electrolysis time is too large. This leads to a concentration profile which is flat in most of the interval with a sharp drop in a very small region near $\xi=0$. This would require a large number of collocation points leading to a very stiff set of ordinary differential equations.

This difficulty can be overcome by the use of a method called spline collocation(28) based on the diffusion boundary concept. This method maintains a fixed low number of collocation points in the interval which is very small initially and will be increased as time increases to account for the thickening of the diffusion layer. In the regions outside this interval, the concentration is flat. As a matter of fact, the spline point can be located as close to the interface as to achieve any desired accuracy(28).

In order to be sure that the concentration gradient at the spline point is zero, the concentration at the Nth collocation point, i.e., the last one before the spline point, is tested to assure that it is within a very small range of the bulk condition. At the time when such a test fails, the spline point is moved further into the solution.

Introducing a spline point, ξ_s, $0 < \xi_s < 1$, a new variable, $z = \xi / \xi_s$, is introduced. The discretized equations we obtained for the case of solution containing cadmium ions are:

$$\left.\frac{dC_1^*}{d\tau}\right|_{z_i} = \left(\frac{1}{\xi_s^2}\right)\left(\frac{D_1}{D_2}\right)\left[\sum_{j=1}^{N+2} B_{i,j} C_1^*(z_j,\tau)\right]$$

$$i=2,\ldots N+1, \qquad (48)$$

and

$$\left.\frac{dC_2^*}{d\tau}\right|_{z_i} = \left(\frac{1}{\xi_s^2}\right)\left[\sum_{j=1}^{N+2} B_{i,j} C_2^*(z_j,\tau)\right] - 2K\left[\tfrac{1}{2}(C_1^*(z_i,\tau) + C_2^*(z_i,\tau)) - \frac{DKsp}{C_2^*(z_i,\tau)^2}\right]$$

$$i=2,\ldots N+1, \qquad (49)$$

For the case of solution containing no cadmium ion,

$$\left.\frac{dC_1^*}{d\tau}\right|_{z_i} = \left(\frac{1}{\xi_s^2}\right)\left(\frac{D_1}{D_2}\right)\left[\sum_{j=1}^{N+2} B_{i,j}C_1^*(z_j,\tau)\right]$$

$$i=2,\ldots N+1, \qquad (50)$$

$$\left.\frac{dC_1^*}{d\tau}\right|_{z_i} = \left(\frac{1}{\xi_s^2}\right)\left[\sum_{j=1}^{N+2} B_{i,j}C_2^*(z_j,\tau)\right]$$

$$i=2,\ldots N+1. \qquad (51)$$

Equations (43) through (46), which come from the four boundary conditions, become:

$$1.\quad \left(\frac{1}{\xi_s}\right)\left(\frac{D_1C_1^b}{\delta}\right)\left[\sum_{j=1}^{N+2} A_{1,j}C_1^*(z_j,\tau)\right] + \Big[K_2(C_1^b)^3C_2^*(z_1,\tau)^3$$

$$-(K_1C_1^b)C_1^*(z_1,\tau)\Big] = 0, \quad \text{for all } \tau > 0, \qquad (52)$$

$$2.\quad 3\left(\frac{D_1}{D_2}\right)\left[\sum_{j=1}^{N+2} A_{1,j}C_1^*(z_j,\tau)\right] + \left[\sum_{j=1}^{N+2} A_{1,j}C_2^*(z_j,\tau)\right] = 0,$$

$$\text{for all } \tau > 0, \qquad (53)$$

$$3.\quad C_1^*(\xi_s,\tau) = C_1^*(z_{N+2},\tau) = 1, \text{ for all } \tau > 0, \qquad (54)$$

$$4.\quad C_2^*(\xi_s,\tau) = C_2^*(z_{N+2},\tau) = C_2^b/C_1^b, \text{ for all } \tau > 0, \qquad (55)$$

The initial conditions become:

I.C.'s:

1. at $\tau=0$, $C_1^*(z_i,\tau)=1$, $i=1,\ldots N+2$,

2. at $\tau=0$, $C_2^*(z_i,\tau)=C_2^b/C_1^b$, $i=1,\ldots N+2$.

The current density should be changed to:

$$I=-\left[\frac{2FD_1C_1^b}{\delta}\right]\left[\frac{\partial C_1^*}{\partial \xi}\right]_{\xi=0}$$

$$=-\left(\frac{1}{\xi_s}\right)\left(\frac{2FD_1C_1^b}{\delta}\right)\left[\frac{\partial C_1^*}{\partial Z}\right]_{z=0}$$

$$=-\left(\frac{1}{\xi_s}\right)\left(\frac{2FD_1C_1^b}{\delta}\right)\sum_{j=1}^{N+2}A_{1,j}C_1^*(z_j,\tau). \qquad (56)$$

5.4 Solution Procedures

For the case of a solution containing cadmium ions, equations (48), (49) and (52) through (55), with the initial conditions, are the working equations used to solve for the concentration profiles of NO_3^- and OH^- ions. The Cd^{+2} ion concentration is calculated by the electroneutrality condition in the solution:

$$C_3^*(z_i,\tau)=\tfrac{1}{2}\left[C_1^*(z_i,\tau)+C_2^*(z_i,\tau)\right] \qquad (57)$$

For the case of a solution containing no cadmium ion, equations (50), (51) and (52) through (55) with the initial conditions, are the working equations.

Equation (56) is used to calculate the current density at each time τ for both cases.

5.5 Computer Program Structure

The computer program for solving the discretized equations consists of a main program and 5 main subroutines. The first main subroutine evaluates the collocation points (roots) of the Jacobi polynomial of order N, as well as the first and second derivatives of the polynomial at the roots. These derivatives are then used in a second main subroutine to calculate the discretization coefficient matrices A and B. The third main subroutine is used to perform a semi-implicit integration using Gear's routine$^{(29)}$. This subroutine calls 4 external subroutines. The first of these contains the explicit expressions (48) and (49) (or (50) and (51) in another case) for the discretized coupled first order differential equations containing the $B_{i,j}$ terms; the second contains the Jacobian matrix for the same equation; the third performs the first stage of Gaussian elimination$^{(30)}$ of the Jacobian matrix; the last performs the back substitution of Gaussian elimination of the Jacobian matrix. The first external subroutine called by the integration subroutine also calls another subroutine coming from the IMSL package. This subroutine solves equations (52) and (53) simultaneously to give the surface concentrations of C_1^* and C_2^*. The IMSL subroutine calls another function which feeds the equations to be solved. Before writing the function, $C_2^*(z_1,\tau)$ (surface concentration of C_2^*) is solved in terms of $C_1^*(z_i,\tau)$, $i=1,\ldots N+2$, and $C_2^*(z_i,\tau)$, $i=1,\ldots N+2$, using equation (53), and then substitute into equation (52) to eliminate $C_2^*(z_1,\tau)$. Thus, only one equation which contains only one unknown, $C_2^*(z_1,\tau)$, is needed. Once we obtain $C_1^*(z_1,\tau)$, $C_2^*(z_1,\tau)$ can be calculated easily.

The Jacobian matrices for both cases can also be evaluated after substituting the expression of $C_2^*(z_1,\tau)$ into equations (48) and (49) (or (50) and (51) in another case). For the case of solution containing no cadmium ion, the Jacobian matrix is:

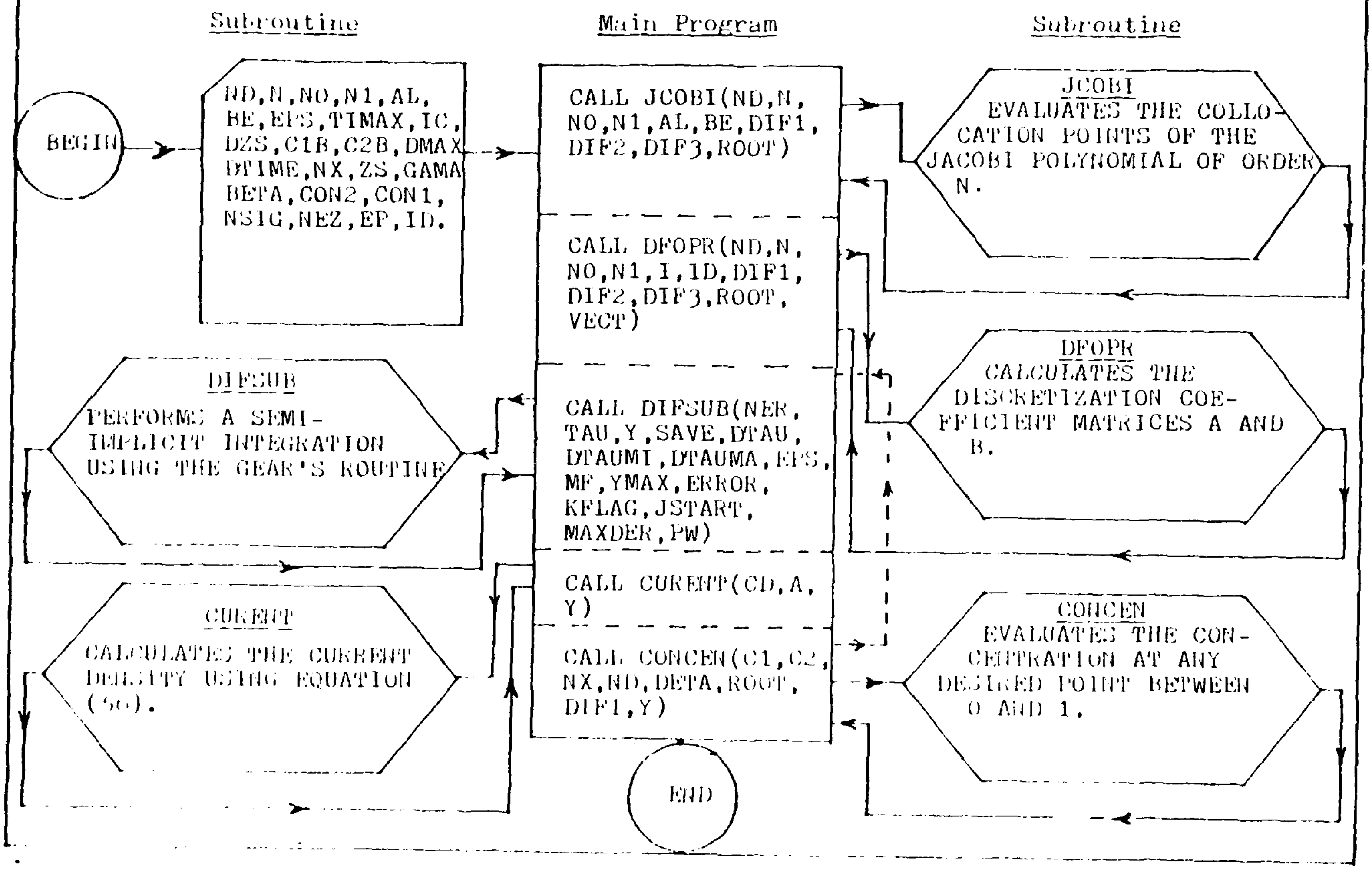
$$J_{i,j}=\left[\begin{array}{c|c} \left(\frac{D_1}{D_2}\right)\left(\frac{1}{\xi_s^{2}}\right) B_{i+1,j+1} & \underline{0} \\ \hline \frac{3B_{i+1-N,1}\left(\frac{D_1}{D_2}\right)A_{1,j+1}}{(A_{1,1})\,\xi_s^{2}} & \left(\frac{1}{\xi_s^{2}}\right)\left[B_{i+1-N,j+1-N}-\frac{(B_{i+1-N,1})(A_{1,j+1-N})}{A_{1,1}}\right] \end{array}\right]$$

which is a 2N by 2N matrix. For the case of solution containing cadmium ions, the Jacobian matrix is the same except that the terms in the diagonal line of the third quadrant are all subtracted by K and the terms in the diagonal line of the fourth quadrant are all subracted by $2K(\frac{1}{2}+(2DKsp/C_2^*(z_{i-N+1},\tau)^3))$.

The values obtained from the integration subroutine are then used in a fourth main subroutine to calculate the current density by equation (56). The last main subroutine is used to evaluate the concentration at any desired point between 0 and 1 by interpolation using the values at the collocation points.

The structure of the whole program is shown in Figure 11. Programs from both cases are listed in Appendix D. Programs herein were executed on an AMDAHL 470/V6 computer.

Figure 11. The Main Structure of the Program



CHAPTER 6

FITTING OF THE THEORETICAL MODEL WITH EXPERIMENTAL DATA

6.1 The Determination of the Electrochemical Reaction Kinetics Parameters

The unknown heterogeneous reaction rate constants which appear in equation (52) were determined from the current-density-vs.-time data obtained in a solution which did not contain cadmium ion. The differential equations (50) and (51) which describe the transport process were solved by computer to determine the rate constants. Comparing equation (31) with equation (31a), one can see that both K_1 and K_2 depend on the applied potential with exponential dependence. Thus, K_1 and K_2 should be constant when the applied potential is maintained at a constant value during the electrolysis. K_1 and K_2 were obtained by comparing the experimental data in the absence of cadmium ion in the electrolyte with the computer-calculated current density data.

The experimental current-density-vs.-time data with the electrolyte containing 0.005M nitrate ions and the applied overpotential of -0.40V was first fitted to the computer-simulated data to obtain the K_1 and K_2 values. Due to the lack of information about the values of K_1 and K_2, rough estimates of K_1 and K_2 were evaluated by substituting the applied potential V, which is equal to the value of the applied overpotential plus the rest potential, to equations (31) and (31a). The estimated values of K_1 and K_2 were increased or decreased until the computer-calculated current-density-vs.-time curve had the same shape as the same curve obtained experimentally. (Note, the background water decomposition current has been subtracted.)

After we obtained the right shape, the anodic reaction rate constant, K_2, was then fixed. By changing K_1, one can make the entire curve shift upward. Conversely, decreasing the K_1 value will decrease the current density at each time point and thus shift the entire curve downward. A set of current-density-vs.-time curves with fixed K_2 values and different values of K_1 are plotted in Figure 12. The values of K_1 and K_2 when the concentration of nitrate ions is 0.005M and the applied overpotential is -0.40V was obtained

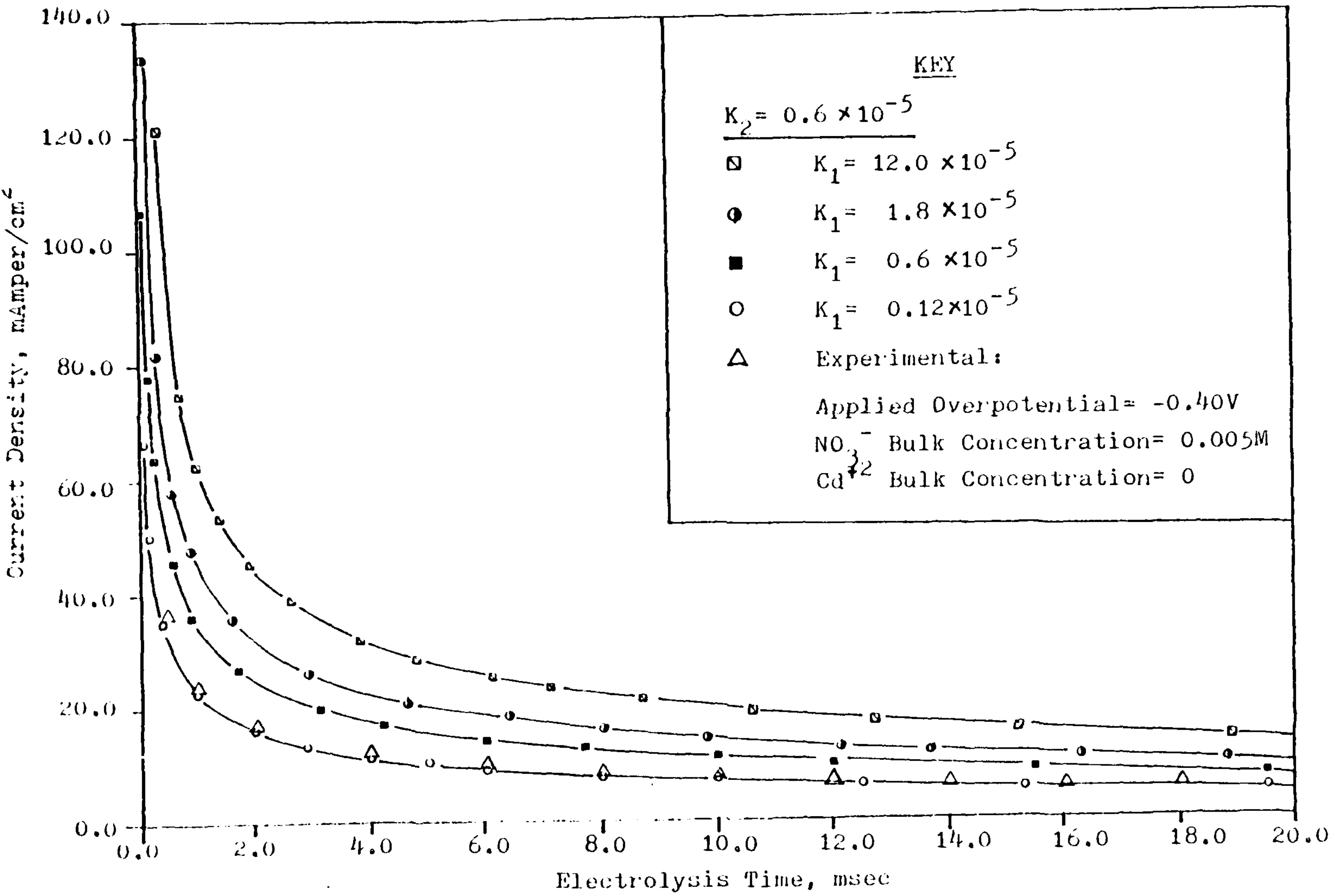


Figure 12: Computer-Simulated Current-Density-vs.-Time Curves with Fixed K_2 and Various K_1's.

by interpolating the experimental curve between those curves in Figure 12. The values of K_1 and K_2 which achieved the best approximation of the experimental data are $K_1 = 0.12 \times 10^{-5}$ and $K_2 = 0.6 \times 10^{-5}$, respectively.

These values were then used to predict the current-density-vs.-time curves at the other ion concentrations. Figure 13 shows the computer-simulated current density curves and experimental curves at various nitrate ion concentrations.

The values of K_1 and K_2 at the applied overpotential of -0.60V were different from those at -0.40V. The same procedure was used in evaluating the values of K_1 and K_2 at the condition of -0.60V. Figure 14 shows a set of calculated current-density-vs.-time curves with fixed K_2 valued and different values of K_1. The value of K_1 at the condition of -0.60V was then obtained in the same way as before. The values of K_1 and K_2 were determined to be 0.10×10^{-5} and 0.50×10^{-6}, respectively. These values were then used to predict the current-density-vs.-time curves at the other ion concentrations. Figure 15 shows the comparison of the predicted and experimental current-density-vs.-time curves.

The reaction rate constants at the applied overpo-

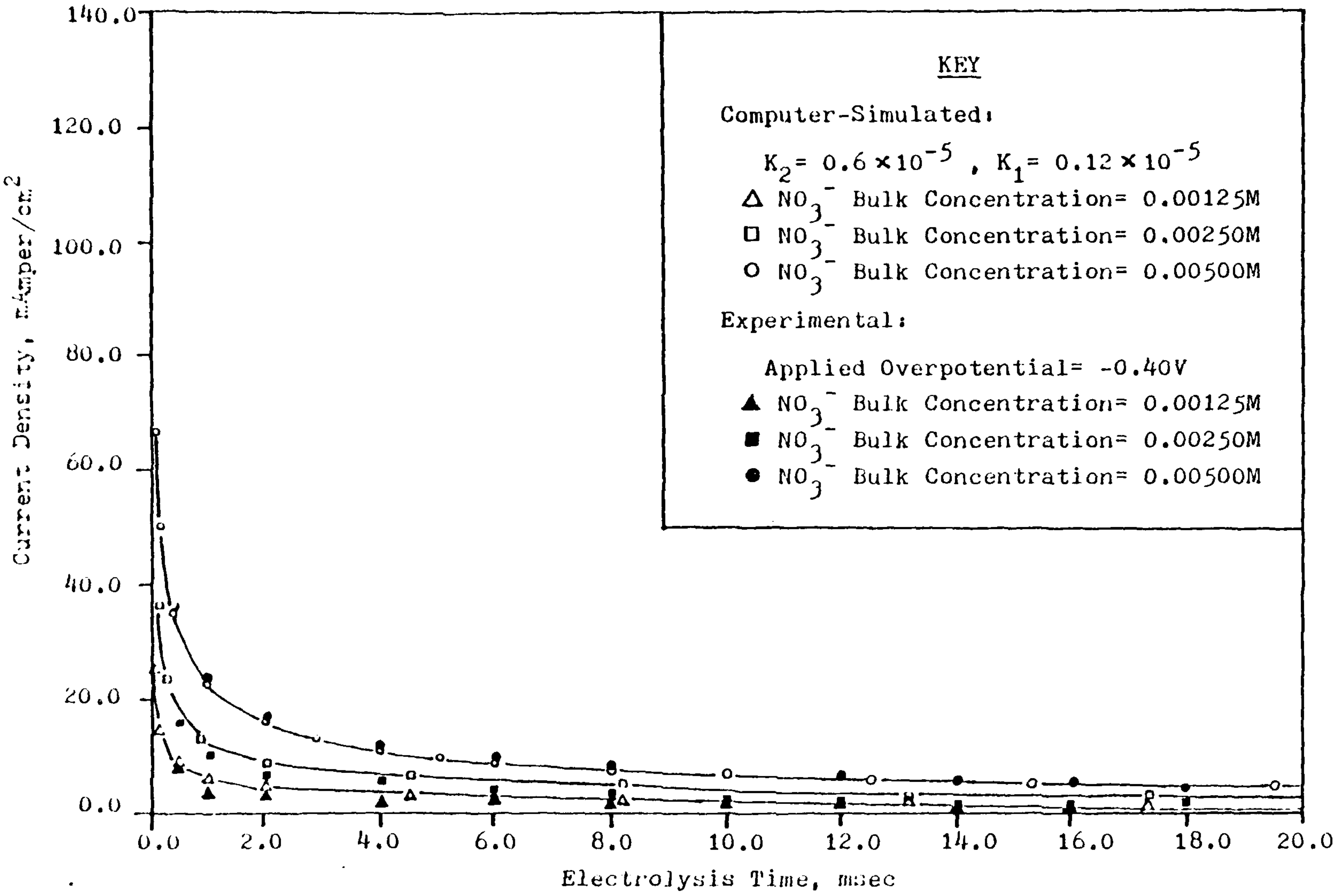


Figure 13: Experimental and Computer-Simulated Current-Density-vs.-Time Curves with Various Nitrate Ion Bulk Concentrations in the Case of Electrolyte Containing No Cadmium Ion.

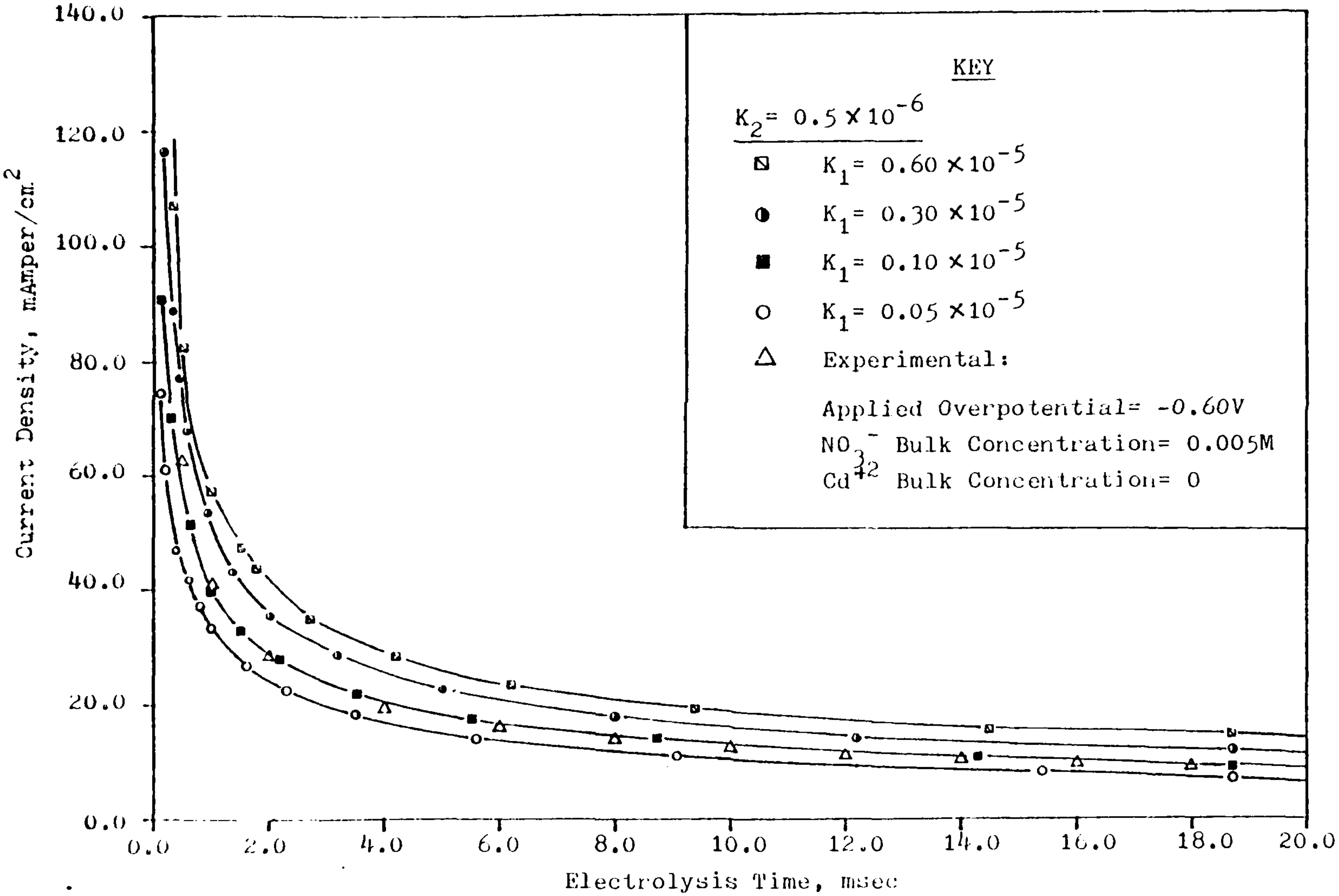


Figure 14: Computer-Simulated Current-Density-vs.-Time Curves with Fixed K_2 and Various K_1's

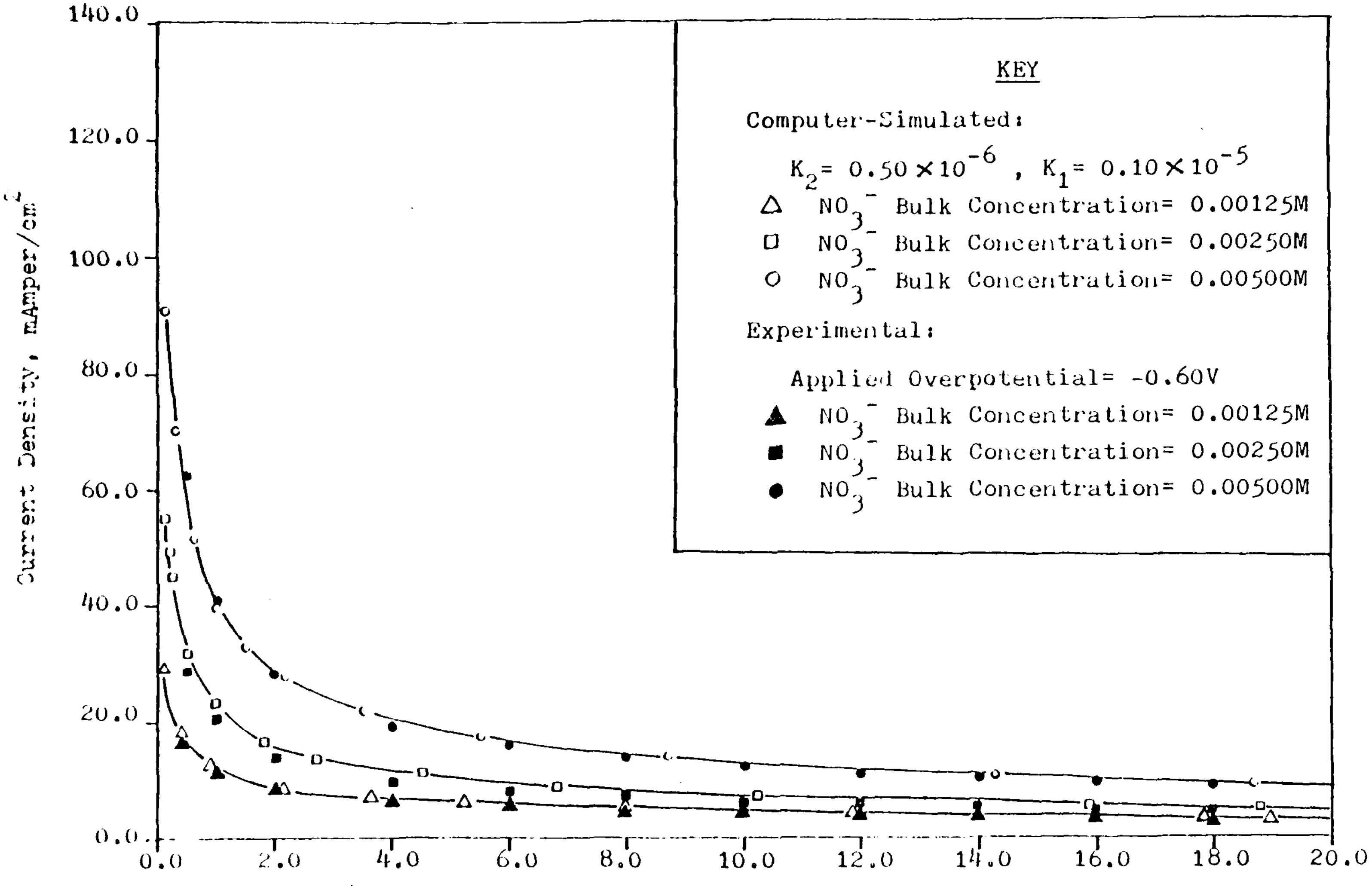


Figure 15: Experimental and Computer-Simulated Current-Density-vs.-Time Curves with Various Nitrate Ion Bulk Concentration in the Case of Electrolyte Containing No Cadmium Ion.

tential of -0.80V were not pursued. The reason, which was discussed previously, is that at this high applied overpotential more complicate sequences of reactions take place. This simple reaction expression can not describe the phenomena.

The heterogeneous rate expression so determined is believed to be a correct one. This claim is supported by the fact that the rate constants, K_1 and K_2, are independent of the bulk concentration at a given potential. This is indeed the case as was shown in Figures 13 and 15.

6.2 The Determination of the Homogeneous Precipitation Reaction Rate Constant

Higher current density was observed when cadmium nitrate was used instead of potassium nitrate as the electrolyte in the electrochemical cell. The hydroxy ion produced by the reduction of nitrate ion coprecipitated with the cadmium ion in the solution. This increased the reduction reaction rate and led to higher current. This homogeneous reaction was assumed to be linearly dependent on the degree of supersaturation of cadmium hydroxide (see Equation (14)). Since the heterogeneous reaction rate constants K_1 and K_2 were determined, the homogeneous rate constant k could be evaluated by fitting the second set of experimental data with the theoretical model to determine the value of k.

Figure 16 shows the current-density-vs.-time curves with various k values while the other parameters were held at a constant value. The current-density-vs.-time data obtained in a 0.0025M cadmium nitrate solution at the applied overpotential of -0.40V is also plotted in Figure 16. The reaction rate constant, k, was then evaluated approximately from Figure 16. The most probable homogeneous reaction rate constant was determined to be 50 sec^{-1}.

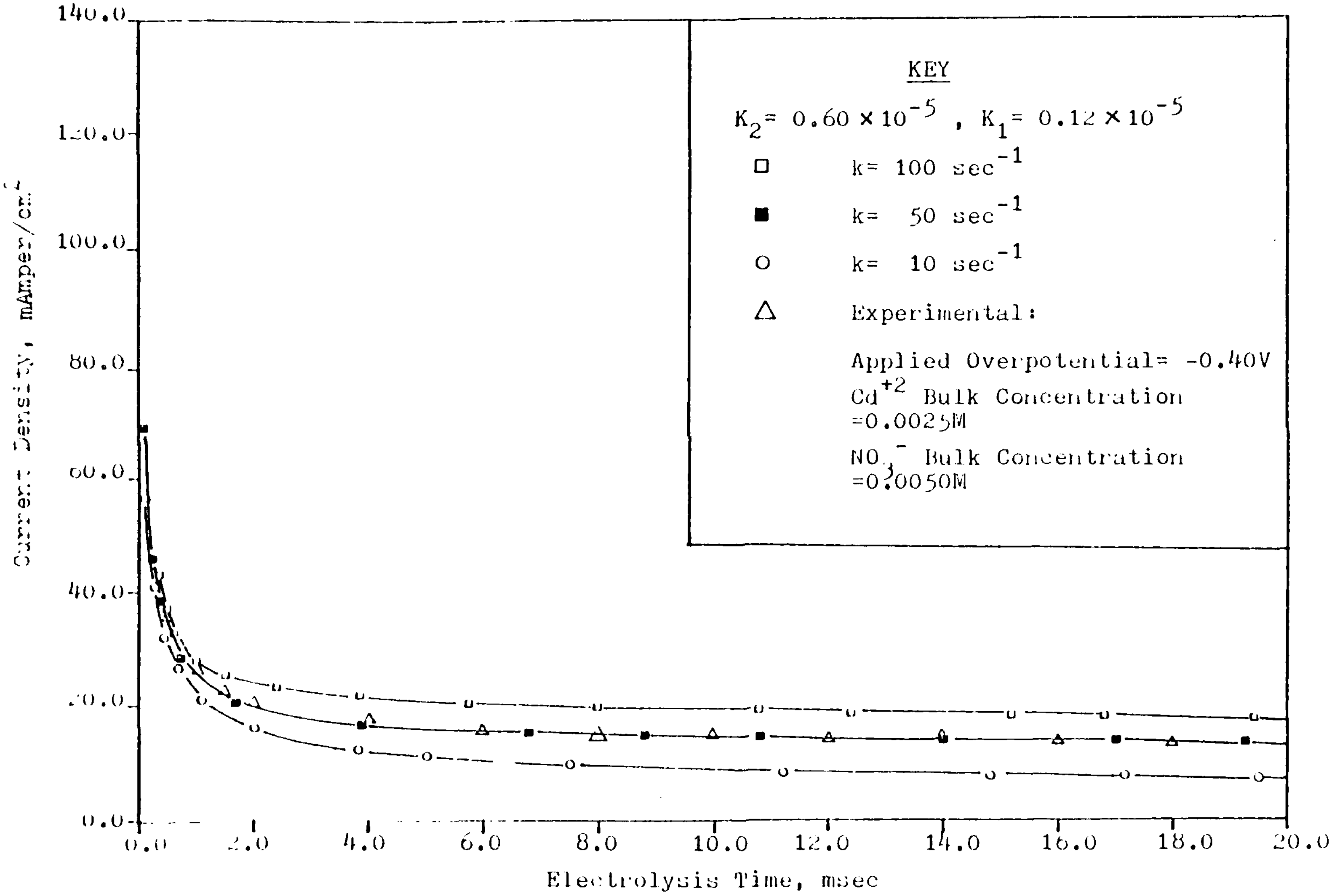


Figure 16: Computer Simulated Current-Density-vs.-Time Curves with Fixed K_1 and K_2 and Various Homogeneous Reaction Rate Constants.

CHAPTER 7

DISCUSSIONS AND CONCLUSIONS

7.1 Surface Concentrations of Various Ions as Functions of Time

The knowledge of the surface ion concentrations can provide information concerning the electrochemical deposition process. Although the surface ion concentrations were not available from the experiment, that information could be generated by computer simulations.

Figure 17 shows the surface concentrations of NO_3^- and OH^- ions as functions of time in the absence of cadmium ion in the solution at two potentials, -0.40V and -0.60V from equilibrium potential and at a NO_3^- bulk concentration of 0.005M. In general, the surface concentration of NO_3^- ions decreases as time increases, while the surface concentration of OH^- ions increases as time increases. This is due to the electrochemical reaction (23), in which one nitrate ion reacts with two electrons and which produces three hydroxy ions.

For the case of -0.40V overpotential, the OH^- concentration increases sharply from the bulk value of nearly zero

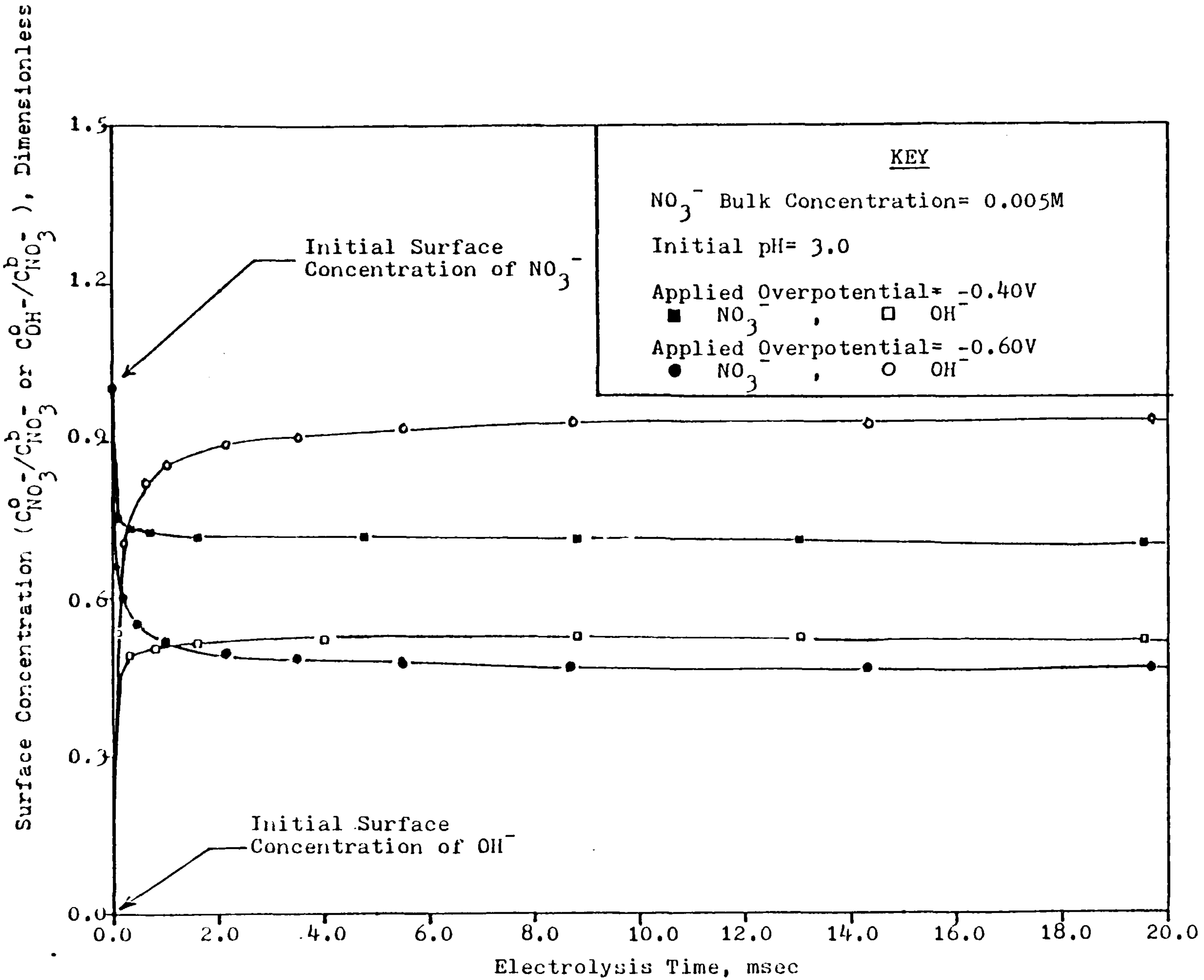


Figure 17: Surface Concentrations of NO_3^- and OH^- Ions as Functions of Time in the Absence of Cadmium Ions in the Solution.

to about 0.5 dimensionless concentration units in less than 1 msec before the hydroxy ions generated are removed effectively by diffusion. Thereafter, the OH^- concentration increases at a slower rate. For NO_3^- ions, the surface concentration drops to about 0.72 dimensionless concentration units from the bulk value of 1.0 in less than 1 msec and then decreases at a slower rate when the diffusion can effectively supply the reactant for the electrode reaction. The sharp changes of the surface concentrations of NO_3^- and OH^- ions cause the sharp decrease of the current density in a short time period in the beginning of the electrolysis.

At a more negative overpotential of -0.60V, the increase in surface OH^- concentration and the decrease of NO_3^- concentration are even more significant and last over a longer time period. The surface concentration of NO_3^- drops to about 0.5 dimensionless concentration units and OH^- concentration increases to about 0.87 dimensionless concentration units in 2.0 msecs. The behavior is the consequence of the higher overall reaction rate at -0.60V. The nitrate ions were consumed at a higher rate which produced more hydroxy ions. Longer induction time is needed for diffusion to effectively supply the reactant from the bulk solution and remove the product from the electrode surface.

Similar profiles of NO_3^- and OH^- surface concentrations at lower bulk NO_3^- concentrations were also obtained. These are shown in Figures 18 and 19.

When the electrolyte contains cadmium ions, the homogeneous precipitation reaction of cadmium ions and hydroxy ions near the electrode surface promotes the electrochemical reaction on the electrode surface in the cathodic direction. This causes the nitrate ions to be consumed at a higher rate than the case when no cadmium is present. This is shown in Figure 20 where the homogeneous reaction rate constant is 50 sec^{-1}. It is interesting to note that the cadmium ion surface concentration increases initially and then starts to decrease. This phenomenon is explained as follows. Immediately after the electrolysis began, NO_3^- ions were consumed by the electrochemical reaction which produced an NO_3^- concentration gradient made the NO_3^- ions in the bulk solution diffused toward the electrode surface. The Cd^{+2} ions, on the other hand, moved with the NO_3^- ions in the same direction in order to maintain the eleconeutrality condition. In the meantime, the OH^- concentration was, however, not so high as to consume all the Cd^{+2} ions brought in by the transport process. The cadmium ions was thus accumulated and resulted in a higher value than its bulk condition. As soon as the surface concentration of OH^- ion raised to some value, the surface concentration of the Cd^{+2} ions starts to decrease because of the abundant supply of OH^- ions consuming the cadmium ions at

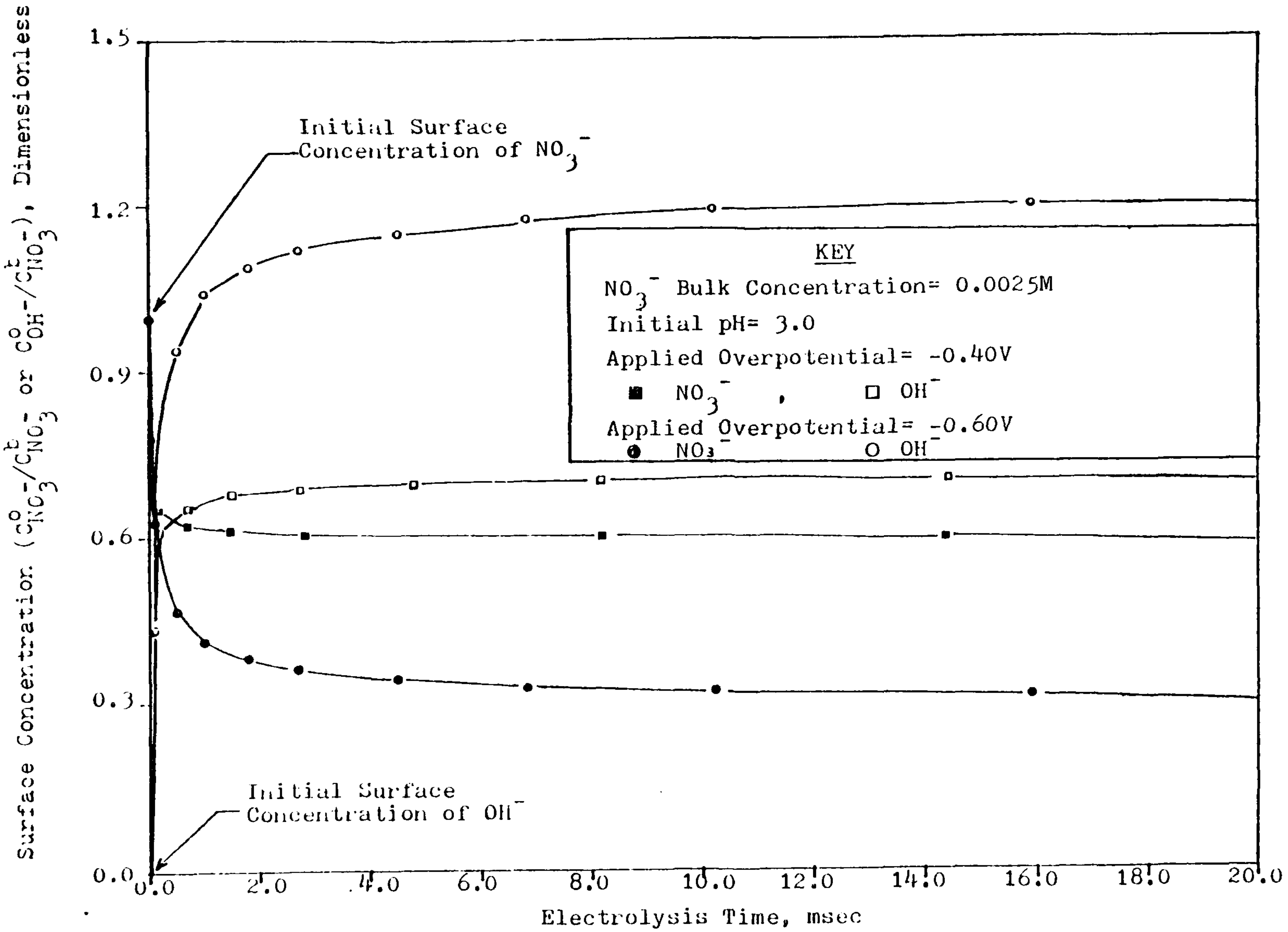


Figure 18: Surface Concentration of NO_3^- and OH^- Ions as Functions of Time in the Absence of Cadmium Ions in the Solution.

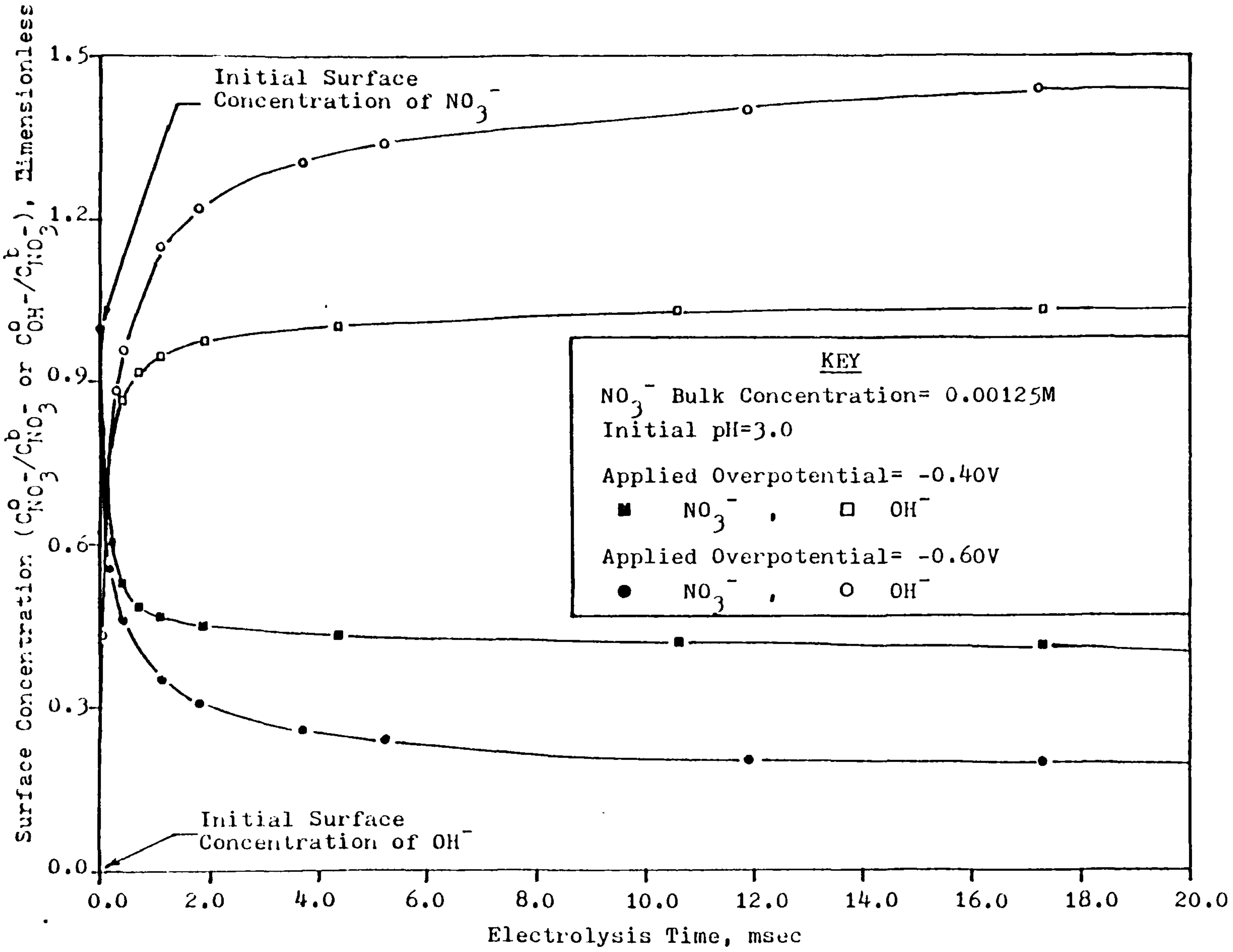


Figure 19: Surface Concentrations of NO_3^- and OH^- Ions as Functions of Time in the Absence of Cadmium Ions in the Solution.

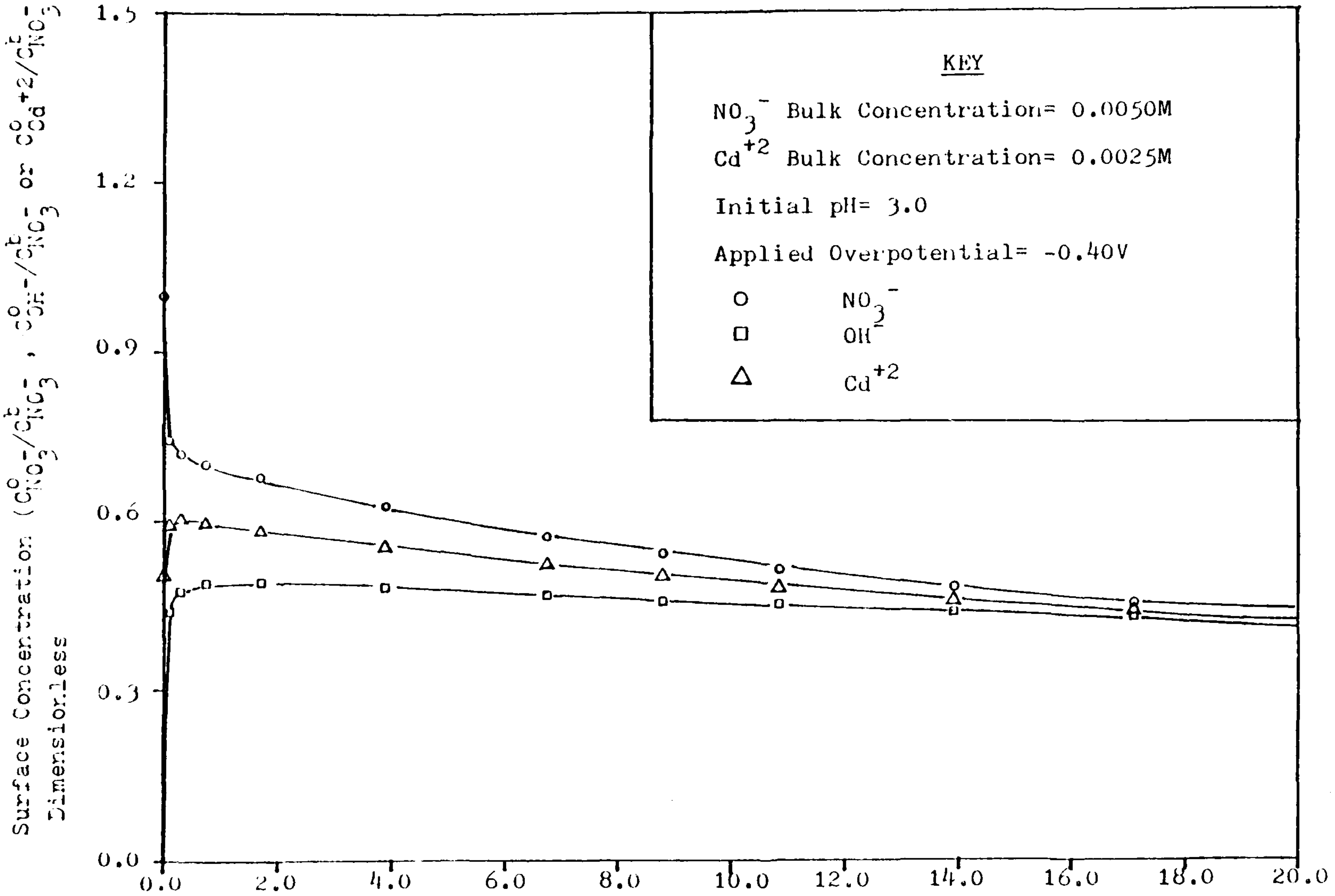


Figure 20: Surface Concentrations of NO_3^- , OH^- and Cd^{+2} Ions as Functions of Time in the Presence of Cadmium Ions in the Solution.

this time.

For the nitrate ions, the surface concentration also decreases as time increases at a rate somewhat larger than that for the case of solution containing no cadmium ion. This is shown in Figure 21. Figure 21 also shows the difference in the surface concentration of the hydroxy ion between those two cases, i.e., in the presence and in the absence of cadmium ions. The initial behaviors of two cases are very similar. After this induction period, the ion concentration for the case of a solution which contains cadmium ions decreases at a more gradual rate as a result of the homogeneous precipitation reaction between cadmium and hydroxy ions.

7.2 Concentration Profiles of Various Ions at Various Time

For the case of solution containing no cadmium ion, the nitrate ions were consumed and the hydroxy ions were produced on the electrode, the concentration gradients were established which made the nitrate ions diffused from the bulk solution toward the electrode surface and the hydroxy ions diffused away from the electrode surface toward the bulk solution. Figures 22 through 27 show the concentration profiles of NO_3^- and OH^- ions with different applied overpotentials at some selected times. From these figures, one can see that the diffusion thickness, δ, increases with time. The diffusion

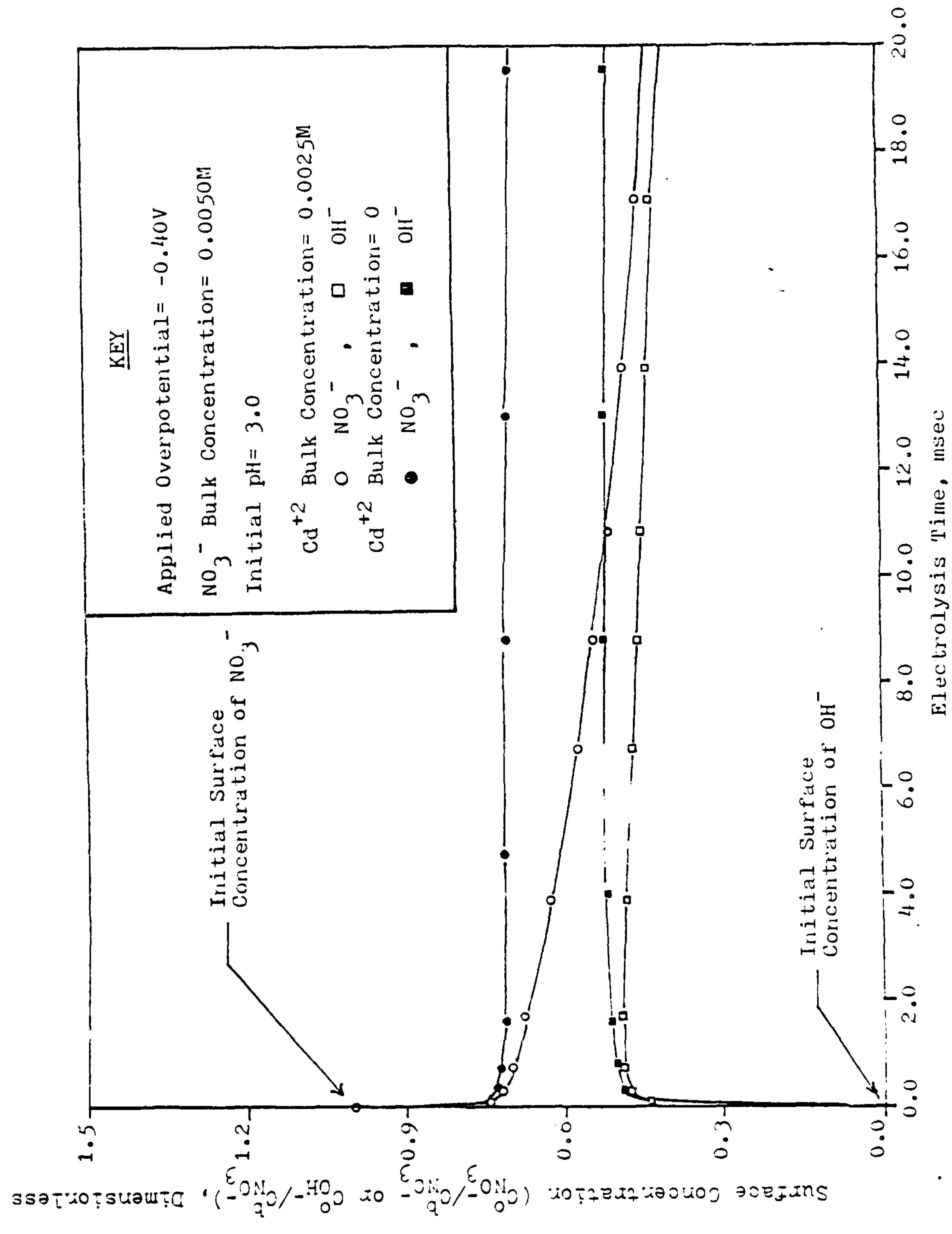


Figure 21: Comparison of the Surface Concentrations of Nitrate and Hydroxy Ions Between Two Cases.

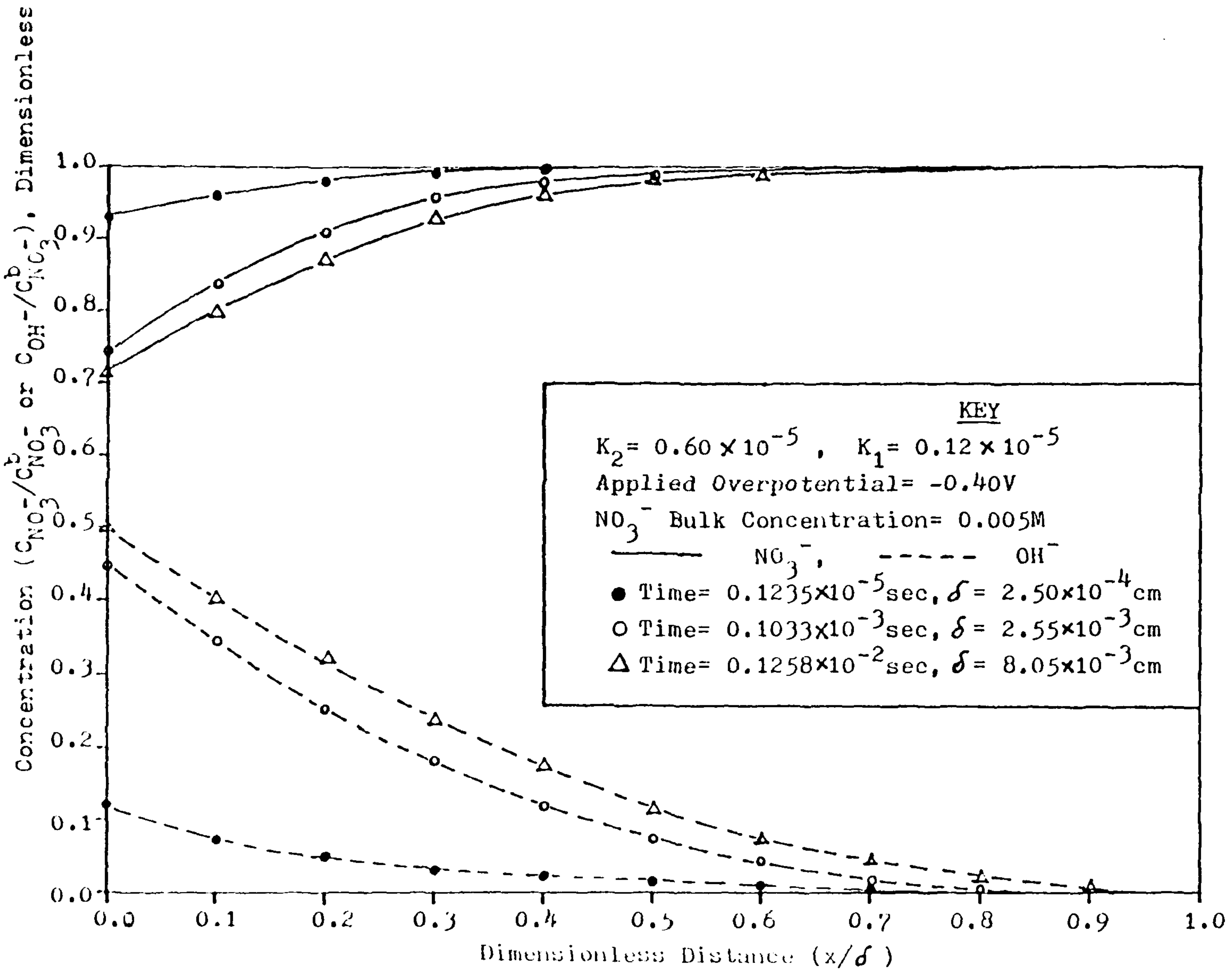


Figure 22 Concentration Profiles of Nitrate and Hydroxy Ions at Various Time for the Case of Solution Containing No Cadmium Ion.

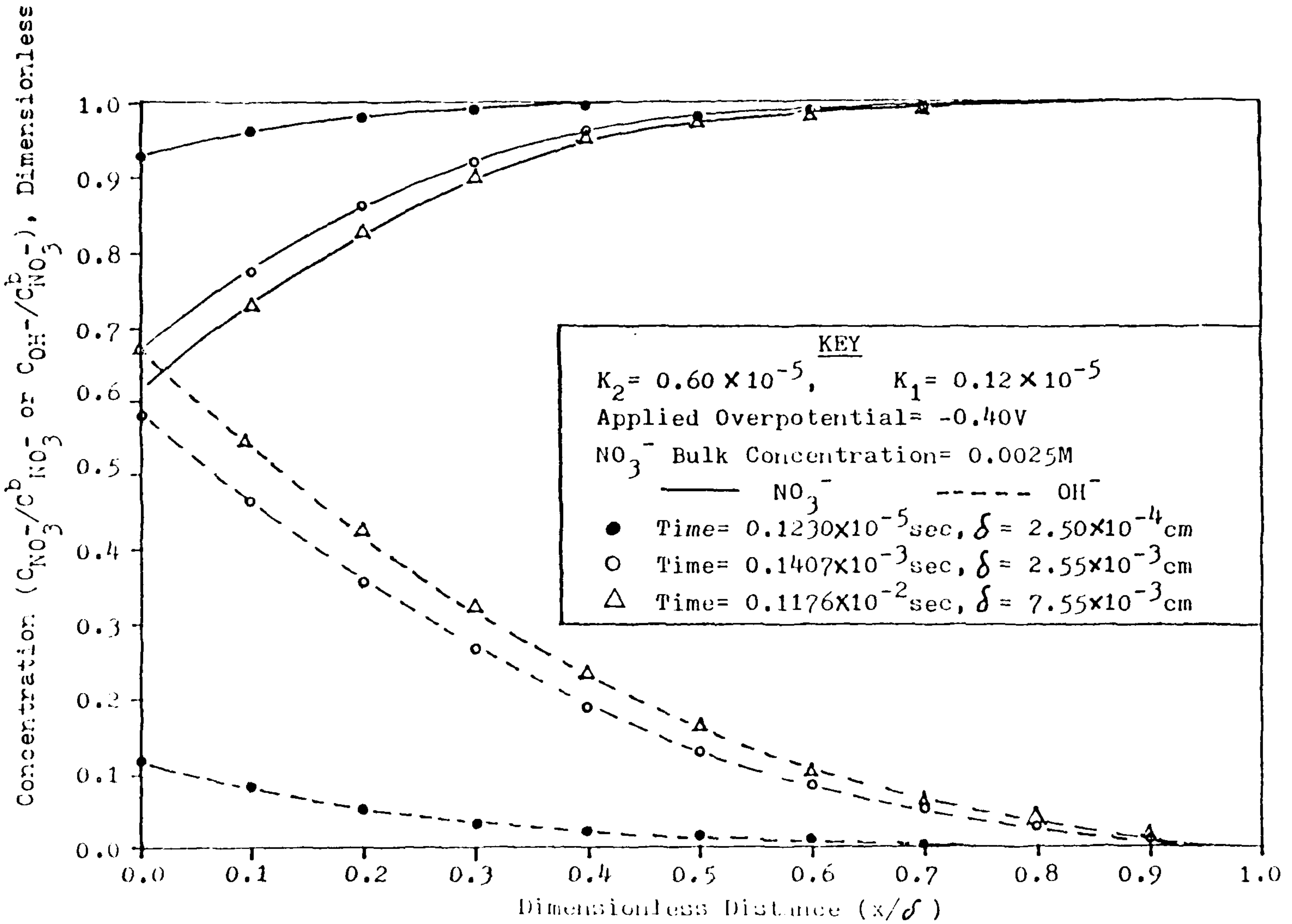


Figure 23: Concentration Profiles of Nitrate and Hydroxy Ions at Various Times for the Case of Solution Containing No Cadmium Ion.

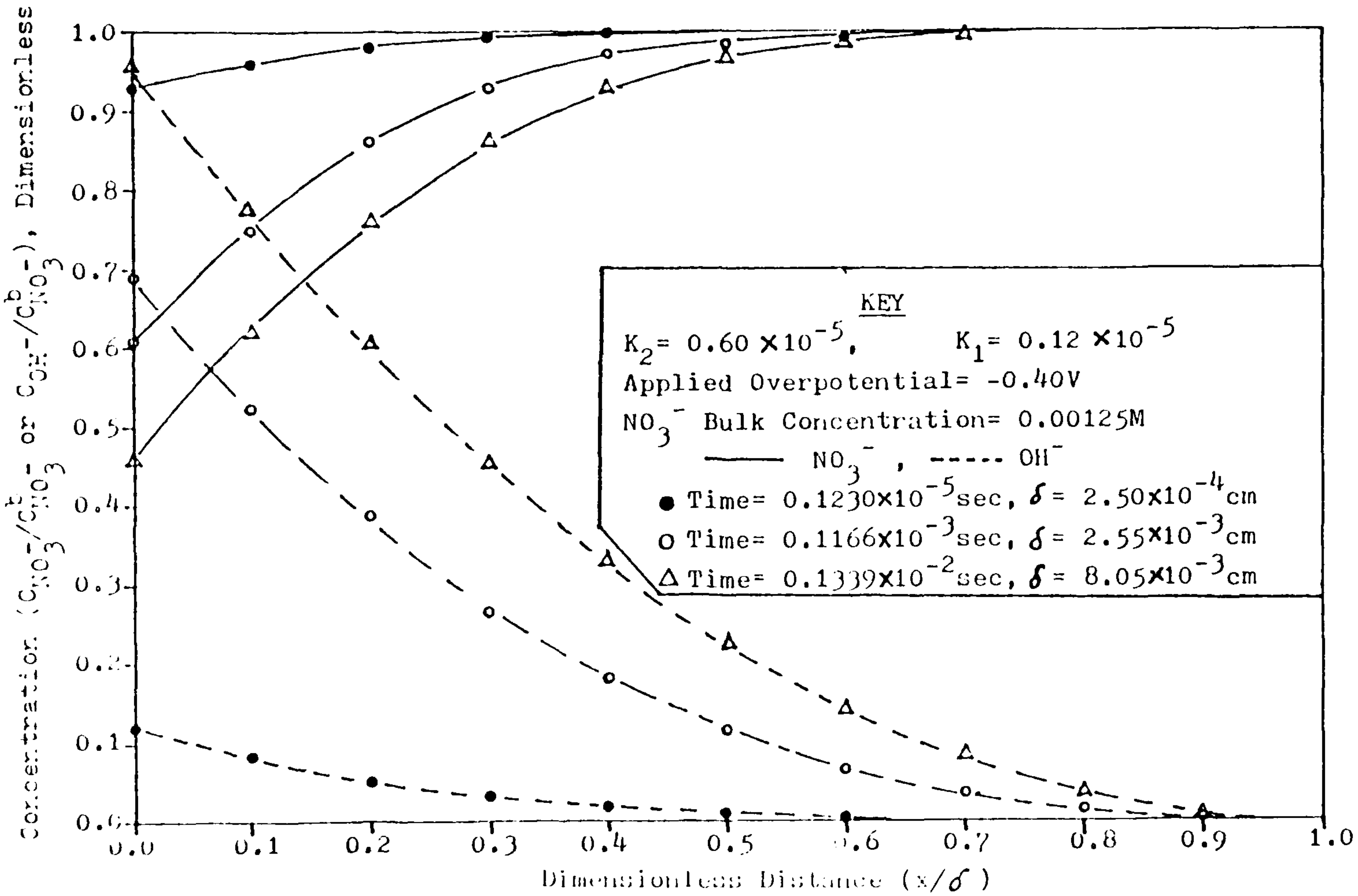


Figure 24: Concentration Profiles of Nitrate and Hydroxy Ions at Various Times for the Case of Solution Containing No Cadmium Ion.

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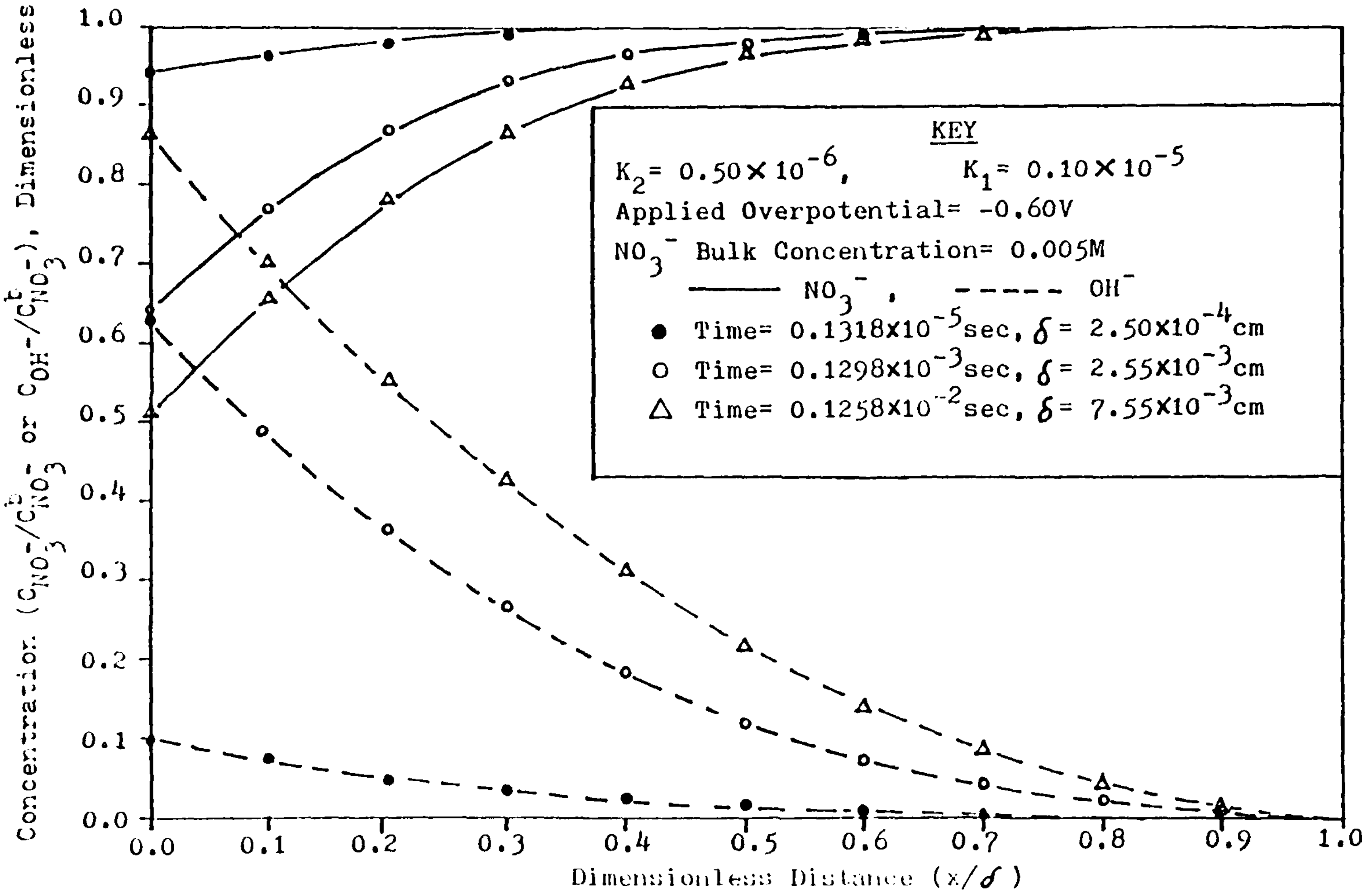

Figure 25: Concentration Profiles of Nitrate and Hydroxy Ions at Various Times for the Case of Solution Containing No Cadmium Ion.

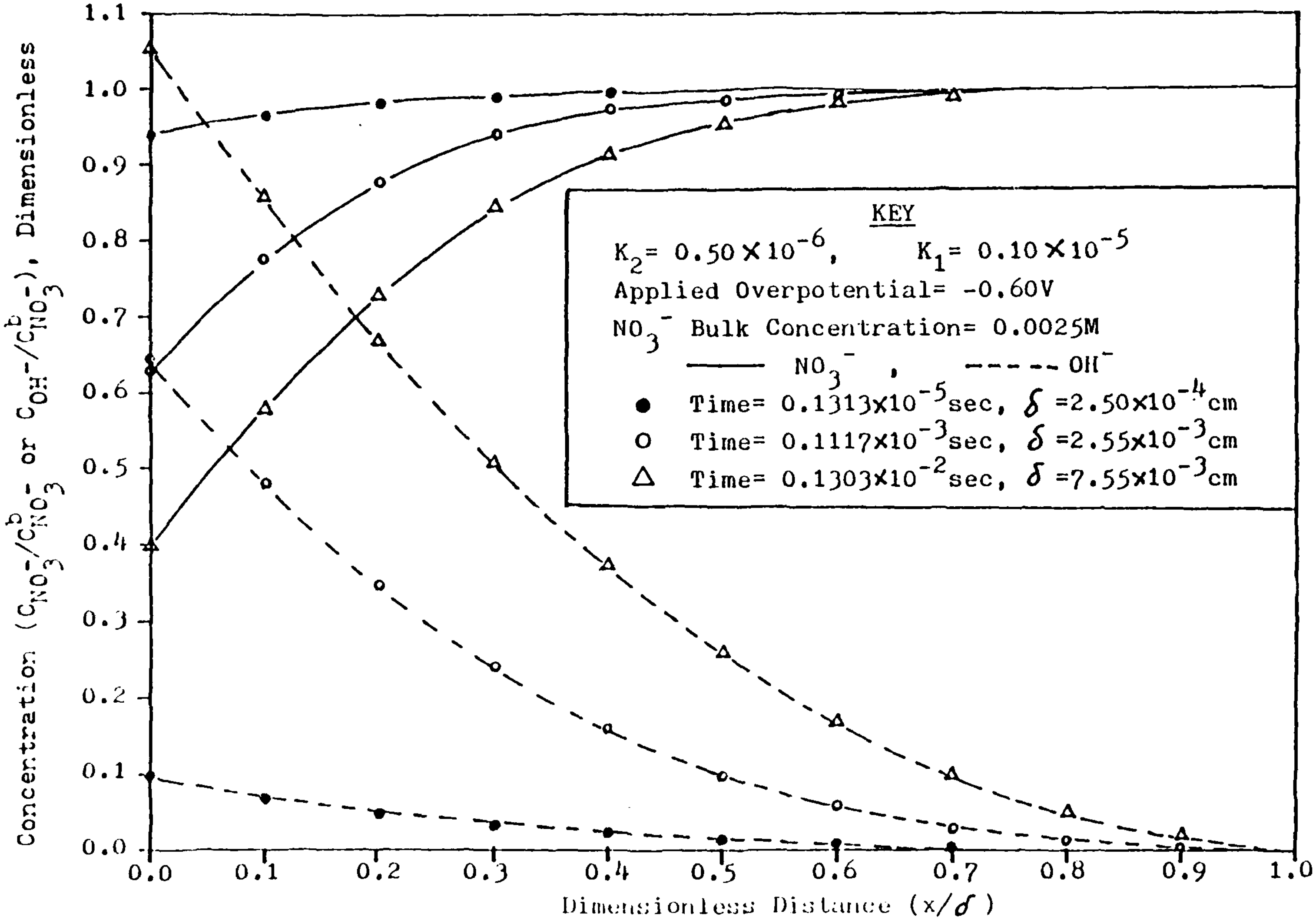

Figure 26: Concentration Profiles of Nitrate and Hydroxy Ions at Various Times for the Case of Solution Containing No Cadmium Ion.

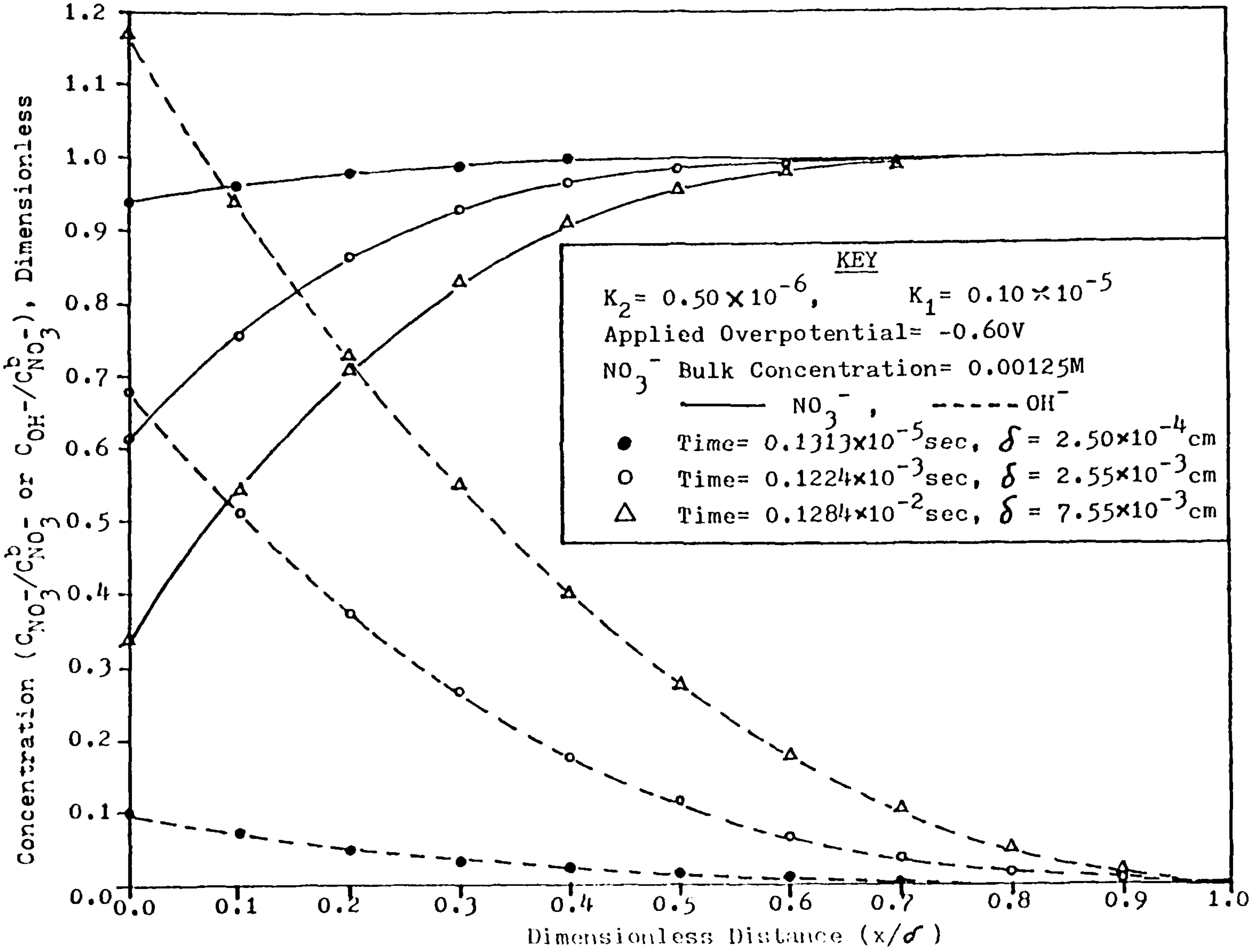

Figure 27: Concentration Profiles of Nitrate and Hydroxy Ions at Various Times for the Case of Solution Containing No Cadmium Ion.

thicknesses at various time are listed in Tables 2 and 3.

The concentration profiles of NO_3^-, OH^- and Cd^{+2} ions at various time for the case of solution containing cadmium ions are shown in Figures 28 and 29. The shape of NO_3^- concentration profiles is the same as that for the case of containing no cadmium ion but the NO_3^- concentration on the surface is somewhat lower than that for the case of containing no cadmium ion. The diffusion thickness increases as time increases.

In the previous discussion of the surface concentration, the surface concentration of OH^- ions increases in the beginning. During that time, OH^- ions diffuse from the electrode surface to the bulk solution. Figure 28 shows that the surface concentration increases and the diffusion layer thickness also increases as time increases. Then the surface concentration starts to drop and the diffusion layer thickness stays at about the same value. This is shown in Figure 30. Table 4 shows the diffusion layer thickness for the diffusion of OH^- ions as a function of time. In Table 4, one can see that the diffusion layer thickness stops increasing as a result of the decreasing surface concentration of OH^- ion.

The Cd^{+2} concentration profiles are shown in Figure 29. As the profiles indicate, for each specific time, when the

Table 2: Diffusion Thickness as a Function of Time for the Case of Solution Containing No Cadmium Ion. The Applied Overpotential is -0.40V. The Nitrate-Ion Bulk Concentration is 0.005M.

Time (sec)	Diffusion Thickness(cm)
0.1235×10^{-5}	0.25×10^{-4}
0.6121×10^{-5}	0.45×10^{-4}
0.1758×10^{-4}	0.80×10^{-4}
0.3572×10^{-4}	0.15×10^{-3}
0.1033×10^{-3}	0.25×10^{-3}
0.4737×10^{-3}	0.50×10^{-3}
0.1258×10^{-2}	0.80×10^{-3}
0.7417×10^{-2}	0.20×10^{-2}
0.3946×10^{-1}	0.45×10^{-2}
0.7032×10^{-1}	0.60×10^{-2}

Table 3: Diffusion Thickness as a Function of Time for the Case of Solution Containing No Cadmium Ion. The Applied Overpotential Is -0.60V. The Nitrate-Ion Bulk Concentration Is 0.005M.

Time (sec)	Diffusion Thickness (cm)
0.1313×10^{-5}	0.25×10^{-4}
0.4982×10^{-5}	0.40×10^{-4}
0.1642×10^{-4}	0.70×10^{-4}
0.3318×10^{-4}	0.10×10^{-3}
0.1298×10^{-3}	0.25×10^{-3}
0.4407×10^{-3}	0.45×10^{-3}
0.1258×10^{-2}	0.75×10^{-3}
0.8718×10^{-2}	0.25×10^{-2}
0.3229×10^{-1}	0.45×10^{-2}
0.7004×10^{-1}	0.65×10^{-2}

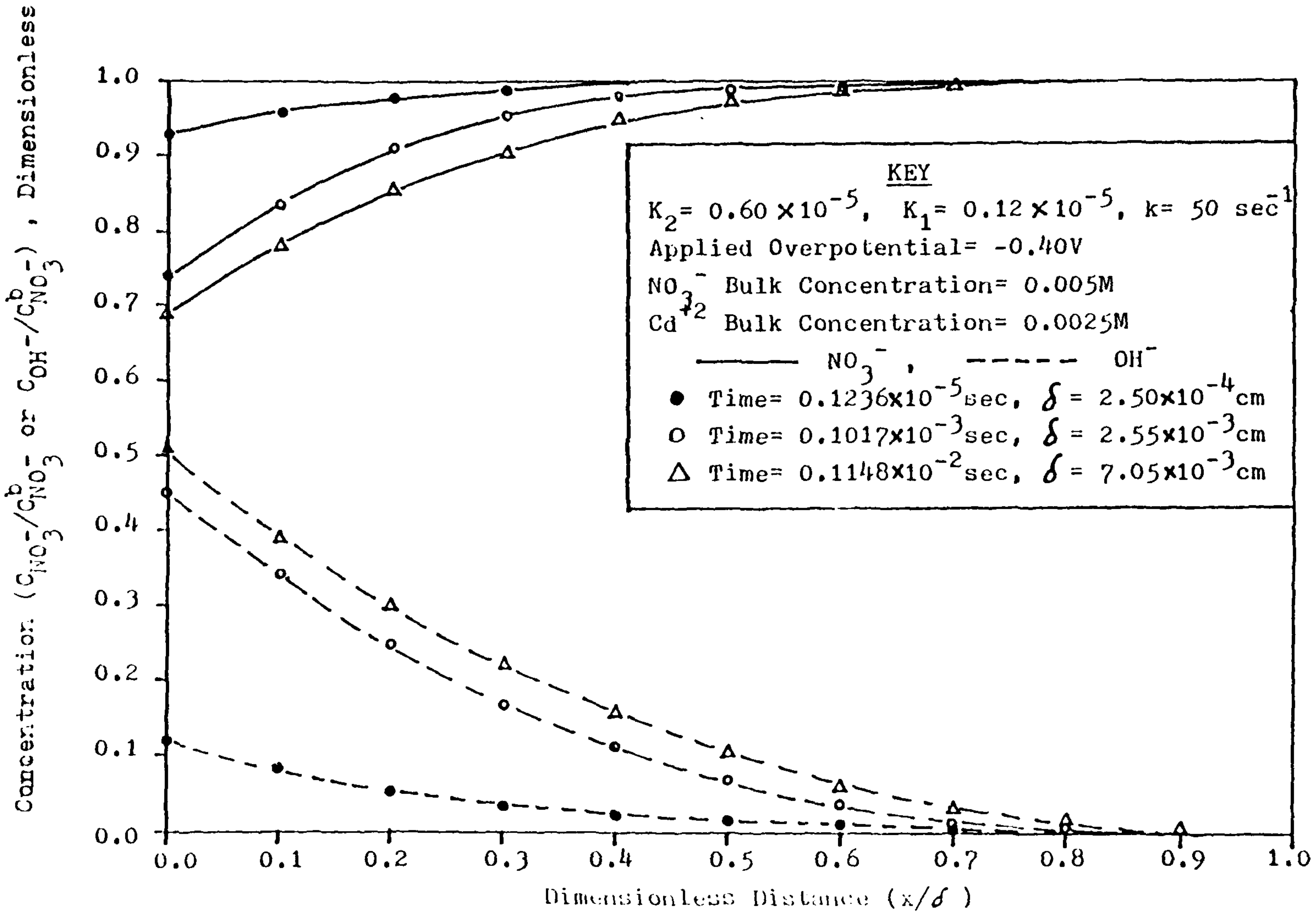

Figure 28: Concentration Profiles of Nitrate and Hydroxy Ions at Various Times for the Case of Solution Containing 0.0025M Cadmium Ions.

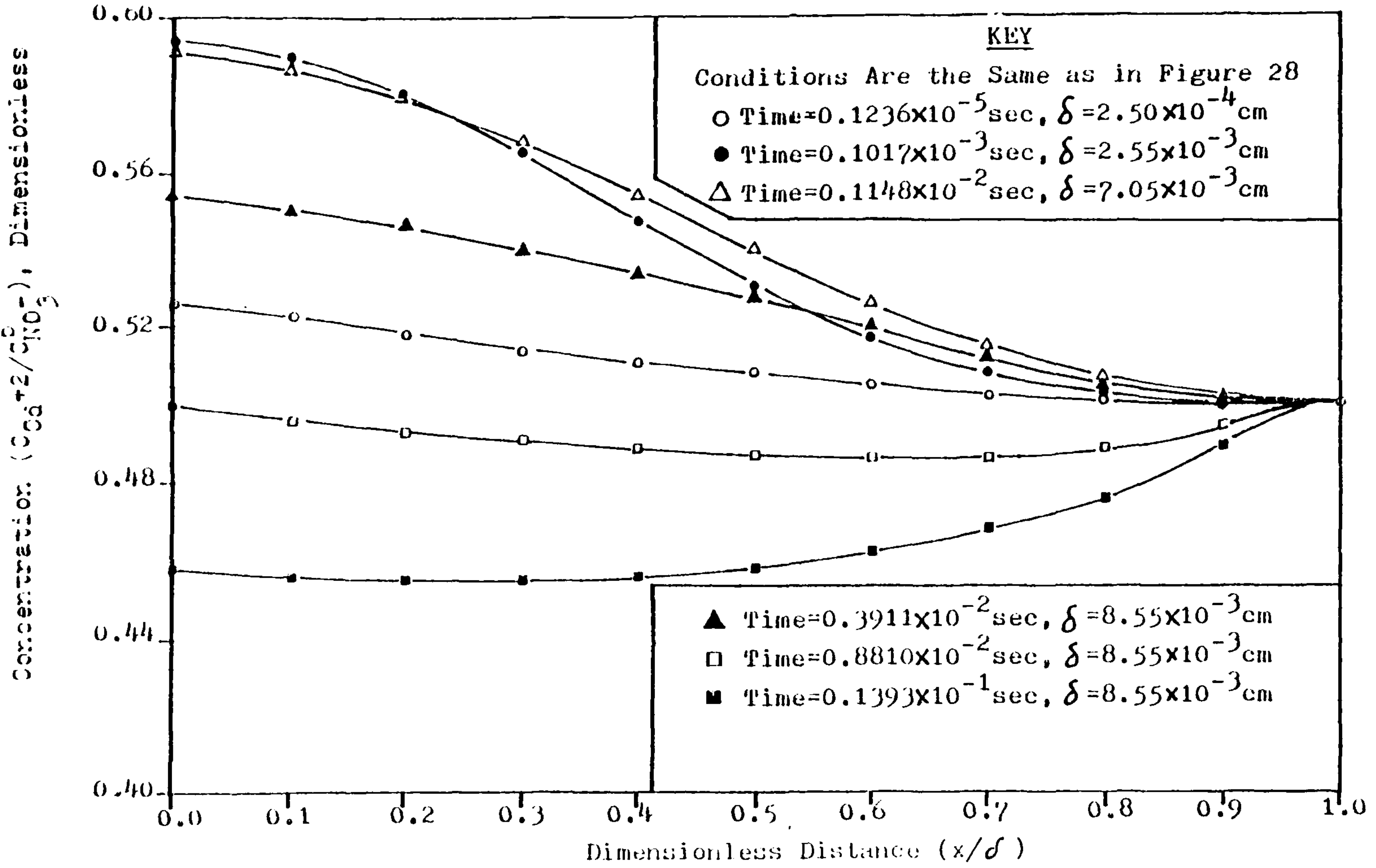

Figure 29: Concentration Profiles of Cadmium Ion at Various Times for the Case of Solution Containing 0.0025M Cadmium Ions.

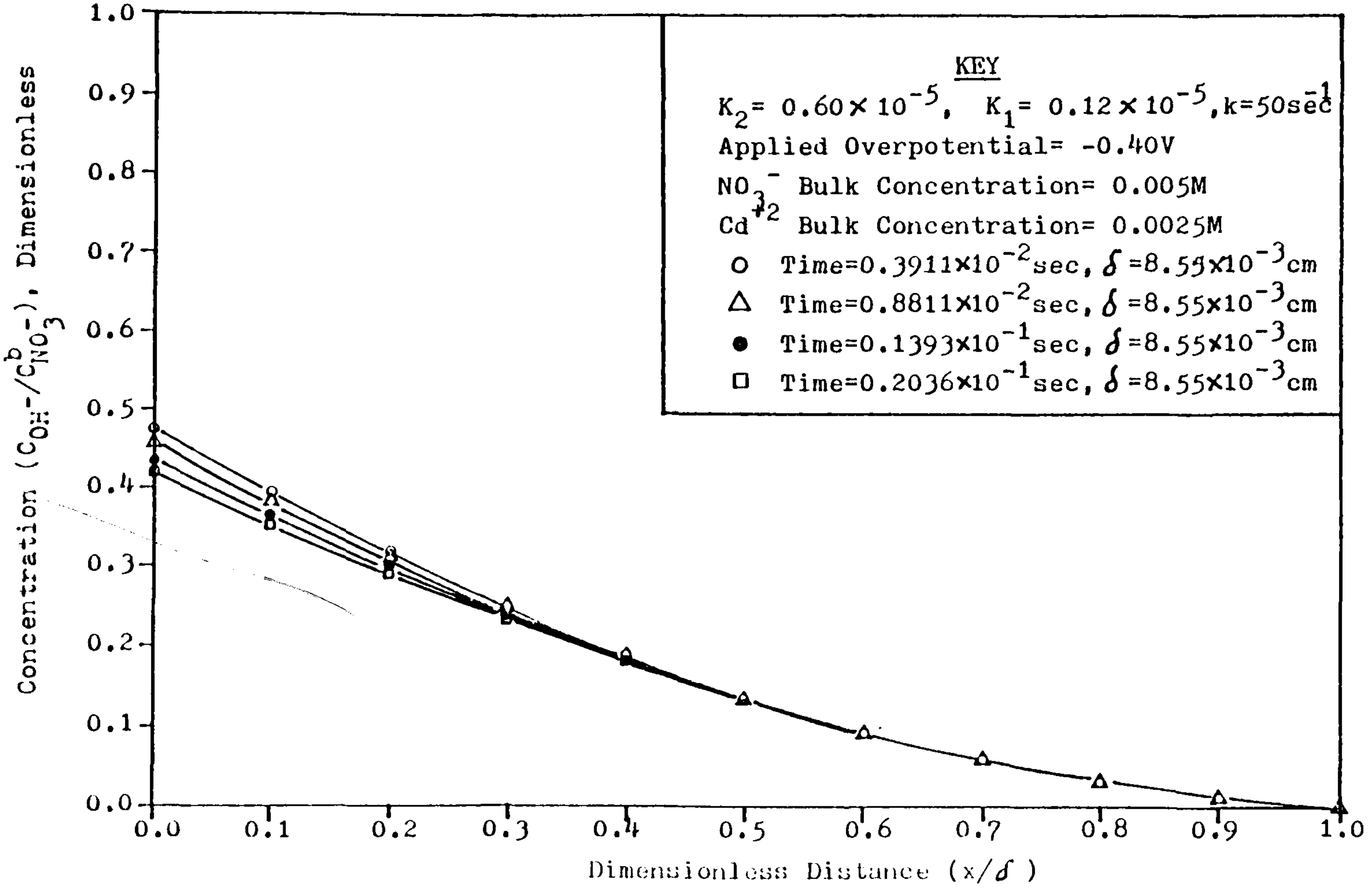

Figure 30: Concentration Profiles of Hydroxy Ion When the Surface Concentration of Hydroxy Ion Starts to Drop.

Table 4: Diffusion Thickness of OH^- Ion as a Function of Time for the Case of Solution Containing Cadmium Ions. The Applied Overpotential Is -0.40V. The Nitrate-Ion Bulk Concentration Is 0.005M. The Cadmium-Ion Bulk Concentration Is 0.0025M.

Time (sec)	Diffusion Thickness(cm)
0.1236×10^{-5}	0.25×10^{-4}
0.6128×10^{-5}	0.45×10^{-4}
0.1798×10^{-4}	0.80×10^{-4}
0.3513×10^{-4}	0.15×10^{-3}
0.1017×10^{-3}	0.25×10^{-3}
0.4856×10^{-3}	0.50×10^{-3}
0.1148×10^{-2}	0.70×10^{-3}
0.8811×10^{-2}	0.85×10^{-3}
0.4050×10^{-1}	0.85×10^{-3}
0.7031×10^{-1}	0.85×10^{-3}

concentration near the electrode is greater than the bulk concentration of Cd^{+2}, its value versus distance from the electrode decreases slowly in the beginning, then faster, and more slowly again before finally reaching its bulk value. At the time when the concentration values near the electrode surface are still larger than the bulk concentration, the concentration decreases to some minimum value at some distance from the electrode surface and then increases until it reaches the bulk value. The location of the minimum concentration point moves toward the electrode surface as time increases. At sufficiently long time, the minimum point finally reaches the electrode surface.

7.3 Conclusions

The transport model for the electrode kinetics and the homogeneous reaction presented previously has already explained very successfully the characterestics of the current density as a function of time for both the case of solution containing cadmium ion and that without cadmium ion. This model was then used to simulate the concentration profiles for various ions involved in the reactions. The behavior of the various ions on the electrode surface and in the solution was obtained. The diffusion processes were also known after examining these concentration profiles carefully. These can be summarized as follows:

1. The current density decays with time after a double-layer charging. The time for this charging is so short that we can not observe it by the experiment. The decay for the current density is a result of the depletion of the nitrate ions on the electrode surface.
2. The current density for the case of a solution containing cadmium ions is greater than that for the case of solution containing no cadmium ion. This is because the precipitation of $Cd(OH)_2$ promotes the electrochemical reaction on the electrode surface by consuming OH^- generated in this reaction.
3. The current density depends on the bulk concentration of nitrate ions and the applied overpotential. Increasing the NO_3^- bulk concentration or the applied overpotential will increase the current density.
4. The applied overpotential is one of the factors which changes the reaction rate of the electrochemical reaction on the electrode surface. Increasing the applied overpotential will increase the overall reaction rate.
5. For the case of solution containing no cadmium ion, the surface concentration of NO_3^- decreases as time increases while the surface concentration of OH^- increases as time increases. This is because NO_3^- ions are consumed to produce the OH^- ions during the electrochemical reaction on the electrode surface.
6. For the case of solution containing cadmium ion, the surface concentration of NO_3^- ion also decreases. The decreasing rate is, however, faster than that for the case

of solution containing no cadmium ion. The surface concentration of OH^- ion increases in the beginning and reaches a maximum. When the production rate of OH^- due to the electrochemical reaction is less than the consumption rate of OH^- due to the precipitation reaction, the surface concentration of OH^- starts to decrease. To maintain electroneutrality, the surface concentration of Cd^{+2} ions will exceed its bulk value and then decrease to the value lower than its bulk value.

7. The diffusion processes for the case of solution containing no cadmium ion is that the nitrate ions diffuse from the bulk solution toward the electrode surface while the hydroxy ions diffuse in the opposite direction.
8. For the case of solution containing cadmium ions, the diffusion directions for both the nitrate ions and hydroxy ions are the same as that for the case of solution containing no cadmium ion. However, the cadmium ions diffuse toward the bulk solution in the beginning and then finally change direction toward the electrode surface.

7.4 Recommendation for Future Works

Although the model has successfully explained the cases of -0.40V and -0.60V, it is not likely valid for the case of -0.80V due to the unexpected characterestics of the current-density-vs.-time curves and the comparison of the current density with the limiting case. When the applied overpotential is as high as -0.80V, the reaction mechanisms and electrode behavior should be identified by doing some further experiments. Furthermore, the current-density-vs.-time data at -0.60V applied overpotential for the case of solution containing cadmium ions is not available yet. It can be obtained by repeating the experimental work we decribed before. Once the data is obtained, the model can be used for comparison with the experimental data.

Finally, the configuration of the electrode in the impregnation process is not as simple as we have used in deriving the model. It is, in fact, a porous electrode in the real case. If a micro-porous electrode is possible to obtain, the experiment can be repeated to obtain the current-density-vs.-time data. Once the data are available, the transport processes can be examined for the condition of porous electrode.

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APPENDIX A.1

THE "BASIC" MAIN PROGRAM USED IN EXPERIMENTAL WORKS

APPENDIX A.1

THE "BASIC" MAIN PROGRAM USED IN EXPERIMENTAL WORKS

```
10 REM**********************************************************************
15 REM*                                                                    *
18 REM*                                                                    *
20 REM*   THIS IS THE BASIC PROGRAM USED IN THE CURRENT VS                 *
25 REM* TIME TRANSIENT EXPERIMENT. THE "MUG" IN STATEMENT                  *
30 REM* 260 IS A SAMPLING SUBROUTINE WRITTEN IN ASSEMBLY                   *
35 REM* LANGUAGE. WHEN "MUG" IS EXECUTED, THE CPU STARTS TO                *
40 REM* SAMPLE THE CURRENT OUTPUT AT EVERY CONSTANT TIME                   *
45 REM* INTERVAL. THE ANALOG SIGNAL IS IMMEDIATELY CONVERTED               *
50 REM* INTO A DIGITAL DATA BY A 12 BIT ADC AND THEN STORED                *
55 REM* IN THE MEMORY. WHEN THE NUMBER OF TIMES IT SAMPLES                 *
60 REM* REACHES A PRESET VALUE, THE SAMPLING ROUTINE IS                    *
64 REM* TERMINATED. THESE DATA ARE THEN CONVERTED INTO                     *
66 REM* DECIMAL NUMBERS AND PRINTED OUT BY A LINE PRINTER.                 *
68 REM*   THE VARIABLES USED IN THIS PROGRAM ARE                           *
70 REM*                                                                    *
72 REM*     X(0)=CLOCK SETTING                                             *
74 REM*     X(1)=SAMPLING TIME INTERVAL IN MICROSECOND                     *
76 REM*     X(2)=CHANNEL NUMBER WHERE THE CURRENT IS                       *
78 REM*          SAMPLED FROM                                              *
80 REM*     M   =NUMBER OF POINTS TO BE SAMPLED                            *
82 REM*   THE ARGUMENTS IN "MUG" SUBROUTINE ARE                            *
84 REM*                                                                    *
86 REM*     IF S=0 THEN EXECUTE TEST PROGRAM                               *
88 REM*     IF S=1 THEN GO TO MUGGER                                       *
90 REM*     N=NUMBER OF VALUES PASSED IN ARRAY X(0)                        *
92 REM*     M=NUMBER OF VALUES TO BE RETURNED IN ARRAY Y(0)                *
93 REM*     X(0) IS THE INPUT ARRAY                                        *
94 REM*     X(0) IS THE INPUT ARRAY                                        *
96 REM*     Y(0) IS THE OUTPUT CURRENT ARRAY                               *
97 REM*                                                                    *
98 REM*                                                                    *
99 REM**********************************************************************
170 CONFIG(SCREEN)
180 DIM X(10),Y(2000),Z(2000),C(300),T(300)
190 S=0
200 N=3
201 REM*
202 REM*
204 REM*******     INPUT DATA      *******
205 REM*
206 REM*
210 PRINT "CLOCK SET,","SAMPLING TIME INTERVAL"
220 INPUT X(0),X(1)
230 K=X(1)
240 PRINT "CHANNEL NUMBER,","NUMBER OF POINTS,","SCALE FACTOR"
250 INPUT X(2),M,F
251 REM*
```

```
252 REM*
254 REM*****  CALL THE MUG SUBROUTINE AND START TO SAMPLE  *****
255 REM*
256 REM*
260 DOIT(MUG,S,N,X(0),M,Y(0))
261 REM*
262 REM*
264 REM***** CONVERT THE CURRENT DATA INTO DECIMAL NUMBERS *****
265 REM*
266 REM*
270 FOR I=0TOM-1
280 Z(I)=(Y(I)-15)/16/2048
290 NEXT I
292 REM*
294 REM*
300 REM*****  CONNECT THE COMPUTER TO THE LINE PRINTER   *****
302 REM*****  DIVIDED THE CURRENT BY THE SURFACE AREA    *****
304 REM*****  0.013 CM2 TO BECOME THE CURRENT DENSITY    *****
305 REM*****  PRINT CURRENT DENSITY VS TIME DATA         *****
306 REM*
307 REM*
310 CONFIG(TTY)
320 PRINT TAB(15),"TIME",TAB(45),"CURRENT DENSITY"
330 PRINT TAB(16),"(SEC)",TAB(50),"(  AMP/CM2)"
340 PRINT;PRINT
350 FOR I=1 TO 19
360 T(I)=K/1000000*I
370 C(I)=-Z(I-1)*F/0.1/0.013
380 PRINT TAB(15),T(I),TAB(50),C(I)
390 NEXT I
400 FOR I=1 TO M/20-1
410 T(I)=K/1000000*(20*I)
420 C(I)=-Z(20*I-1)*F/0.1/0.013
430 PRINT TAB(15),T(I),TAB(50),C(I)
440 NEXT I
450 END
```

APPENDIX A.2

THE ASSEMBLY SUBROUTINE "MUG" USED IN THE MAIN PROGRAM

Address	Contents	Instructions	Comments
0300	CD	CAL 0390	Clear clocks
0301	90		
0302	03		
0303	D3	Out E1	Stop ADC
0304	E1		
0305	3E	MBI A,34	
0306	34		
0307	D3	Out E9	Clock 0, Mode 2, 2 Byte Load
0308	E9		
0309	2A	MHLD HL,0406	"HL" points to N(0)
030A	06		
030B	04		
030C	7E	MB A,M	
030D	D3	Out EF	Load LSBYT to clock 0
030E	EF		
030F	23	INC HL	

Address	Contents	Instructions	Comments
0310	7E	MB A,M	
0311	D3	Out EF	Load MSBYT to clock 0
0312	EF		
0313	23	INC HL	
0314	3E	MBI A,74	
0315	74		
0316	D3	Out E9	Clock 1, Mode 2, 2 Byte Load
0317	E9		
0318	7E	MB A,M	
0319	D3	Out EB	Load LSBYT to clock 1
031A	EB		
031B	23	INC HL	
031C	7E	MB A,M	
031D	D3	Out EB	Load MSBYT to clock 1
031E	EB		
031F	23	INC HL	

```
Address   Contents   Instructions     Comments

0320      3E         MBI A,10         Trigger (Go high)
0321      10
0322      D3         Out E5
0323      E5
0324      3A         MAD A,0404       Load LSBYT
0325      04
0326      04
0327      4F         MB C,A
0328      3A         MAD A,0405       Load MSBYT
0329      05
032A      04
032B      47         MB B,A           Number of points= .BC.
032C      7E         MB A,M
032D      2A         MHLD HL,0408     Address of output array
032E      08
032F      04
```

Address	Contents	Instructions	Comments
0330	D3	Out E7	Start clock & ADC
0331	E7		
0332	3E	MBI A,00	Trigger (Go low)
0333	00		
0334	D3	Out E5	
0335	E5		
0336	DB	In E0	Read ADC status
0337	E0		
0338	1F	RR CRY	Is it holding yet?
0339	D2	JUM0336,NCRY	
033A	36		
033B	03		
033C	DB	In E0	Look for not busy
033D	E0		
033E	1F	RR CRY	
033F	DA	JUM033C,CRY	It is holding now!

Address	Contents	Instructions	Comments
0340	3C		
0341	03		
0342	DB	In E6	Read LSBYT (Conversion complete)
0343	E6		
0344	77	MB M,A	Plant the LSBYT to memory
0345	23	INC HL	Point to next location
0346	DB	In E4	Read MSBYT
0347	E4		
0348	77	MB M,A	Plant the MSBYT to memory
0349	23	INC HL	
034A	0B	DCR BC	Decrease the number of points
034B	79	MB A,C	
034C	B0	IR B	
034D	C2	JUM0336,NZOT	
034E	36		
034F	03		
0350	C9	RET	Return to main program

APPENDIX B

LISTING OF EXPERIMENTAL DATA

Table B.1 Current-Density-vs.-Time Data for the Case of Solution Containing No Cadmium Ion. Nitrate-Ion Bulk Concentration= 0.005M, Initial pH=3.0, Applied Overpotential= -0.40V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (m AMP/CM2)
.0001	184.043
.0002	102.163
.0003	75.4957
.0004	60.8473
.0005	51.8329
.0006	45.4476
.0007	40.9404
.0008	37.56
.0009	34.5552
.001	32.3016
.0011	30.7992
.0012	29.2968
.0013	27.7944
.0014	26.6676
.0015	25.9164
.0016	25.1652
.0017	24.0384
.0018	23.2872
.0019	22.9116
.002	22.1603
.004	16.5263
.006	13.8972
.008	12.3947
.01	10.8923
.012	10.1411
.014	9.76561
.016	9.01438
.018	8.63876
.02	8.26317
.022	7.88761
.024	7.51201
.026	7.51201
.028	6.76081
.03	7.13641
.032	6.76081
.034	6.76081
.036	6.38521
.038	6.38521
.04	6.00961

Table B.2 Current-Density-vs.-Time Data for the Case of Solution Containing No Cadmium Ion, Nitrate-Ion Bulk Concentration= 0.005M, Initial pH= 3.0, Applied Overpotential= -0.60V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (MLAMP/CM2
.0001	292.593
.0002	178.034
.0003	135.966
.0004	113.43
.0005	99.1584
.0006	89.0169
.0007	81.1292
.0008	75.1201
.0009	70.6129
.001	66.4813
.0011	62.7253
.0012	60.0961
.0013	57.4669
.0014	55.5889
.0015	53.3353
.0016	51.4573
.0017	49.9549
.0018	48.4524
.0019	46.95
.002	46.1988
.004	32.6772
.006	27.4188
.008	24.0384
.01	21.7848
.012	19.9068
.014	18.78
.016	17.2776
.018	16.5263
.02	15.3996
.022	15.3996
.024	14.2727
.026	13.8972
.028	13.146
.03	13.146
.032	12.3947
.034	12.0192
.036	11.6436
.038	11.6436
.04	11.268

Table B.3 Current-Density-vs.-Time Data for the Case of Solution Containing No Cadmium Ion. Nitrate-Ion Bulk Concentration= 0.005M, Initial pH= 3.0, Applied Overpotential= -0.80V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (m AMP/CM2)
.0001	424.804
.0002	282.826
.0003	224.609
.0004	191.18
.0005	169.02
.0006	152.493
.0007	139.723
.0008	129.582
.0009	120.567
.001	113.806
.0011	107.421
.0012	102.163
.0013	97.6561
.0014	93.1484
.0015	89.7684
.0016	86.3876
.0017	83.0076
.0018	80.3784
.0019	77.7492
.002	75.4957
.004	51.0816
.006	41.6316
.008	37.1844
.01	33.804
.012	31.5504
.014	29.6724
.016	28.5456
.018	27.4188
.02	26.6676
.022	25.5408
.024	24.7896
.026	24.0384
.028	23.6628
.03	22.9116
.032	22.536
.034	21.7848
.036	21.7848
.038	21.4092
.04	20.658

Table B.4 Current-Density-vs.-Time Data for the Case of Solution Containing No Cadmium Ion, Nitrate-Ion Bulk Concentration= 0.0025M, Initial pH=3.0, Applied Overpotential= -0.40V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (mAMP/CM2)
.0001	138.913
.0002	58.5936
.0003	43.5696
.0004	35.3064
.0005	29.6724
.0006	25.9164
.0007	23.2871
.0008	21.0336
.0009	19.5312
.001	18.0288
.0011	16.5263
.0012	16.1507
.0013	15.024
.0014	14.2727
.0015	13.8972
.0016	13.146
.0017	12.7703
.0018	12.3947
.0019	11.6436
.002	11.6436
.004	7.88761
.006	6.76081
.008	5.634
.01	5.2584
.012	4.5072
.014	4.5072
.016	4.1316
.018	4.1316
.02	3.756
.022	3.756
.024	3.756
.026	3.3804
.028	3.3804
.03	3.0048
.032	3.3804
.034	3.0048
.036	3.0048
.038	3.0048
.04	3.0048

Table B.5 Current-Density-vs.-Time Data for the Case of Solution Containing No Cadmium Ion. Nitrate-Ion Bulk Concentration= 0.0025M, Initial pH=3.0, Applied Overpotential=-0.60V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (mAMP/CM2)
.0001	217.848
.0002	120.567
.0003	88.6415
.0004	72.8663
.0005	62.3496
.0006	55.5889
.0007	51.0816
.0008	46.95
.0009	43.9453
.001	41.6916
.0011	39.438
.0012	38.3112
.0013	36.4332
.0014	34.9308
.0015	34.1796
.0016	33.0528
.0017	32.3016
.0018	31.5504
.0019	30.4236
.002	30.048
.004	22.536
.006	20.1823
.008	18.4043
.01	17.2776
.012	16.1507
.014	15.3996
.016	14.6483
.018	13.8972
.02	13.5216
.022	13.146
.024	12.7703
.026	12.0192
.028	12.0192
.03	11.268
.032	11.6436
.034	10.8923
.036	10.8923
.038	10.5167
.04	10.5167

Table B.6 Current-Density-vs.-Time Data for the Case of Solution Containing No Cadmium Ion. Nitrate-Ion Bulk Concentration= 0.0025M, Initial pH=3.0, Applied Overpotential= -0.80V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (mAMP/CM2)
.0001	342.923
.0002	207.706
.0003	162.634
.0004	139.347
.0005	123.947
.0006	113.055
.0007	104.792
.0008	97.6561
.0009	92.3976
.001	87.5146
.0011	83.383
.0012	80.0023
.0013	76.6225
.0014	73.9933
.0015	70.9885
.0016	68.7349
.0017	66.8569
.0018	64.2276
.0019	62.7253
.002	61.2229
.004	40.9404
.006	33.0528
.008	28.17
.01	25.9164
.012	23.6628
.014	22.536
.016	20.658
.018	20.2823
.02	18.78
.022	18.4043
.024	17.2778
.026	16.902
.028	16.1507
.03	15.7752
.032	15.024
.034	14.6483
.036	14.2727
.038	13.8972
.04	13.5216

Table 3.7 Current-Density-vs.-Time Data for the Case of Solution Containing No Cadmium Ion. Nitrate-Ion Bulk Concentration= 0.00125M, Initial pH=3.0, Applied Overpotential= -0.40V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (M AMP CM2)
.0001	96.9046
.0002	49.5793
.0003	34.9306
.0004	27.4188
.0005	23.2872
.0006	19.9068
.0007	18.0288
.0008	16.1507
.0009	15.024
.001	14.2727
.0011	13.146
.0012	12.3947
.0013	12.3947
.0014	11.268
.0015	11.268
.0016	10.8923
.0017	10.1411
.0018	10.1411
.0019	10.1411
.002	9.76561
.004	7.13641
.006	6.00961
.008	5.634
.01	4.8828
.012	4.8828
.014	4.1316
.016	4.1316
.018	3.756
.02	4.1316
.022	3.3804
.024	3.3804
.026	3.3804
.028	3.3804
.03	3.0048
.032	3.3804
.034	2.6292
.036	3.0048
.038	2.6292
.04	3.0048

Table 3.8 Current-Density-vs.-Time Data for the Case of Solution Containing No Cadmium Ion. Nitrate-Ion Bulk Concentration= 0.00125M, Initial pH=3.0, Applied Overpotential= -0.60V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (M AMP/CM2)
.0001	199.443
.0002	104.04
.0003	75.4957
.0004	61.5985
.0005	53.3353
.0006	48.0769
.0007	44.3288
.0008	41.316
.0009	39.0624
.001	36.8088
.0011	35.682
.0012	34.1796
.0013	32.6772
.0014	31.926
.0015	30.7992
.0016	29.6724
.0017	29.2968
.0018	28.17
.0019	28.17
.002	27.4188
.004	20.658
.006	18.4043
.008	16.5263
.01	15.7752
.012	14.6483
.014	13.8972
.016	13.146
.018	12.7703
.02	12.0192
.022	12.0192
.024	11.268
.026	11.268
.028	10.5167
.03	10.8927
.032	10.1411
.034	10.1411
.036	9.76561
.038	9.76561
.04	9.79

Table 3.9 Current-Density-vs.-Time Data for the Case of Solution Containing No Cadmium Ion. Nitrate-Ion Bulk Concentration= 0.00125M, Initial pH=3.0, Applied Overpotential= -0.80V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (M AMP/CM2)
.0001	330.153
.0002	184.043
.0003	141.976
.0004	123.196
.0005	111.177
.0006	102.508
.0007	96.1508
.0008	90.8533
.0009	86.3873
.001	83.0076
.0011	79.6269
.0012	76.6225
.0013	73.9933
.0014	71.3641
.0015	69.1105
.0016	66.8569
.0017	64.6033
.0018	62.7253
.0019	60.8473
.002	58.9693
.004	36.3112
.006	30.4236
.008	25.9164
.01	22.9116
.012	21.0336
.014	19.1556
.016	18.4043
.018	17.2776
.02	16.5263
.022	15.7752
.024	15.3996
.026	14.6483
.028	14.6483
.03	13.8972
.032	13.8972
.034	13.146
.036	13.146
.038	12.7703
.04	12.7703

Table B.10 Background Current Density of Water, Initial pH= 3.0, Applied Overpotential= -0.40V, Rest Potential= -0.354V.

TIME (SEC)	CURRENT DENSITY (M AMP/CM2)
.0001	53.3353
.0002	30.048
.0003	21.7848
.0004	17.6532
.0005	14.6483
.0006	12.7703
.0007	11.6436
.0008	10.5167
.0009	9.76561
.001	9.39
.0011	8.26315
.0012	8.26315
.0013	7.88761
.0014	7.13641
.0015	7.13641
.0016	6.76081
.0017	6.38521
.0018	6.38521
.0019	6.00961
.002	6.00961
.004	4.5072
.006	3.756
.008	3.3804
.01	3.0048
.012	3.0048
.014	2.6292
.016	2.6292
.018	2.2536
.02	2.2536
.022	2.2536
.024	2.2536
.026	1.878
.028	2.2536
.03	1.878
.032	2.2536
.034	1.878
.036	2.2536
.038	1.878
.04	1.878

Table 3.11 Background Current Density of Water. Initial pH= 3.0, Applied Overpotential= -0.607V, Rest Potential= -0.354V.

TIME (SEC)	CURRENT DENSITY (µ AMP/CM2)
.0001	128.83
.0002	68.3593
.0003	50.706
.0004	41.316
.0005	36.0576
.0006	32.6772
.0007	30.048
.0008	28.17
.0009	26.6675
.001	25.1652
.0011	24.414
.0012	23.2872
.0013	22.1603
.0014	21.7848
.0015	21.0336
.0016	20.658
.0017	20.2823
.0018	19.5312
.0019	19.1556
.002	18.78
.004	14.2727
.006	12.3947
.008	11.268
.01	10.8923
.012	10.1411
.014	9.76561
.016	9.39
.018	9.39
.02	8.63876
.022	8.63876
.024	8.26315
.026	8.26315
.028	7.88761
.03	7.88761
.032	7.51201
.034	7.51201
.036	7.13641
.038	7.51201
.04	7.13641

Table B.12 Background Current Density of Water. Initial pH= 3.0, Applied Overpotential= -0.80V, Rest Potential= -0.354V.

TIME (SEC)	CURRENT DENSITY (mAMP/CM2)
.0001	247.145
.0002	135.216
.0003	93.5246
.0004	72.1153
.0005	60.0961
.0006	52.584
.0007	47.7013
.0008	43.9453
.0009	41.316
.001	38.6868
.0011	37.1844
.0012	35.682
.0013	34.1796
.0014	33.4284
.0015	32.3016
.0016	31.5504
.0017	30.7992
.0018	30.048
.0019	29.6724
.002	28.9212
.004	22.536
.006	19.9068
.008	18.0288
.01	16.5263
.012	15.3996
.014	14.6483
.016	13.8972
.018	13.5216
.02	12.7703
.022	12.3947
.024	11.6436
.026	11.6436
.028	10.8923
.03	10.8923
.032	10.5167
.034	10.5167
.036	9.76561
.038	9.76561
.04	9.39

Table 3.13 Current-Density-vs.-Time Data for the Case of Solution Containing Cadmium Ions. Nitrate-Ion Bulk Concentration= 0.005M, Cadmium-Ion Bulk Concentration= 0.0025M, Initial pH= 3.0, Applied Overpotential= -0.40V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (mAMP CM2)
.0001	226.862
.0002	138.972
.0003	105.167
.0004	86.763
.0005	74.7445
.0006	66.1057
.0007	60.0961
.0008	55.2133
.0009	51.4573
.001	48.0769
.0011	45.072
.0012	43.194
.0013	40.9404
.0014	39.438
.0015	38.3112
.0016	36.8088
.0017	35.682
.0018	34.5552
.0019	33.4284
.002	33.0528
.004	24.7896
.006	22.1603
.008	20.2823
.01	19.9068
.012	19.1556
.014	19.1556
.016	18.78
.018	18.4043
.02	18.0288
.022	17.2776
.024	16.902
.026	16.1507
.028	15.3996
.03	14.4483
.032	13.8972
.034	13.146
.036	13.146
.038	12.3947
.04	12.0192

Table B. 14 Current-Density-vs.Time Data for the Case of Solution Containing Cadmium Ions. Nitrate-Ion Bulk Concentration= 0.005M, Cadmium-Ion Bulk Concentration= 0.0025M, Initial pH= 3.0, Applied Overpotential= -0.60V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (mAMP/CM2)
.0001	343.552
.0002	226.466
.0003	179.506
.0004	154.371
.0005	137.845
.0006	125.826
.0007	116.436
.0008	108.548
.0009	102.538
.001	97.29
.0011	92.773
.0012	89.3923
.0013	86.0123
.0014	83.383
.0015	81.1292
.0016	78.8761
.0017	77.373
.0018	75.4957
.0019	73.9933
.002	72.4909
.004	54.0865
.006	43.5696
.008	37.1844
.01	33.4284
.012	30.048
.014	28.17
.016	25.9164
.018	24.7896
.02	23.2872
.022	22.536
.024	21.4092
.026	20.658
.028	19.9068
.03	19.1556
.032	18.4043
.034	18.0288
.036	17.6532
.038	16.902
.04	16.5263

Table B.15 Current-Density-vs.-Time Data for the Case of Solution Containing Cadmium Ions. Nitrate-Ion Bulk Concentration= 0.005M, Cadmium-Ion Bulk Concentration= 0.0025M, Initial pH= 3.0, Applied Overpotential= -0.80V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (m AMP/CM2)
.0001	480.393
.0002	336.578
.0003	272.686
.0004	234.374
.0005	208.458
.0006	190.653
.0007	176.156
.0008	166.015
.0009	157.752
.001	150.619
.0011	144.981
.0012	139.347
.0013	134.464
.0014	130.333
.0015	125.826
.0016	122.449
.0017	119.065
.0018	116.06
.0019	113.806
.002	110.801
.004	84.51
.006	72.1153
.008	64.6033
.01	59.3449
.012	55.5889
.014	52.584
.016	49.9549
.018	47.7013
.02	45.8233
.022	44.3208
.024	42.8184
.026	41.6915
.028	40.5648
.03	39.8136
.032	38.6868
.034	37.9356
.036	36.8088
.038	36.4332
.04	35.7064

Table B.16 Current-Density-vs.-Time Data for the Case of Solution Containing Cadmium Ions. Nitrate-Ion Bulk Concentration= 0.0025M, Cadmium-Ion Bulk Concentration= 0.00125M, Initial pH= 3.0, Applied Overpotential= -0.40V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (mAMP/CM2)
.0001	126.953
.0002	70.2373
.0003	51.0816
.0004	40.5648
.0005	34.5552
.0006	30.048
.0007	27.0432
.0008	25.1652
.0009	22.9116
.001	21.4092
.0011	20.658
.0012	19.1556
.0013	18.78
.0014	17.6532
.0015	16.902
.0016	16.5263
.0017	16.1507
.0018	15.3996
.0019	15.3996
.002	14.6483
.004	10.8923
.006	9.39
.008	8.63876
.01	7.88761
.012	7.51201
.014	6.76081
.016	6.76081
.018	6.38521
.02	6.00961
.022	6.00961
.024	5.634
.026	5.634
.028	5.2584
.03	5.2584
.032	5.2584
.034	5.2584
.036	4.8828
.038	4.8828
.04	4.5072

Table 3.17 Current-Density-vs.-Time Data for the Case of Solution Containing Cadmium Ions. Nitrate-Ion Bulk Concentration= 0.0025M, Cadmium-Ion Bulk Concentration= 0.00125M, Initial pH= 3.0, Applied Overpotential= -0.60V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (mAMP/CM2)
.0001	233.623
.0002	134.84
.0003	102.914
.0004	86.0123
.0005	75.8713
.0006	68.3593
.0007	63.1009
.0008	58.9693
.0009	55.5889
.001	52.584
.0011	50.3304
.0012	48.0769
.0013	46.5744
.0014	45.4476
.0015	43.9453
.0016	42.8184
.0017	41.6916
.0018	40.5648
.0019	40.1892
.002	39.0624
.004	31.926
.006	28.5456
.008	26.292
.01	24.0384
.012	22.536
.014	21.0336
.016	19.5312
.018	18.78
.02	17.6532
.022	16.902
.024	16.1507
.026	15.7752
.028	15.024
.03	14.6483
.032	13.8972
.034	13.8972
.036	13.146
.038	13.146
.04	12.3947

Table 3.18 Current-Density-vs.-Time Data for the Case of Solution Containing Cadmium Ions. Nitrate-Ion Bulk Concentration= 0.0025M, Cadmium-Ion Bulk Concentration= 0.00125M, Initial pH= 3.0, Applied Overpotential= -0.30V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (mAMP/CM2)
.0001	353.064
.0002	230.993
.0003	184.795
.0004	159.254
.0005	143.183
.0006	131.084
.0007	122.449
.0008	117.684
.0009	110.85
.001	105.543
.0011	101.836
.0012	97.28
.0013	94.2753
.0014	91.2707
.0015	88.6415
.0016	86.3876
.0017	83.7584
.0018	81.8807
.0019	79.6269
.002	77.373
.004	54.462
.006	44.3208
.008	39.0624
.01	34.9308
.012	32.6772
.014	30.4236
.016	28.9212
.018	27.4188
.02	26.292
.022	25.1652
.024	24.0384
.026	23.2872
.028	22.9116
.03	21.7848
.032	21.4092
.034	20.658
.036	19.9068
.038	19.5312
.04	19.1556

Table 3.19 Current-Density-vs.-Time Data for the Case of Solution Containing Cadmium Ions. Nitrate-Ion Bulk Concentration= 0.00125M, Cadmium-Ion Bulk Concentration= 0.000625M, Initial pH= 3.0, Applied Overpotential= -0.40V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (mAMP/CM2)
.0001	108.173
.0002	61.9741
.0003	45.4476
.0004	36.8088
.0005	30.4236
.0006	26.6676
.0007	23.2872
.0008	21.0036
.0009	19.5312
.001	17.6532
.0011	16.5263
.0012	15.7752
.0013	14.6483
.0014	14.2727
.0015	13.5216
.0016	12.7703
.0017	12.7703
.0018	12.0192
.0019	11.6436
.002	11.268
.004	7.88761
.006	6.76081
.008	5.634
.01	5.2584
.012	4.8828
.014	4.8828
.016	4.1316
.018	4.1316
.02	4.1316
.022	4.1316
.024	3.756
.026	3.756
.028	3.3804
.03	3.3804
.032	3.3804
.034	3.3804
.036	3.3804
.038	3.3804
.04	3.3804

Table B.20 Current-Density-vs.-Time Data for the Case of Solution Containing Cadmium Ions. Nitrate-Ion Bulk Concentration= 0.00125M, Cadmium-Ion Bulk Concentration= 0.00625M, Initial pH= 3.0, Applied Overpotential= -0.60V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (mAMP/CM2)
.0001	205.077
.0002	122.82
.0003	91.6461
.0004	75.1201
.0005	64.6033
.0006	57.4669
.0007	52.584
.0008	48.4524
.0009	45.8233
.001	43.194
.0011	40.9404
.0012	39.438
.0013	37.56
.0014	36.4332
.0015	35.3064
.0016	34.1796
.0017	33.4284
.0018	32.3016
.0019	31.5504
.002	30.7992
.004	22.536
.006	19.9068
.008	17.6532
.01	16.902
.012	15.7752
.014	15.3996
.016	14.6483
.018	14.2727
.02	13.5216
.022	13.5216
.024	13.146
.026	12.7703
.028	12.3947
.03	12.0192
.032	12.0192
.034	11.6436
.036	11.6436
.038	11.268
.04	11.268

Table 3.21 Current-Density-vs.-Time Data for the Case of Solution Containing Cadmium Ions. Nitrate-Ion Bulk Concentration= 0.00125M, Cadmium-Ion Bulk Concentration= 0.00625M, Initial pH= 3.0, Applied Overpotential= -0.80V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (mAMP/CM2)
.0001	347.806
.0002	230.618
.0003	183.293
.0004	157.752
.0005	140.474
.0006	128.83
.0007	119.44
.0008	111.928
.0009	106.294
.001	101.411
.0011	96.9046
.0012	93.5246
.0013	90.1438
.0014	87.5146
.0015	84.8853
.0016	82.2561
.0017	80.7538
.0018	78.5
.0019	76.6225
.002	75.1201
.004	51.0816
.006	40.5648
.008	34.5552
.01	31.1748
.012	28.5456
.014	26.6676
.016	25.1652
.018	23.6628
.02	22.536
.022	22.1603
.024	21.0336
.026	20.2823
.028	19.9068
.03	19.1556
.032	18.78
.034	18.0288
.036	18.0288
.038	17.2776
.04	17.2776

Table 3.22 Background Current Density of Water in the Presence of Cadmium Ion. Cadmium-Ion Bulk Concentration= 0,0025M, Initial pH= 3.0, Applied Overpotential= -0.40V, Rest Potential = -0.354V.

TIME (SEC)	CURRENT DENSITY (mAMP/CM2)
.0001	110.05
.0002	63.1009
.0003	48.0769
.0004	39.438
.0005	33.0528
.0006	28.17
.0007	25.5408
.0008	22.536
.0009	20.658
.001	19.1556
.0011	17.2776
.0012	16.5263
.0013	15.3956
.0014	14.2727
.0015	14.2727
.0016	13.146
.0017	12.3947
.0018	12.3947
.0019	11.6436
.002	11.268
.004	7.51201
.006	6.00961
.008	5.634
.01	4.8828
.012	4.5072
.014	4.1316
.016	4.1316
.018	3.756
.02	3.756
.022	3.3804
.024	3.756
.026	3.3804
.028	3.3804
.03	3.0048
.032	3.3804
.034	2.6292
.036	3.3804
.038	2.6292
.04	3.0048

APPENDIX C

A BRIEF REVIEW OF ORTHOGONAL COLLOCATION METHOD

The method of weighted residuals, MWR, is a general method for obtaining solutions to equations of change, in our case, Fick's second law. In the MWR, one assumes a trial function, usually a set of weighted polynomials, substitutes this trial function into the differential equation and then selects the coefficients of the polynomial terms by specifying that the residual be zero, on the average, at certain points. If one evaluates the differential equation at the zeros of an orthogonal polynomial, the residual will of necessity be exactly zero at these collocation points. By increasing the number of collocation points, the trial function would satisfy the differential equation at more and more points(1).

The polynomials selected for this work are "shifted" Jacobi polynomials defined by

$$\int_0^1 x^{\beta}(1-x)^{\alpha} P_n^{(\alpha,\beta)}(x)\, P_m^{(\alpha,\beta)}(x)\, dx = 0 \qquad (1)$$

A general diffusion problem can be formulated as

$$\frac{\partial y}{\partial t} = D\frac{\partial^2 y}{\partial x^2} + f(y),\ 0 \leq x \leq 1,\ 0 < t \qquad (2)$$

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(1) B.A. Finlayson & Richard Bellman (Ed.), 'Mathematics in Science and Engineering', Vol. 87, Academic Press, New York, 1972, pp 9.

with the boundary conditions of the form

$$y(0,t)=g(t) \tag{3}$$

$$y(1,t)=h(t) \tag{4}$$

and initial condition such as

$$y(x,0)=p(x) \tag{5}$$

For a mass transfer problem D would be a dimensionless diffusion coefficient and f(y) would be homogeneous reaction term. Geometric considerations indicate that $\alpha=\beta=0$ and mathematical considerations indicate that a suitable but not unique trial function is$^{(2)}$

$$y(x,t)=(1-x)y(0,t)+xy(1,t)+x(1-x)\sum_{j=1}^{N}a_j(t)P_{j-1}(x) \tag{6}$$

The P_{j-1} of equation (6) refers to one member of a complete set of polynomials. Table C.1 lists some Legendre polynomials, the special case of equation (1) where $\alpha=\beta=0$, and their roots . Note that a Legendre polynomial of degree N has N real, distinct roots on the interval $0<x<1$.

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(2) B.A. Finlayson & Richard Bellman (Ed.), 'Mathematics in Science and Engineering', Vol. 87, Academic Press, New York, 1972, pp 105.

TABLE C.1 Legendre Polynomial and Their Roots(3).

N	P_{N-1}	Roots of P_{N-1}
1	$-1+2x$	0.500000000
2	$1-6x+6x^2$	0.211324865 0.788675135
3	$-1+12x-30x^2+20x^3$	0.112701665 0.500000000 0.887298335
4	$1-20x+90x^2-140x^3+70x^4$	0.069431844 0.330009478 0.669990522 0.930568156

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(3) John Villadsen, 'Selected Approximation Method for Chemical Engineering Problems', Reproset, Copenhagen, Denmark, 1970, pp A3 and A4.

It is evident that regardless of the value of N chosen one can always rewrite eqn.(6) in the general form

$$y(x,t)=\sum_{j=1}^{N+2} x^{j-1} b_j(t) \qquad (7)$$

One could at this point, as is normally the case in using MWR, obtain the coefficients $b_j(t)$ by substitution of eqn.(7) in the differential equation whose solution is desired. However, the computer programming is greatly simplified when they are written in terms of the solution of the differential equation at the collocation points, $y(x_i,t)$ where $i=1,2,3...N+2$, and each x_i is one of the N roots of the polynomial or one of the two boundary values. So in terms of the N+2 collocation points we may write:

$$y(x_i,t)=\sum_{j=1}^{N+2} x_i^{j-1} b_j(t) \qquad (8)$$

We now have an approximating polynomial function which we will force to fit our partial differential eqn.(2) at the N+2 collocation points (i.e. choose the $b_j(t)$ so that our partial differential equation is satisfied). In order to do this we will need both the first and second derivatives with respect to x. These derivatives can be calculated explicitly in terms of x since we have already defined the dependence of y upon the spatial coordinate,eqn.(6)and (8).

It is easily seen that if one considers all the collocation points, x_i, equation (8) represents one member of a set of equations:

$$y(x_1,t)=\sum_{j=1}^{N+2} x_1^{j-1} b_j(t) \tag{9}$$

$$y(x_2,t)=\sum_{j=1}^{N+2} x_2^{j-1} b_j(t) \tag{10}$$

$$y(x_{N+2},t)=\sum_{j=1}^{N+2} x_{N+2}^{j-1} b_j(t) \tag{11}$$

One can see that the left-hand side is a vector of the trial solution evaluated at the collocation points. Since the term involving x_i^{j-1} depends on both i and j, a matrix will represent this term. The $b_j(t)$ will naturally be a vector. If we let a single bar represent a vector and a bouble bar a matrix, then the set of eqns.(9) through(11) can be written as one equation in this simplified notation:

$$\overline{y(t)}=\overline{\overline{Q}}\cdot\overline{b(t)} \tag{12}$$

where $Q_{i,j}=x_i^{j-1}$

The first and second derivatives with respect to x may then be obtained from equation (12):

$$\overline{\frac{dy(t)}{dx}}=\overline{\overline{C}}\cdot\overline{b(t)} \tag{13}$$

$$\overline{\frac{d^2 y(t)}{dx^2}} = \overline{\overline{D}} \cdot \overline{b(t)} \qquad (14)$$

where $C_{i,j} = \left.\frac{dx^{j-1}}{dx}\right|_{x_i}$ and $D_{i,j} = \left.\frac{d^2 x^{j-1}}{dx^2}\right|_{x_i}$

It is now simple to solve for $\overline{b(t)}$ the vector of $b_j(t)$ coefficients, since simple rules of matrix algebra apply in this notation. Equation (12) yields

$$\overline{b(t)} = \overline{\overline{Q}}^{-1} \, \overline{y(t)}$$

Substituting this into eqns.(13) and(14) gives

$$\overline{\frac{dy(t)}{dx}} = \overline{\overline{C}} \, \overline{\overline{Q}}^{-1} \, \overline{y(t)} = \overline{\overline{A}} \, \overline{y(t)} \qquad (15)$$

$$\overline{\frac{d^2 y(t)}{dx^2}} = \overline{\overline{D}} \, \overline{\overline{Q}}^{-1} \, \overline{y(t)} = \overline{\overline{B}} \, \overline{y(t)} \qquad (16)$$

where $\overline{\overline{A}} = \overline{\overline{C}} \, \overline{\overline{Q}}^{-1}$ and $\overline{\overline{B}} = \overline{\overline{D}} \, \overline{\overline{Q}}^{-1}$ or in terms of the i-th collocation point, after some simple matrix multiplication,

$$\left.\frac{dy(x,t)}{dx}\right|_{x_i} = \sum_{j=1}^{N+2} A_{i,j} \, y(x_j,t) \qquad (17)$$

$$\left.\frac{d^2 y(x,t)}{dx^2}\right|_{x_i} = \sum_{j=1}^{N+2} B_{i,j} \, y(x_j,t) \qquad (18)$$

One can therefore express the spatial derivatives in terms of the trial function at the N+2 collocation points.

Equation (16) can be directly applied to some diffusion process such as that described by eqns.(2) through (5). Equation (2) becomes

$$\overline{\frac{dy(t)}{dt}} = k\overline{\overline{B}}\ \overline{y(t)} + \overline{f(y(t))} \qquad (19)$$

where the vector $\overline{dy(t)}/dt$ represents the set of time derivatives at the N+2 collocation points. We note that there is no explicit spatial (x) dependence in eqn.(19). By assuming an explicit polynomial in x, eqn.(6), and evaluating it at specific values, the collocation points, the problem is reduced from a partial differential equation with two independent variables to a set of ordinary differential equations.

One can expand eqn.(19) into its separate members to solve the problem. For the i-th collocation point we can write, according to eqn.(19),

$$\left.\frac{dy(x,t)}{dt}\right|_{x_i} = k\left(\sum_{j=1}^{N+2} B_{i,j}\, y(x_j,t)\right) + f(y(x_i,t)) \qquad (20)$$

for i= 1,2,3,...N+2.

One now considers the conditions at the boundaries $x_1=0$ and $x_{N+2}=1$. Since these values are known from the original problem i.e. eqns.(3) and (4) one can subtitute the boundary conditions in eqn.(20) to obtain

$$\left.\frac{dy(x,t)}{dt}\right|_{x_i} = k\left[B_{i,1}\cdot g(t)+ B_{i,N+2}\cdot h(t)+ \sum_{j=1}^{N+1} B_{i,j}y(x_j,t)\right] + f(y(x_i,t))$$

for i = 2,3,4...N+1.

One should note that g(t) and h(t) are included so that the boundary conditions may be time dependent in which case g(t) and h(t) would be known or easily obtained. The diffusion problem has been transformed into a set of N simultaneous first order ordinary differential equations in N unknowns with initial conditions and can be solved numerically by a number of standard methods on a computer.

Evaluation of the current at an electrode, $i= nFAD\left.\frac{\partial c}{\partial x}\right|_{x=0}$, can be obtained directly from eqn.(17) once the concentration profile is obtained.

APPENDIX D

COMPUTER PROGRAMS USING ORTHOGONAL COLLOCATION METHOD

```
C****************************************************************C
C                                                                C
C   THIS PROGRAM SOLVES EQUATIONS (50) THROUGH (55) WITH TWO     C
C   INITIAL CONDITIONS USING SPLINE COLLOCATION METHOD FOR THE   C
C   CASE OF THE ELECTROLYTE CONTAINING NO CADMIUM ION.           C
C   EQUATIONS (50) AND (51) ARE DISCRETIZED FIRST-ORDER          C
C   ORDINARY DIFFERENTIAL EQUATIONS WHICH ARE SOLVED BY AN       C
C   SEMI-IMPLICIT INTEGRATION SUBROUTINE CALLED DIFSUB USING     C
C   GEAR'S ROUTINE. EQUATIONS (52) THROUGH (53) ARE SOLVED       C
C   SIMULTANEOUSLY BY A SUBROUTINE CALLED ZSYSTM WHICH COMES     C
C   FROM IMSL SUBROUTINE PACKAGE TO OBTAIN THE SURFACE           C
C   CONCENTRATIONS OF NITRATE AND HYDROXY IONS. EQUATIONS (54)   C
C   AND (55) ARE THEIR BULK VALUES. THE CONCENTRATION PROFILES   C
C   THUS OBTAINED ARE THEN USED TO CALCULATE THE CURRENT         C
C   DENSITY BY EQUATION (56). THE CURRENT DENSITY DATA ARE       C
C   THEN USED TO FIT WITH THE EXPERIMENTAL DATA TO IDENTIFY      C
C   THE CATHODIC AND ANODIC REACTION RATE CONSTANTS OF THE       C
C   SURFACE REACTION.                                            C
C                                                                C
C       --------------- NOMENCLATURE ---------------             C
C                                                                C
C   NX=NUMBER OF POINTS IN X DIRECTION.                          C
C   N=NUMBER OF INTERIOR COLLOCATION POINTS.                     C
C   NT=NUMBER OF TOTAL COLLOCATION POINTS INCLUDING TWO          C
C       BOUNDARY POINTS.                                         C
C   Y(1,1),Y(1,2),...Y(1,N)=CONCENTRATIONS OF NITRATE ION AT     C
C                           N INTERIOR COLLOCATION POINTS.       C
C   Y(1,N+1),Y(1,N+2),...Y(1,2*N)=CONCENTRATIONS OF HYDROXY      C
C                                 ION AT N INTERIOR COLLOCATION  C
C                                 POINTS.                        C
C   C1(1),C1(2),...C1(NX)=CONCENTRATION OF NITRATE ION AT EACH   C
C                         POINT IN X DIRECTION.                  C
C   C2(1),C2(2),...C2(NX)=CONCENTRATION OF HYDROXY ION AT EACH   C
C                         POINT IN X DIRECTION.                  C
C   XS(1)=SURFACE CONCENTRATION OF NITRATE ION.                  C
C   XS(2)=SURFACE CONCENTRATION OF HYDROXY ION.                  C
C   C1B=BULK CONCENTRATION OF NITRATE ION.                       C
C   C2B=BULK CONCENTRATION OF HYDROXY ION.                       C
C   DMAX=DIFFUSION THICKNESS, CM.                                C
C   ZS=LOCATION OF THE SPLINE POINT, 0 < ZS < 1 .                C
C   DZS=INCREMENT OF THE SPLINE POINT, ZS.                       C
C   TIMAX=MAXIMUM TIME TO BE INTEGRATED, SEC.                    C
C   DTIME=TIME INCREMENT, SEC.                                   C
C   TAUMAX=DIMENSIONLESS MAXIMUM TIME TO BE INTEGRATED.          C
C   TAU=DIMENSIONLESS TIME                                       C
C   DTAU=DIMENSIONLESS TIME INCREMENT                            C
C   GAMA=REACTION ORDER OF HYDROXY ION.                          C
C   BETA=REACTION ORDER OF NITRATE ION.                          C
C   CON2=HETEROGENEOUS REACTION RATE CONSTANT IN ANODIC          C
C         DIRECTION.                                             C
C   CON1=HETEROGENEOUS REACTION RATE CONSTANT IN CATHODIC        C
C         DIRECTION.                                             C
C   CD=CURRENT DENSITY, AMP/CM**2.                               C
```

```
C    THE DIFFUSION COEFFICIENTS OF THE NITRATE AND HYDROXY            C
C    IONS ARE 1.902E-5 AND 5.260E-5CM2/SEC,RESPECTIVELY.              C
C                                                                     C
C*********************************************************************C


      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(20,20),B(20,20),C1(60),C2(60),C(20),Y(8,20),YMAX(20),
     1          DIF1(20),DIF2(20),DIF3(20),ROOT(20),VECT(20),ERROR(20),
     2          SAVE(24,20),PW(400),XS(2),XX(1),WA(3),BAR(1)
      EXTERNAL AUX2
      COMMON/L1/COEF1,COEF5
      COMMON/L2/COEF2
      COMMON/L3/N,NT
      COMMON/L4/A,B
      COMMON/L5/XS
      COMMON/L6/COEF4
      COMMON/L7/NSIG,NEZ,EP
      COMMON/L8/COEF3,CON1,CON2,GAMA,BETA
      COMMON/L9/Y
C
C     ------- INPUT DATA -------
C
      READ(5,310) ND,N,N0,N1,AL,BE,EPS,TIMAX,IC,DZS
      READ(5,320) C1B,C2B,DMAX,DTIME,NX,ZS
      READ(5,330) GAMA,BETA,CON2,CON1
      READ(5,340) NSIG,NEZ,EP
C
C     ------- CALCULATE SOME CONSTANTS TO BE USED IN THE PROGRAM -----
C
       COEF1=(1.902D-5)/5.26D-5
       COEF2=C2B/C1B
       COEF3=(1.902D-5)*C1B/DMAX/ZS
       COEF4=2.*(1.902D-5)*C1B*96487./DMAX/ZS
       COEF5=1./ZS/ZS
      DX=DMAX/(NX-1)
      DTAU=(5.26D-5)*DTIME/DMAX/DMAX
      TAUMAX=(5.26D-5)*TIMAX/DMAX/DMAX
      SDTAU=DTAU
      DETA=1./(NX-1)
      NT=N+N0+N1
      NER=2*N
C
C     ------- SET INITIAL DIMENSIONLESS TIME=0. -------
C
      TAU=0.
C
C     ------- DEFINE THE MAXIMUM AND MINIMUM DIMENSIONLESS
C             TIME INCREMENT TO BE USED IN THE INTEGRATION
C             SUBROUTINE DIFSUB -------
C
      DTAUMI=.001*DTAU
      DTAUMA=2.0*DTAU
      WRITE(6,350)
```

```
C
C     ------- EVALUATE THE COLLOCATION POINTS(ROOTS) OF THE
C             JACOBI POLYNOMIAL OF ORDER N, AS WELL AS THE
C             FIRST AND SECOND DERIVATIVES OF THE POLYNOMIAL
C             AT THE ROOTS. -------
C
      CALL JCOBI(ND,N,NO,N1,AL,BE,DIF1,DIF2,DIF3,ROOT)
       WRITE(6,350)  (ROOT(J),J=1,NT)
C
C     ------- CALCULATE THE DISCRETIZATION COEFFICIENT MATRIX A -------
C
      ID=1
       DO 20 I=1,NT
        CALL DFOPR(ND,N,NO,N1,I,ID,DIF1,DIF2,DIF3,ROOT,VECT)
         DO 10 J=1,NT
   10     A(I,J)=VECT(J)
   20  CONTINUE
C
C     ------- CALCULATE THE DISCRETIZATION COEFFICIENT MATRIX B -------
C
      ID=2
       DO 40 I=1,NT
        CALL DFOPR(ND,N,NO,N1,I,ID,DIF1,DIF2,DIF3,ROOT,VECT)
         DO 30 J=1,NT
   30     B(I,J)=VECT(J)
   40  CONTINUE
C
C     ------- INPUT THE VALUES OF ARGUMENTS TO BE USED IN THE
C             INTEGRATION SUBROUTINE DIFSUB -------
C
      MF=1
      JSTART=0
      MAXDER=7
      DO 45 I=1,NER
       YMAX(I)=1.0
   45 CONTINUE
      I=0
C
C     ------- INPUT THE INITIAL CONDITIONS -------
C
      DO 50 J=1,N
       Y(1,J)=1.
       Y(1,J+N)=COEF2
   50 CONTINUE
      XS(1)=1.
      XS(2)=COEF2
      WRITE(6,390)
   60 TIME=TAU*DMAX*DMAX/(5.26D-5)
C
C     ------- CALCULATE AND PRINT THE CURRENT DENSITY AT THIS TIME
C             PRINT THE CONCENTRATIONS OF NITRATE AND HYDROXY IONS
C             AT THE NT COLLOCATION POINTS -------
C
      CALL CURENT(CD,A,Y)
```

```
       WRITE(6,300) TIME,CD,XS(1),XS(2),KFLAG,ITERN,ZS
       WRITE(6,700) (Y(1,L),L=1,NEQ)
C
C     ------- EVALUATE AND PRINT THE CONCENTRATIONS OF
C             NITRATE AND HYDROXY IONS AT EACH POINT
C             IN X DIRECTION AT THIS TIME -------
C
      CALL CONCEN(C1,C2,NX,ND,DETA,ROOT,DIF1,Y)
       WRITE(6,230) (C1(J),J=1,NX)
       WRITE(6,250) (C2(J),J=1,NX)
C
C     ------- CHECK IF THE INTEGRATION TIME AT THIS MOMENT REACHES
C             THE MAXMIUM TIME TO BE INTEGRATED -------
C
      IF(TAU.GE.TAUMAX) GO TO 190
   85 I=I+1
      IF(I.EQ.1) GO TO 90
C
C
C     ------- TEST IF THE CONCENTRATION OF NITRATE ION AT THE NTH
C             COLLOCATION POINT,IE, THE LAST ONE BEFORE THE SPLINE
C             POINT IS WITHIN 0.0001 DIMENSIONLESS CONCENTRATION
C             UNIT OF THE BOUNDARY CONDITION. -------
C
C
      IF((1.-Y(1,5)).LT.0.0001) GO TO 90
C
C     ------- IF THE TEST FAILS, THE SPLINE POINT IS INCREASED,IE,
C             MOVED FURTHER INTO THE SOLUTION. -------
C
       CALL CHANGE(ZS,DZS,COEF3,COEF4,COEF5,FACTOR,DTAU,DTAUMI,DTAUMA,
     1             JSTART)
C
C
C     ------- EVALUATE THE CONCENTRATIONS OF NITRATE AND HYDROXY
C             IONS AT THE COLLOCATION POINTS AT THE NEW COORDINATE
C             DUE TO THE INCREASE OF THE SPLINE POINT. -------
C
C
       CALL EXPAND(Y,ROOT,DIF1,FACTOR,ND)
C
C
C     ------- INTEGRATE EQUATIONS (50) AND (51) USING THE CONCENTRATIONS
C             AT THE COLLOCATION POINTS AT THIS TIME TO OBTAIN THE
C             CONCENTRATIONS AT THE SUCCESSIVE TIME -------
C
C
   90 CALL DIFSUB(NEQ,TAU,Y,SAVE,DTAU,DTAUMI,DTAUMA,EPS,MF,YMAX,
     1             ERROR,KFLAG,JSTART,MAXDER,PW)
        IF(KFLAG.LT.0) GO TO 190
        DTAUMI=.001*DTAU
        DTAUMA=2.0*DTAU
      IF(I.GE.2) GO TO 93
      IF(Y(1,1).GT.1..OR.Y(1,2).GT.1..OR.Y(1,3).GT.1..OR.Y(1,4).GT.1.
```

```
     1  .OR.DABS(Y(1,5)-1.).GT.0.0004) GO TO 90
        GO TO 95
   93   M1=I/IC
        M2=M1*IC
        IF(I.EQ.M2.OR.TAU.GE.TAUMAX) GO TO 95
         GO TO 85
C
C       ------- CALCULATE THE SURFACE CONCENTRATIONS -------
C
   95   XX(1)=Y(1,1)
        ITERN=500
        CALL ZSYSTM(AUX2,EP,NSIG,NEZ,XX,ITERN,WA,BAR,IER)
         XS(1)=XX(1)
         XS(2)=-3.*COEF1*(A(1,1)*XX(1)+A(1,NT)*1.0)/A(1,1)-A(1,NT)/A(1,1)
     1        *COEF2
         DO 150 J=1,N
          XS(2)=XS(2)-3.*COEF1*A(1,J+1)*Y(1,J)/A(1,1)-A(1,J+1)
     1         *Y(1,J+N)/A(1,1)
  150    CONTINUE
         GO TO 60
  190   WRITE(6,240) DX,SDTAU,NX,DTAU,DTIME,DMAX,AL,BE,ZS,EPS,KFLAG,
     1               EP,NSIG
        WRITE(6,245) BETA,GAMA,CON1,CON2
C
C       ------- FORMATS FOR INPUT AND OUTPUT STATEMENTS -------
C
  230   FORMAT(/,25X,'NO3-',1X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4
     1         /30X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4
     2         /30X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4)
  240   FORMAT(//,5X,'X INTERVAL=',D12.4,32X,'INITIAL TAU STEP SIZE='
     1         ,D12.4/5X,'NO OF POINTS IN X DIR= ',I3,29X,
     2         'LAST TAU STEP SIZE=  ',D12.4/5X,'REAL TIME INTERVAL=  '
     3         ,D10.4,24X,'DIFUSION LENGTH= ',D10.4//5X,'AL=  ',F7.2,30X,
     4         'BE=  ',F7.2,25X,'ZS=  ',F7.4//5X,'EPS=  ',D10.2,27X,
     5         'KFLAG=  ',I3//5X,'EP =  ',D10.2,27X,'NSIG=   ',I3)
  245   FORMAT(//,5X,'REACTION ORDER OF NO3- ION  =',F7.2,25X,
     1         'REACTION ORDER OF OH- ION  =',F7.2//5X,'1ST CONSTANT ='
     2         ,D12.4,25X,'2ND CONSTANT  =',D12.4)
  250   FORMAT(/,25X,'OH-',2X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4
     1         /30X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4
     2         /30X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4)
  310   FORMAT(4I3,2F5.1,2D10.2,I5,F8.4)
  320   FORMAT(4D12.5,I7,F7.4)
  330   FORMAT(2F7.2,2D12.4)
  340   FORMAT(2I5,D12.4)
  350   FORMAT(15X,10F10.6)
  360   FORMAT(//,D12.4,1X,D12.4,2X,2D30.10,2I5,F20.7)
  370   FORMAT(/,2X,6F20.6/2X,6F20.6)
  380   FORMAT(2X,'COLLOCATION POINTS: ')
  390   FORMAT(//,3X,'TIME',12X,'CURRENT',45X,'ION CONCENTRATION')
  700   FORMAT(30X,10F10.5/30X,10F10.5)
        STOP
        END
```

```
      SUBROUTINE JCOBI(ND,N,N0,N1,AL,BE,DIF1,DIF2,DIF3,ROOT)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION DIF1(ND),DIF2(ND),DIF3(ND),ROOT(ND)

C*******************************************************************C
C                                                                   C
C   SUBROUTINE EVALUATES THE COLLOCATION POINTS(ROOTS) OF THE      C
C   JACOBI POLYNOMIAL OF ORDER N AS WELL AS THE FIRST, SECOND       C
C   AND THIRD DERIVATIVES OF THE POLYNOMIAL AT THE ROOTS.           C
C                                                                   C
C   --- INPUT PARAMETERS ---                                        C
C                                                                   C
C   INTEGER ND=THE DIMENSION OF VECTORS DIF1,DIF2,DIF3,ROOT.        C
C   INTEGER N=THE DEGREE OF THE JACOBI POLYNOMIAL, I.E., THE        C
C              NUMBER OF INTERIOR COLLOCATION POINTS.               C
C   INTEGER N0=DECIDES WHETHER X=0 IS INCLUDED AS A COLLOCATION     C
C               POINT. N0 MUST BE SET EQUAL TO 1 (INCLUDING X=0)    C
C               OR 0 (EXCLUDING THIS POINT).                        C
C   INTEGER N1=AS FOR N0, BUT FOR THE POINT X=1.                    C
C   REAL AL,BE=THE PARAMETERS OF THE JACOBI POLYNOMIAL.             C
C                                                                   C
C   --- OUTPUT PARAMETERS ---                                       C
C                                                                   C
C   REAL ARRAY ROOT=ONE-DIMENSIONAL VECTOR CONTAINING ON EXIT       C
C                    THE N+N0+N1 ZEROS OF THE POLYNOMIAL USED       C
C                    IN THE COLLOCATION ROUTINE.                    C
C   REAL ARRAY      =THREE ONE-DIMENSIONAL VECTORS CONTAINING       C
C   DIF1,DIF2,DIF3   ON EXIT THE FIRST, SECOND, AND THIRD           C
C                    DERIVATIVES OF THE POLYNOMIAL AT THE ZEROS.    C
C                                                                   C
C*******************************************************************C


C
C   ------- FIRST EVALUATION OF COEFFICIENTS IN RECURSION FORMULAS --
C   ------- RECURSION COEFFICIENTS ARE STORED IN DIF1 AND DIF2     --
C
      AB=AL+BE
      AD=BE-AL
      AP=BE*AL
      DIF1(1)=(AD/(AB+2)+1)/2
      DIF2(1)=0
      IF(N.LT.2) GO TO 15
      DO 12 I=2,N
      Z1=I-1
      Z=AB+2*Z1
      DIF1(I)=(AB*AD/Z/(Z+2)+1)/2
      IF(I.NE.2) GO TO 10
      DIF2(I)=(AB+AP+Z1)/Z/Z/(Z+1)
      GO TO 12
   10 Z=Z*Z
      Y=Z1*(AB+Z1)
```

```
      Y=Z*(AB+Z)
      DIF2(I)=Y/Z/(Z-1)
   12 CONTINUE
C
C     ------- ROOT DETERMINATION BY NEWTON METHOD WITH SUPPRESSION
C             OF PREVIOUSLY DETERMINED ROOTS   -------
C
   15 X=0
      DO 35 I=1,N
   20 XD=0
      XN=1
      XD1=0
      XN1=0
      DO 22 J=1,N
      XP=(DIF1(J)-X)*XN-DIF2(J)*XD
      XP1=(DIF1(J)-X)*XN1-DIF2(J)*XD1-XN
      XD=XN
      XD1=XN1
      XN=XP
   22 XN1=XP1
      ZC=1
      Z=XN/XN1
      IF(I.EQ.1)GO TO 30
      DO 25 J=2,I
   25 ZC=ZC-Z/(X-ROOT(J-1))
   30 Z=Z/ZC
      X=X-Z
      IF(DABS(Z).GT.1.D-09)GO TO 20
      ROOT(I)=X
      X=X+.0001
   35 CONTINUE
C
C     ------- ADD EVENTUAL COLLOCATION POINTS AT X=0 OR X=1 -------
C
      NT=N+N0+N1
      IF(N0.EQ.0) GO TO 45
      DO 40 I=1,N
      J=N+1-I
   40 ROOT(J+1)=ROOT(J)
      ROOT(1)=0
   45 IF(N1.EQ.1) ROOT(NT)=1
C
C     ------- NOW EVALUATE DERIVATIVES OF POLYNOMIAL -------
C
      DO 50 I=1,NT
      X=ROOT(I)
      DIF1(I)=1
      DIF2(I)=0
      DIF3(I)=0
      DO 50 J=1,NT
      IF(J.EQ.I) GO TO 50
      Y=X-ROOT(J)
      DIF3(I)=Y*DIF3(I)+3*DIF2(I)
      DIF2(I)=Y*DIF2(I)+2*DIF1(I)
```

```
      DIF1(I)=Y*DIF1(I)
   50 CONTINUE
      RETURN
      END

      SUBROUTINE DFOPR(ND,N,N0,N1,I,ID,DIF1,DIF2,DIF3,ROOT,VECT)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION DIF1(ND),DIF2(ND),DIF3(ND),ROOT(ND),VECT(ND)

C*****************************************************************C
C                                                                 C
C   SUBROUTINE EVALUATES DISCRETIZATION COEFFICIENT MATRICES      C
C   AND GAUSSIAN QUADRATURE WEIGHTS, NOMALIZED TO SUM 1.          C
C                                                                 C
C   --- INPUT PARAMETERS ---                                      C
C                                                                 C
C   INTEGER N, N0, N1=AS IN SUBROUTINE JCOBI.                     C
C   INTEGER I=THE INDEX OF THE NODE FOR WHICH THE WEIGHTS ARE     C
C             TO BE CALCULATED.                                   C
C   INTEGER ID=INDICATOR. ID=1 GIVES THE WEIGHTS FOR DY/DX,       C
C              ID=2 GIVES THE WEIGHTS FOR D2Y/DX2, AND ID=3       C
C              GIVES THE GAUSSIAN WEIGHTS. THE VALUE OF I IS      C
C              IRRELEVANT IN THE LAST CASE.                       C
C   REAL ARRAY ROOT,                                              C
C   DIF1,DIF2,DIF3  =THE ONE-DIMENSIONAL VECTORS COMPUTED IN      C
C                    SUBROUTINE JCOBI.                            C
C                                                                 C
C   --- OUTPUT PARAMETERS ---                                     C
C                                                                 C
C   REAL ARRAY VECT=THE COMPUTED VECTOR OF WEIGHTS.               C
C                                                                 C
C*****************************************************************C

      NT=N+N0+N1
      IF(ID.EQ.3) GO TO 10
      DO 20 J=1,NT
      IF(J.NE.I) GO TO 21
      IF(ID.NE.1) GO TO 5
      VECT(I)=DIF2(I)/DIF1(I)/2
      GO TO 20
    5 VECT(I)=DIF3(I)/DIF1(I)/3
      GO TO 20
   21 Y=ROOT(I)-ROOT(J)
      VECT(J)=DIF1(I)/DIF1(J)/Y
      IF(ID.EQ.2) VECT(J)=VECT(J)*(DIF2(I)/DIF1(I)-2/Y)
   20 CONTINUE
      GO TO 50
   10 Y=0
      DO 25 J=1,NT
      X=ROOT(J)
      AX=X*(1-X)
      IF(N0.EQ.0) AX=AX/X/X
      IF(N1.EQ.0) AX=AX/(1-X)/(1-X)
```

```
      VECT(J)=AX/DIF1(J)**2
   25 Y=Y+VECT(J)
      DO 60 J=1,NT
   60 VECT(J)=VECT(J)/Y
   50 RETURN
      END


      SUBROUTINE INTRP(ND,NT,X,ROOT,DIF1,XINTP)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION ROOT(ND),DIF1(ND),XINTP(ND)

C*********************************************************************C
C                                                                     C
C    SUBROUTINE EVALUATES THE LAGRANGIAN INTERPOLATION COEFFICIENTS   C
C                                                                     C
C    --- INPUT PARAMETERS ---                                         C
C                                                                     C
C    INTEGER NT=THE TOTAL NUMBER OF COLLOCATION POINTS (=N+N0+N1)     C
C               FOR WHICH THE VALUE OF THE DEPENDENT VARIABLE Y       C
C               IS KNOWN.                                             C
C    REAL X=THE ABSCISSA X WHERE Y(X) IS DESIRED.                     C
C    REAL ARRAY                                                       C
C    ROOT,DIF1 =COLLOCATION POINTS AND DERIVATIVES OF NODE            C
C               POLYNOMIAL, DERIVED IN SUBROUTINE JCOBI.              C
C                                                                     C
C    --- OUTPUT PARAMETERS ---                                        C
C                                                                     C
C    REAL ARRAY XINTP=THE VECTOR OF INTERPOLATION WEIGHTS.            C
C                                                                     C
C*********************************************************************C

      POL=1
      DO 5 I=1,NT
      Y=X-ROOT(I)
      XINTP(I)=0
      IF(Y.EQ.0.D0) XINTP(I)=1
    5 POL=POL*Y
      IF(POL.EQ.0.D0)GO TO 10
      DO 6 I=1,NT
    6 XINTP(I)=POL/DIF1(I)/(X-ROOT(I))
   10 RETURN
      END


      SUBROUTINE DIFSUB(N,T,Y,SAVE,H,HMIN,HMAX,EPS,MF,YMAX,ERROR,KFLAG,
     1                  JSTART,MAXDER,PW)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION Y(8,20),YMAX(20), SAVE(24,20),ERROR(20),PW(400),
     3          A(8),PERTST(7,2,3)
      DIMENSION B(20),PJL(20,20),X(20)

C*********************************************************************C
C                                                                     C
```

```
C     SUBROUTINE INTEGRATES A SET OF N ORDINARY DIFFERENTIAL FIRST
C     ORDER EQUATIONS AS DESCRIBED IN EQUATIONS (50) AND (51) OVER
C     ONE STEP OF LENGTH H AT EACH CALL. H MAY BE INCREASED OR
C     DECREASED WITHIN THE RANGE HMIN TO HMAX IN ORDER TO ACHIEVE
C     AS LARGE A STEP AS POSSIBLE WHILE NOT COMMITTING A SINGLE
C     STEP ERROR WHICH IS LARGER THAN EPS IN THE L-2 NORM, WHERE
C     EACH COMPONENT OF THE ERROR IS DIVIDED BY THE COMPONENTS OF
C     YMAX.
C
C     THE PROGRAM CALLS FOUR SUBROUTINES NAMED
C          DIFFUN(T,Y,DY)
C          MATINV(PW,N,M,J)
C          SOLVE(NN,PUL,B,X)
C          PEDERV(T,Y,PW,M)
C     THE FIRST,DIFFUN,EVALUATES THE DERIVATIVES OF THE DEPENDENT
C     VARIABLES STORED IN Y(1,I) FOR I=1 TO N, AND STORES THE
C     DERIVATIVES IN THE ARRAY DY. THE SECOND IS CALLED ONLY IF
C     MF IS SET TO 1 OR 2 FOR STIFF METHODS. IT PERFORMS A FIRST
C     STAGE OF GAUSSIAN ELIMINATION ROUTINE OF THE N BY N MATRIX
C     STORED IN THE ARRAY PW(M,M). SOLVE PERFORMS THE BACK
C     SUBSTITUTION PROCESS OF THE GAUSSIAN ELIMINATION ROUTINE.
C     PEDERV IS USED ONLY IF MF IS 1, AND STORES THE PARTIAL
C     DERIVATIVES OF THE DIFFERENTIAL EQUATIONS PROVIDED BY DIFFUN.
C
C     --- PARAMETERS ---
C
C     N=THE NUMBER OF FIRST ORDER DIFFERENTIAL EQUATIONS.
C     T=THE INDEPENDENT VARIABLE.
C     Y=AN 8 BY N ARRAY CONTAINING THE DEPENDENT VARIABLES AND
C       THEIR SCALED DERIVATIVES. THE DEPENDENT VARIABLES ARE
C        STORED IN Y(1,I), I=1 TO N.
C     SAVE=A BLOCK OF AT LEAST 12*N FLOATING POINT LOCATIONS USED
C          BY THE SUBROUTINE.
C     H=THE STEP SIZE TO BE ATTEMPTED ON THE NEXT STEP.
C     HMIN=THE MINIMUM STEP SIZE THAT WILL BE USED FOR THE
C          INTEGRATION.
C     HMAX=THE MAXIMUM SIZE TO WHICH THE STEP WILL BE INCREASED.
C     EPS=THE ERROR TEST CONSTANT.
C     MF=THE METHOD INDICATOR.
C          0           AN ADAMS PREDICTOR CORRECTOR IS USED.
C          1           A MULTI-STEP METHOD SUITABLE FOR STIFF SYSTEMS
C                      IS USED.
C          2           THE SAME AS CASE 1, EXCEPT THAT THIS SUBROUTINE
C                      COMPUTES THE PARTIAL DERIVATIVES BY NUMERICAL
C                      DIFFERENCING OF THE DERIVATIVES.
C     YMAX=AN ARRAY OF N LOCATIONS WHICH CONTAINS THE MAXIMUM OF
C          EACH Y SEEN SO FAR.
C     ERROR=AN ARRAY OF N ELEMENTS WHICH CONTAINS THE ESTIMATED
C           ONE STEP ERROR IN EACH COMPONENT.
C     KFLAG=A COMPLETION CODE. 1 MEANS THE STEP WAS SUCCESSFUL.
C     JSTART=AN INPUT INDICATOR.
C     MAXDER=THE MAXIMUM DERIVATIVE THAT SHOULD BE USED.
C     PW=A BLOCK OF AT LEAST N**2 FLOATING POINT LOCATIONS.
C
```

```
C*********************************************************************C
      DATA PERTST /2.0,4.5,7.333,10.42,13.7,17.15,1.0,
     1        2.0,12.0,24.0,37.89,53.33,70.08,87.97,
     2        3.0,6.0,9.167,12.5,15.98,1.0,1.0,
     3        12.0,24.0,37.89,53.33,70.08,87.97,1.0,
     4        1.,1.,0.5,0.1667,0.04133,0.008267,1.0,
     5        1.0,1.0,2.0,1.0,.3157,.07407,.0139/
      DATA A(2)/-1.0/
      IRET=1
      KFLAG = 1
      IF (JSTART.LE.0) GO TO 140
  100 DO 110 I=1,N
        DO 110 J=1,K
  110     SAVE(J,I) = Y(J,I)
      HOLD = HNEW
      IF (H.EQ.HOLD) GO TO 130
  120 RACUM = H/HOLD
      IRET1 = 1
      GO TO 750
  130 NQOLD = NQ
      TOLD = T
      RACUM = 1.0
      IF (JSTART.GT.0) GO TO 250
      GO TO 170
  140 IF (JSTART.EQ.-1) GO TO 160
       NQ =1
      N3 = N
      N1 = N*10
      N2 = N1 + 1
      N4 = N**2
      N5 = N1 + N
      N6 = N5 + 1
      CALL DIFFUN(T,Y,SAVE(N2,1))
      DO 150 I = 1,N
  150   Y(2,I) = SAVE(N1+I,1)*H
      HNEW = H
      K = 2
      GO TO 100
  160 IF (NQ.EQ.NQOLD) JSTART = 1
      T = TOLD
      NQ = NQOLD
      K = NQ + 1
      GO TO 120
  170 IF (MF.EQ.0) GO TO 180
      IF (NQ.GT.6) GO TO 190
      GO TO (221,222,223,224,225,226),NQ
  180 IF (NQ.GT.7) GO TO 190
      GO TO (211,212,213,214,215,216,217),NQ
  190 KFLAG = -2
      RETURN
  211 A(1) = -1.0
      GO TO 230
  212 A(1) = -0.500000000000
```

```
      A(3) = -0.500000000
      GO TO 230
  213 A(1) = -0.4166666666666667
      A(3) = -0.750000000
      A(4) = -0.1666666666666667
      GO TO 230
  214 A(1) = -0.375000000
      A(3) = -0.9166666666666667
      A(4) = -0.3333333333333333
      A(5) = -0.0416666666666666667
      GO TO 230
  215 A(1) = -0.34861111111111111
      A(3) = -1.041666666666667
      A(4) = -0.43611111111111111
      A(5) = -0.1041666666666667
      A(6) = -0.008333333333333333
      GO TO 230
  216 A(1) = -0.32936111111111111
      A(3) = -1.1416666666666667
      A(4) = -0.625000000
      A(5) = -0.17708333333333333
      A(6) = -0.02500000000
      A(7) = 0.001388888888888889
      GO TO 230
  217 A(1) = -0.3155919312169312
      A(3) = -1.225000000
      A(4) = -0.7518518518518519
      A(5) = -0.2552083333333333
      A(6) = -0.04861111111111111
      A(7) = -0.0048611111111111111
      A(8) = -0.0001984126984126984
      GO TO 230
  221 A(1) = -1.000000000
      GO TO 230
  222 A(1) = -0.6666666666666667
      A(3) = -0.3333333333333333
      GO TO 230
  223 A(1) = -0.5454545454545455
      A(3) = A(1)
      A(4) = -0.09090909090909091
      GO TO 230
  224 A(1) = -0.480000000
      A(3) = -0.700000000
      A(4) = -0.200000000
      A(5) = -0.020000000
      GO TO 230
  225 A(1) = -0.437956204379562
      A(3) = -0.8211678832116788
      A(4) = -0.3102189781021898
      A(5) = -0.035474452554744526
      A(6) = -0.00106496350364963504
      GO TO 230
  226 A(1) = -0.4081632653061225
      A(3) = -0.9206349206349206
```

```
      A(4)  =  -0.41666666666666667
      A(5)  =  -0.0992047619047619
      A(6)  =  -0.0119047619047619
      A(7)  =  -0.000566893424036282
  230 K = NQ+1
      IDOUB = K
      MTYP = (4 - MF)/2
      ENQ2 = .5/FLOAT(NQ + 1)
      ENQ3 = .5/FLOAT(NQ + 2)
      ENQ1 = .5/FLOAT(NQ)
      PEPSH = EPS
      EUP = (PERTST(NQ,MTYP,2)*PEPSH)**2
      E = (PERTST(NQ,MTYP,1)*PEPSH)**2
      EDWN = (PERTST(NQ,MTYP,3)*PEPSH)**2
      IF (EDWN.EQ.0) GO TO 780
      BND = EPS*ENQ3/DFLOAT(N)
  240 IWEVAL = MF
      GO TO  (250,680),IRET
  250 T = T + H
      DO 260 J = 2,K
        DO 260 J1 = J,K
          J2 = K - J1 + J - 1
          DO 260 I = 1,N
  260          Y(J2,I)  = Y(J2,I)  + Y(J2+1,I)
      DO 270 I = 1,N
  270   ERROR(I)  = 0.0
      DO 430 L = 1,3
          CALL DIFFUN (T,Y,SAVE(N2,1))
      IF (IWEVAL.LT.1) GO TO 350
        IF (MF.EQ.2) GO TO 310
        CALL PEDERV(T,Y,PW,N3)
        R = A(1)*H
        DO 280 I = 1,N4
  280     PW(I)  = PW(I)*R
  290    DO 300 I = 1,N
  300     PW(I*(N3+1)-N3)  = 1.0 + PW(I*(N3+1)-N3)
      IWEVAL = -1
      CALL MATINV(PW,N,N3,J1,PUL)
        IF (J1.GT.0) GO TO 350
        GO TO 440
  310   DO 320 I = 1,N
  320    SAVE(9,I)  = Y(1,I)
        DO 340 J = 1,N
           R = EPS*DMAX1(EPS,DABS(SAVE(9,J)))
          Y(1,J)  = Y(1,J)  + R
          D = A(1)*H/R
          CALL DIFFUN(T,Y,SAVE(N6,1))
          DO 330 I = 1,N
  330       PW(I+(J-1)*N3)  =  (SAVE(N5+I,1)  - SAVE(N1+I,1))*D
  340     Y(I,J)  = SAVE(9,J)
       GO TO 290
  350      IF (MF.NE.0) GO TO 370
          DO 360 I = 1,N
  360       SAVE(9,I)  = Y(2,I)  - SAVE(N1+I,1)*H
```

```
          GO TO 410
370       DO 380 I = 1,N
380     SAVE(N5+I,1) = Y (2,I) - SAVE(N1+I,1)*H
      CALL SOLVE (N ,PJL,SAVE(N5+1,1),X)
      DO 399 J=1,N
399   SAVE(9,J)=X(J)
410       NT = N
        DO 420 I = 1,N
          Y(1,I) = Y(1,I)+A(1)*SAVE(9,I)
          Y(2,I) = Y(2,I) - SAVE(9,I)
          ERROR(I) = ERROR(I) + SAVE(9,I)
        IF (DABS(SAVE(9,I)).LE.(BND*YMAX(I))) NT = NT-1
420       CONTINUE
        IF (NT.LE.0) GO TO 490
430     CONTINUE
440   T = TOLD
      IF ((H.LE.(HMIN*1.00001)).AND.((IWEVAL-MTYP).LT.-1)) GO TO 460
      IF ((MF.EQ.0).OR.(IWEVAL.NE.0)) RACUM = RACUM*.25D0
      IWEVAL = MF
       IRET1 = 2
       GO TO 750
460   KFLAG = -3
470   DO 480 I =1,N
        DO 480 J = 1,K
480       Y(J,I) = SAVE(J,I)
      H = HOLD
      NQ = NQOLD
      JSTART = NQ
      RETURN
490   D = 0.0
      DO 500 I = 1,N
500     D = D + (ERROR(I)/YMAX(I))**2
      IWEVAL = 0
      IF (D.GT.E) GO TO 540
      IF (K.LT.3) GO TO 520
      DO 510 J = 3,K
        DO 510 I = 1,N
510       Y(J,I) = Y(J,I) + A(J)*ERROR(I)
520   KFLAG = +1
      HNEW = H
      IF (IDOUB.LE.1) GO TO 550
      IDOUB = IDOUB - 1
      IF (IDOUB.GT.1)GO TO 700
      DO 530 I = 1,N
530     SAVE(10,I) = ERROR(I)
      GO TO 700
540   KFLAG = KFLAG - 2
      IF (H.LE.(HMIN*1.00001)) GO TO 740
      T = TOLD
      IF (KFLAG.LT.-5) GO TO 720
550   PR2 = (D/E)**ENQ2*1.2
      PR3 = 1.E+20
      IF ((NQ.GE.MAXDER).OR.(KFLAG.LE.-1)) GO TO 570
      D = 0.0
```

```
    DO 560 I= 1,N
560   D = D + ((ERROR(I) - SAVE(10,I))/YMAX(I))**2
    PR3 = (D/EUP)**ENQ3*1.4
570 PR1 = 1.E+20
    IF (NQ.LE.1) GO TO 590
    D = 0.0
    DO 580 I = 1,N
580   D = D + (Y(K,I)/YMAX(I))**2
    PR1 = (D/EDWN)**ENQ1*1.3
590 CONTINUE
    IF (PR2.LE.PR3) GO TO 650
    IF (PR3.LT.PR1) GO TO 660
600 R = 1.0/AMAX1(PR1,1.E-4)
    NEWQ = NQ-1
610 IDOUB =  10
    IF ((KFLAG.EQ.1).AND.(R.LT.(1.1))) GO TO 700
    IF (NEWQ.LE.NQ) GO TO 630
    DO 620 I = 1,N
620   Y(NEWQ+1,I) = ERROR(I)*A(K)/DFLOAT(K)
630 K = NEWQ + 1
    IF (KFLAG.EQ.1) GO TO 670
    RACUM = RACUM*R
    IRET = 3
    GO TO 750
640 IF (NEWQ.EQ.NQ) GO TO 250
    NQ = NEWQ
    GO TO 170
650 IF (PR2.GT.PR1) GO TO 600
    NEWQ = NQ
    R = 1.0/AMAX1(PR2,1.E-4)
    GO TO 610
660 R = 1.0/AMAX1(PR3,1.E-4)
    NEWQ = NQ + 1
    GO TO 610
670 IRET = 2
    R = DMIN1(R,HMAX/DABS(H))
    H = H*R
    HNEW = H
    IF (NQ.EQ.NEWQ) GO TO 680
    NQ = NEWQ
    GO TO 170
680 R1 = 1.0
    DO 690 J = 2,K
      R1 = R1*R
      DO 690 I = 1,N
690     Y(J,I) = Y(J,I)*R1
    IDOUB = K
700 DO 710 I = 1,N
710   YMAX(I) = DMAX1(YMAX(I),DABS(Y(1,I)))
    JSTART = NQ
    RETURN
720 IF (NQ.EQ.1) GO TO 760
    CALL DIFFUN(T,Y,SAVE(N2,1))
     R = H/HOLD
```

```
      DO 730 I = 1,N
        Y(1,I) = SAVE(1,I)
        SAVE(2,I) = HOLD*SAVE(N1+I,1)
  730   Y(2,I) = SAVE(2,I)*R
      NQ = 1
      KFLAG = 1
      GO TO 170
  740 KFLAG = -1
      HNEW = H
      JSTART = NQ
      RETURN
  750 RACUM = DMAX1(DABS(HMIN/HOLD),RACUM)
      RACUM = DMIN1(RACUM,DABS(HMAX/HOLD))
      R1 = 1.0
      DO 760 J = 2,K
        R1 = R1*RACUM
        DO 760 I = 1,N
  760     Y(J,I)= SAVE(J,I)*R1
      H = HOLD*RACUM
      DO 770 I = 1,N
  770   Y(1,I) = SAVE(1,I)
      IDOUB = K
      GO TO (130,250,640),IRET1
  780 KFLAG = -4
      GO TO 470
      END


      SUBROUTINE DIFFUN(T,YY,DYY)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION DYY(20),YY(8,20),A(20,20),B(20,20),C(20),XX(1),WA(3),
     1          QAR(20)

C*****************************************************************C
C                                                                 C
C   SUBROUTINE CALLED BY DIFSUB EVALUATES THE DERIVATIVES OF      C
C   DEPENDENT VARIABLES STORED IN YY(1,I),I=1,2*N, AND STORES     C
C   THE DERIVATIVES IN THE ARRAY DYY. T IS THE INDEPENDENT        C
C   VARIABLE.                                                     C
C                                                                 C
C*****************************************************************C

      EXTERNAL AUX1
      COMMON/L1/COEF1,COEF5
      COMMON/L2/COEF2
      COMMON/L3/N,NT
      COMMON/L4/A,B
      COMMON/L7/NSIG,NEQ,EP
      II=2*N
      DO 30 I=1,II
       QAR(I)=YY(1,I)
   30 CONTINUE
C
C   ------- CALCULATE THE VALUES ON THE SURFACE (X=0) -------
```

```
C
      XX(1)=YY(1,1)
      ITERM=500
      CALL ZSYSTM(AJX1,EP,NSIG,NEL,XX,ITERM,WA,PAR,IER)
      CT=-3.*COEF1*(A(1,1)*XX(1)+A(1,NT)*1.)/A(1,1)-A(1,NT)/A(1,1)*COEF2
      DO 45 I=1,N
       C(I)=B(I+1,1)*CT+B(I+1,NT)*COEF2
   45 CONTINUE
C
C  ------- STORE THE DERIVATIVES IN ARRAY DYY -------
C
      DO 120 J=1,N
       DYY(J)=B(J+1,1)*XX(1)+B(J+1,NT)*1.
       DYY(J+N)=C(J)
        DO 110 K=1,N
         DYY(J)=DYY(J)+B(J+1,K+1)*YY(1,K)
         DYY(J+N)=DYY(J+N)-3.*B(J+1,1)*COEF1*A(1,K+1)*YY(1,K)/A(1,1)
     1             +(B(J+1,K+1)-B(J+1,1)*A(1,K+1)/A(1,1))*YY(1,K+N)
  110   CONTINUE
       DYY(J)=COEF1*COEF5*DYY(J)
       DYY(J+N)=DYY(J+N)*COEF5
  120 CONTINUE
      RETURN
      END


      SUBROUTINE PEDERV(X,Y,PW,N3)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION  Y(8,20),PW(400),A(20,20),B(20,20)

C*********************************************************************C
C                                                                     C
C   SUBROUTINE CALLED BY DIFSUB STORES THE PARTIAL                    C
C   DERIVATIVES OF THE DIFFERENIAL EQUATIONS PROVIDED IN              C
C   SUBROUTINE DIFFUN. THE PARTIAL DERIVATIVES (THE JACOBIAN)         C
C   WERE EVALUATED IN THE LAST SECTION IN CHAPTER 5.                  C
C                                                                     C
C*********************************************************************C

      COMMON/L1/COEF1,COEF5
      COMMON/L3/N,NT
      COMMON/L4/A,B
      DO 10 KK=1,N
       DO 20 II=1,N
       PW(II+(2*KK-2)*N)=COEF1*COEF5*B(II+1,KK+1)
       PW(II+(2*KK-1)*N)=-COEF5*3.*B(II+1,1)*COEF1*A(1,KK+1)/A(1,1)
       PW(II+2*N*N+(2*KK-2)*N)=0.
   20  PW(II+2*N*N+(2*KK-1)*N)=(B(II+1,KK+1)-B(II+1,1)*A(1,KK+1)/A(1,1))
     1                           *COEF5
   10 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE DECOMP(NN,A,UL,J2)
      DIMENSION A(20,20),UL(20,20),SCALES(20),IPS(20)

C****************************************************************C
C                                                                C
C   SUBROUTINE CALLED BY MATINV PERFORMS A FIRST STAGE OF        C
C   GAUSSIAN ELIMINATION ROUTINE.                                C
C                                                                C
C****************************************************************C

      COMMON IPS
      J2=1
      N=NN
      DO 5 I=1,N
         IPS(I) = I
      ROWNRM= 0.0
         DO 2 J = 1,N
            UL(I,J) = A(I,J)
            IF (ROWNRM-ABS(UL(I,J)))  1,2,2
   1        ROWNRM = ABS(UL(I,J))
    2   CONTINUE
         IF (ROWNRM) 3,4,3
    3    SCALES(I) = 1.0/ROWNRM
      GO TO 5
   4    CALL SING(1)
      J2=-1
        SCALES(I) = 0.0
    5 CONTINUE
      NM1 = N-1
      DO 17 K = 1,NM1
         BIG = 0.0
         DO 11 I = K,N
            IP = IPS(I)
            SIZE = ABS(UL(IP,K))*SCALES(IP)
            IF (SIZE-BIG)11,11,10
  10          BIG = SIZE
                 IDXPIV = I
  11     CONTINUE
         IF (BIG) 13,12,13
   12       CALL SING(2)
      J2=-1
            GO TO 17
  13     IF (IDXPIV-K) 14,15,14
  14        J = IPS(K)
            IPS(K) = IPS(IDXPIV)
            IPS(IDXPIV) = J
  15     KP = IPS(K)
         PIVOT = UL(KP,K)
         KP1 = K+1
         DO 16 I = KP1,N
            IP = IPS(I)
            EM = -UL(IP,K)/PIVOT
            UL(IP,K) = -EM
            DO 16 J = KP1,N
```

```
                   UL(IP,J) = UL(IP,J) + EM*UL(KP,J)
  16       CONTINUE
   17 CONTINUE
      KP = IPS(N)
      IF (UL(KP,N)) 19,18,19
   18 CALL SING(2)
      J2=-1
   19 RETURN
      END


      SUBROUTINE SOLVE (NN ,PUL,B,X)
      IMPLICIT  REAL*8 (A-H,O-Z)
      DIMENSION PUL(20,20), B(20),X(20), IPS(20)
C***************************************************************C
C                                                               C
C   SUBROUTINE CALLED BY DIFSUB PERFORMS THE SECOND STAGE       C
C   (THE BACK SUBSTITUTION PROCESS) OF THE GAUSSIAN             C
C   ELIMINATION ROUTINE.                                        C
C                                                               C
C***************************************************************C
      COMMON IPS
      N = NN
      NP1 = N+1
      IP = IPS(1)
      X(1) = B(IP)
      DO 2 I = 2,N
         IP = IPS(I)
         IM1 = I-1
         SUM = 0.0
         DO 1 J = 1,IM1
    1       SUM = SUM + PUL (IP,J)*X(J)
    2 X(I) = B(IP)-SUM
      IP = IPS(N)
      X(N) = X(N)/PUL(IP,N)
      DO 4 IBACK = 2,N
      I = NP1-IBACK
         IP = IPS(I)
         IP1 = I+1
         SUM = 0.0
         DO 3 J = IP1,N
    3       SUM = SUM + PUL(IP,J)*X(J)
    4 X(I) = (X(I)-SUM)/PUL(IP,I)
      RETURN
      END


      SUBROUTINE SING (IWHY)
C***************************************************************C
C                                                               C
C   SUBROUTINE CALLED BY DECOMP INDICATES THE ERRORS IN         C
```

```
C   PERFORMING THE GAUSSIAN ELIMINATION ROUTINE.                      C
C                                                                     C
C*******************************************************************C

 11  FORMAT(54H0MATRIX WITH ZERO ROW IN DECOMPOSE.                     )
 12 FORMAT(54H0SINGULAR MATRIX IN DECOMPOSE.  ZERO DIVIDE IN SOLVE.    )
 13 FORMAT(54H0NO CONVERGENCE IN IMPRUV.  MATRIX IS NEARLY SINGULAR.   )
    NOUT = 3
    GO TO (1,2,3), IWHY
  1 WRITE (NOUT,11)
    GO TO 10
  2 WRITE (NOUT,12)
    GO TO 10
  3 WRITE (NOUT,13)
 10 RETURN
    END


    SUBROUTINE MATINV(PW,N,N3,J1,UL)
    DIMENSION PW(400),A(20,20),UL(20,20)

C*******************************************************************C
C                                                                   C
C   SUBROUTINE CALLED BY DIFSUB PERFORMS THE FIRST STAGE OF         C
C   GAUSSIAN ELIMINATION ROUTINE OF THE MATRIX STORED IN            C
C   THE ARRAY PW.                                                   C
C                                                                   C
C*******************************************************************C

    DO 1 I = 1,N
       DO 1 J = 1,N
  1 A(I,J) = PW(I+(J-1)*N3)
    CALL DECOMP(N,A,UL,J1)
    RETURN
    END


    SUBROUTINE CURENT(CD,A,Y)
    IMPLICIT REAL*8(A-H,O-Z)
    DIMENSION A(20,20),Y(8,20),XS(2)

C*******************************************************************C
C                                                                   C
C   SUBROUTINE CALCULATES THE CURRENT DENSITY BY EQUATION           C
C   (56).                                                           C
C                                                                   C
C   --- PARAMETERS ---                                              C
C                                                                   C
C   CD=CURRENT DENSITY, AMP/CM**2                                   C
C   A=DISCRETIZATION COEFFICIENT MATRIX, A.                         C
C   Y=CONCENTRATIONS AT THE COLLOCATION POINTS.                     C
C                                                                   C
C*******************************************************************C
```

```
      COMMON/L3/N,NT
      COMMON/L5/XS
      COMMON/L6/COEF4
      CD=-COEF4*(A(1,1)*XS(1)+A(1,NT))
      DO 50 J=1,N
       CD=CD-COEF4*A(1,J+1)*Y(1,J)
   50 CONTINUE
      RETURN
      END


      SUBROUTINE CONCEN(C1,C2,NX,ND,DETA,ROOT,DIF1,Y)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION C1(60),C2(60),ROOT(20),DIF1(20),Y(3,20),XS(2),XINTP(20)

C*********************************************************************C
C                                                                     C
C   SUBROUTINE EVALUATES THE CONCENTRATION AT EACH DESIRED            C
C   POINT IN X DIRECTION BY AN INTERPOLATION ROUTINE USING            C
C   THE KNOWN CONCENTRATIONS AT THE COLLOCATION POINTS.               C
C                                                                     C
C   --- PARAMETERS ---                                                C
C                                                                     C
C   C1,C2=CONCENTRATIONS OF NITRATE AND HYDROXY IONS,                 C
C         RESPECTIVELY, IN DIMENSIONLESS UNIT.                        C
C   DETA=X INTERVAL, DIMENSIONLESS, 0 < DETA < 1.                     C
C                                                                     C
C*********************************************************************C

      COMMON/L2/COEF2
      COMMON/L3/N,NT
      COMMON/L5/XS
      DO 80 J=1,NX
       ETA=DETA*(J-1)
       CALL INTRP(ND,NT,ETA,ROOT,DIF1,XINTP)
       C1(J)=XINTP(1)*XS(1)+XINTP(NT)*1.
       C2(J)=XINTP(1)*XS(2)+XINTP(NT)*COEF2
        DO 70 K=1,N
         C1(J)=C1(J)+XINTP(K+1)*Y(1,K)
   70    C2(J)=C2(J)+XINTP(K+1)*Y(1,K+N)
   80 CONTINUE
      RETURN
      END


      SUBROUTINE CHANGE(ZS,DZS,COEF3,COEF4,COEF5,FACTOR,ETAJ,ETAJM1,
     1                      ETAJMA,JSTART)
      IMPLICIT REAL*8(A-H,O-Z)

C*********************************************************************C
C                                                                     C
C   SUBROUTINE INCREASES THE SPLINE POINT, ZS, AND THE OTHER          C
C   PARAMETERS WHICH MAY CHANGE DUE TO THE INCREASE OF THE            C
C   SPLINE POINT.                                                     C
```

```
C                                                                      C
C*********************************************************************C

      SAVZS=ZS
      IF(ZS.GE.0.001.AND.ZS.LT.0.010) DZS=0.0005
      IF(ZS.GE.0.010.AND.ZS.LT.0.100) DZS=0.005
      IF(ZS.GE.0.100) DZS=0.05
      ZS=ZS+DZS
      FACTOR=ZS/SAVZS
      COEF3=COEF3/FACTOR
      COEF4=COEF4/FACTOR
      COEF5=COEF5/FACTOR/FACTOR
      DTAU=DTAU/100.
      DTAUMI=.001*DTAU
      DTAUMA=2.0*DTAU
      JSTART=0
      RETURN
      END


      SUBROUTINE EXPAND(Y,ROOT,DIF1,FACTOR,ND)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION Y(8,20),ROOT(20),DIF1(20),YINTP(20),SY(20),XS(2)

C*********************************************************************C
C                                                                      C
C   SUBROUTINE EVALUATES THE CONCENTRATIONS AT THE COLLOCATION         C
C   POINTS IN THE NEW COORDINATE DUE TO THE CHANGE OF THE              C
C   SPLINE POINT.                                                      C
C                                                                      C
C*********************************************************************C

      COMMON/L2/COEF2
      COMMON/L3/N,NT
      COMMON/L5/XS
      DO 70 I=1,N
       SY(I)=Y(1,I)
   70  SY(I+N)=Y(1,I+N)
      DO 100 I=1,N
       RE=ROOT(I+1)*FACTOR
       IF(RE.GT.1.0) GO TO 90
       CALL INTRP(ND,NT,RE,ROOT,DIF1,YINTP)
       Y(1,I)=YINTP(1)*XS(1)+YINTP(NT)*1.0
       Y(1,I+N)=YINTP(1)*XS(2)+YINTP(NT)*COEF2
        DO 80 K=1,N
         Y(1,I)=Y(1,I)+YINTP(K+1)*SY(K)
   80    Y(1,I+N)=Y(1,I+N)+YINTP(K+1)*SY(K+N)
       GO TO 100
   90  Y(1,I)=1.0
       Y(1,I+N)=COEF2
  100 CONTINUE
      RETURN
      END
```

```
      FUNCTION AUX1(XX,K,QAR)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(20,20),B(20,20),XX(1),QAR(20)
C**************************************************************C
C                                                              C
C    AUX1 IS THE NAME OF THE FUNCTION CALLED BY ZSYSTM IN      C
C    THE SUBROUTINE DIFFUN TO FURNISH THE VALUES OF EQUATIONS  C
C    (52) AND (53).                                            C
C                                                              C
C**************************************************************C
      COMMON/L1/COEF1,COEF5
      COMMON/L2/COEF2
      COMMON/L3/N,NT
      COMMON/L4/A,B
      COMMON/L8/COEF3,CON1,CON2,GAMA,BETA
      QAR(20)=-3.*COEF1*(A(1,1)*XX(1)+A(1,NT)*1.0)/A(1,1)-A(1,NT)/A(1,1)
     1        *COEF2
      DO 500 J=1,N
        QAR(20)=QAR(20)-3.*COEF1*A(1,J+1)*QAR(J)/A(1,1)-A(1,J+1)
     1           *QAR(J+N)/A(1,1)
 500  CONTINUE
      IF(QAR(20).LT.0.) QAR(20)=0.
      AUX1=A(1,1)*XX(1)+A(1,NT)*1.+(CON2*(QAR(20)**GAMA)-CON1*
     1     (XX(1)**BETA))/COEF3
      DO 600 J=1,N
 600    AUX1=AUX1+A(1,J+1)*QAR(J)
      RETURN
      END


      FUNCTION AUX2(XX,K,BAR)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(20,20),B(20,20),Y(8,20),XX(1),BAR(1)
C**************************************************************C
C                                                              C
C    AUX2 IS THE NAME OF THE FUNCTION CALLED BY ZSYSTM IN      C
C    THE MAIN PROGRAM TO FURNISH THE VALUES OF EQUATIONS       C
C    (52) AND (53).                                            C
C                                                              C
C**************************************************************C
      COMMON/L1/COEF1,COEF5
      COMMON/L2/COEF2
      COMMON/L3/N,NT
      COMMON/L4/A,B
      COMMON/L8/COEF3,CON1,CON2,GAMA,BETA
      COMMON/L9/Y
      BAR(1)=-3.*COEF1*(A(1,1)*XX(1)+A(1,NT)*1.0)/A(1,1)-A(1,NT)/A(1,1)
     1       *COEF2
      DO 500 J=1,N
```

```
      BAR(1)=BAR(1)-3.*COEF1*A(1,J+1)*Y(1,J)/A(1,1)-A(1,J+1)
     1         *Y(1,J+N)/A(1,1)
  500 CONTINUE
      IF(BAR(1).LT.0.) BAR(1)=0.
      AUX2=A(1,1)*XX(1)+A(1,NT)*1.+(CON2*(BAR(1)**GAMMA)-CON1*
     1      (XX(1)**BETA))/COEF3
      DO 600 J=1,N
  600   AUX2=AUX2+A(1,J+1)*Y(1,J)
      RETURN
      END
```

```
C*************************************************************************C
C                                                                         C
C    THIS PROGRAM SOLVES EQUATIONS (48), (49), AND (52) THROUGH          C
C    (55) WITH TWO INITIAL CONDITIONS USING SPLINE COLLOCATION           C
C    METHOD FOR THE CASE OF THE ELECTROLYTE CONTAINING CADMIUM           C
C    IONS. IN THIS CASE, THE TWO SUBROUTINES, DIFFUN AND PEDERV,         C
C    CALLED BY THE INTEGRATION SUBROUTINE, DIFSUB, HAVE TO BE            C
C    CHANGED. MEANWHILE, THE MAIN PROGRAM AS WELL AS THE OTHER           C
C    SUBROUTINES STAY THE SAME. THE CONCENTRATION PROFILE OF             C
C    THE CADMIUM ION MAY BE OBTAINED BY THE ELECTRONEUTRALITY            C
C    CONDITION. THE CURRENT DENSITY DATA ARE CALCULATED IN THE           C
C    SAME WAY BY EQUATION (56). THE HETEROGENEOUS REACTION RATE          C
C    CONSTANTS OBTAINED BY LAST PROGRAM ARE USED TO IDENTIFY             C
C    THE HOMOGENEOUS REACTION RATE CONSTANT BY FITTING THE               C
C    CALCULATED CURRENT DENSITY DATA WITH THE EXPERIMENTAL               C
C    DATA.                                                                C
C                                                                         C
C        -------  ADDITIONAL NOMENCLATURE  -------                       C
C                                                                         C
C    SMALLK=HOMOGENEOUS REACTION RATE CONSTANT, 1/SEC.                   C
C    DBIGK=DIMENSIONLESS HOMOGENEOUS REACTION RATE CONSTANT,             C
C          DBIGK=SMALLK*DMAX**2/5.26E-5.                                  C
C    DKSP=DIMENSIONLESS SOLUBILITY PRODUCT OF CADMIUM HYDROXIDE,         C
C         DKSP=2.0E-23/C1B**3.                                            C
C                                                                         C
C*************************************************************************C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(20,20),B(20,20),C1(60),C2(60),C(20),Y(8,20),
     1          DIF1(20),DIF2(20),DIF3(20),ROOT(20),VECT(20),ERROR(20),
     2          YMAX(20),SAVE(24,20),PW(400),XS(2),XX(1),WA(3),BAR(1)
      EXTERNAL AUX2
      COMMON/L1/COEF1,COEF5
      COMMON/L2/COEF2
      COMMON/L3/[illegible],NT
      COMMON/L4/A,B
      COMMON/L5/XS
      COMMON/L6/COEF4
      COMMON/L7/NSIG,NEZ,EP
      COMMON/L8/COEF3,CON1,CON2,GAMA,BETA
      COMMON/L9/[illegible]
      COMMON/L10/DBIGK,DKSP
C
C     ------- INPUT DATA -------
C
      READ(5,310) ND,N,NO,N1,AL,BE,EPS,TIMAX,IC,DES
      READ(5,320) C1B,C2B,DMAX,DTIME,NK,ES
      READ(5,330) GAMA,BETA,CON2,CON1,SMALLK
      READ(5,340) NSIG,NEZ,EP
C
C     ------- CALCULATE SOME CONSTANTS TO BE USED IN THE PROGRAM -----
C
       COEF1=(1.902D-5)/5.26D-5
       COEF2=C2B/C1B
```

```
       COEF3=(1.902D-5)*C1B/DMAX/ZS
       COEF4=2.*(1.902D-5)*C1B*96487./DMAX/ZS
       COEF5=1./ZS/ZS
      DBIGK=SMALLK*DMAX*DMAX/5.26D-5
      DKSP=(2.D-23)/(C1B**3.)
      DX=DMAX/(NX-1)
      DTAU=(5.26D-5)*DTIME/DMAX/DMAX
      TAUMAX=(5.26D-5)*TIMAX/DMAX/DMAX
      SDTAU=DTAU
      DETA=1./(NX-1)
      NT=N+N0+N1
      NER=2*N
C
C     ------- SET INITIAL DIMENSIONLESS TIME=0. -------
C
      TAU=0.
C
C     ------- DEFINE THE MAXIMUM AND MINIMUM DIMENSIONLESS
C             TIME INCREMENT TO BE USED IN THE INTEGRATION
C             SUBROUTINE DIFSUB -------
C
      DTAUMI=.001*DTAU
      DTAUMA=2.0*DTAU
      WRITE(6,360)
C
C     ------- EVALUATE THE COLLOCATION POINTS(ROOTS) OF THE
C             JACOBI POLYNOMIAL OF ORDER N, AS WELL AS THE
C             FIRST AND SECOND DERIVATIVES OF THE POLYNOMIAL
C             AT THE ROOTS. -------
C
      CALL JCOBI(ND,N,N0,N1,AL,BE,DIF1,DIF2,DIF3,ROOT)
       WRITE(6,350) (ROOT(J),J=1,NT)
C
C     ------- CALCULATE THE DISCRETIZATION COEFFICIENT MATRIX A -------
C
      ID=1
       DO 20 I=1,NT
        CALL DFOPR(ND,N,N0,N1,I,ID,DIF1,DIF2,DIF3,ROOT,VECT)
         DO 10 J=1,NT
   10     A(I,J)=VECT(J)
   20  CONTINUE
C
C     ------- CALCULATE THE DISCRETIZATION COEFFICIENT MATRIX B -------
C
      ID=2
       DO 40 I=1,NT
        CALL DFOPR(ND,N,N0,N1,I,ID,DIF1,DIF2,DIF3,ROOT,VECT)
         DO 30 J=1,NT
   30     B(I,J)=VECT(J)
   40  CONTINUE
C
C     ------- INPUT THE VALUES OF ARGUMENTS TO BE USED IN THE
C             INTEGRATION SUBROUTINE DIFSUB -------
C
```

```
      MF=1
      JSTART=0
      ISTOP=0
      MAXDER=7
      DO 47 I=1,NEB
   47  YMAX(I)=1.0
      I=0
C
C     ------- INPUT THE INITIAL CONDITIONS -------
C
      DO 50 J=1,N
       Y(1,J)=1.
   50  Y(1,J+N)=COEF2
      XS(1)=1.
      XS(2)=COEF2
      WRITE(6,390)
   60 TIME=TAU*DMAX*DMAX/(5.26D-5)
C
C     ------- CALCULATE AND PRINT THE CURRENT DENSITY AT THIS TIME
C             PRINT THE CONCENTRATIONS OF NITRATE AND HYDROXY IONS
C             AT THE NT COLLOCATION POINTS -------
C
      CALL CURENT(CD,A,Y)
       WRITE(6,360) TIME,CD,XS(1),XS(2),KFLAG,ITERN,ZS
       WRITE(6,700) (Y(1,L),L=1,NEB)
C
C     ------- EVALUATE AND PRINT THE CONCENTRATIONS OF
C             NITRATE AND HYDROXY IONS AT EACH POINT
C             IN X DIRECTION AT THIS TIME -------
C
      CALL CONCEN(C1,C2,NX,ND,DETA,ROOT,DIF1,Y)
       WRITE(6,230) (C1(J),J=1,NX)
       WRITE(6,250) (C2(J),J=1,NX)
C
C     ------- CHECK IF THE INTEGRATION TIME AT THIS MOMENT REACHES
C             THE MAXMIUM TIME TO BE INTEGRATED -------
C
      IF(TAU.GE.TAUMAX) GO TO 190
   85 I=I+1
      IF(I.EQ.1) GO TO 90
      IF(ISTOP.EQ.1) GO TO 90
C
C
C     ------- TEST IF THE CONCENTRATION OF NITRATE ION AT THE NTH
C             COLLOCATION POINT,IE, THE LAST ONE BEFORE THE SPLINE
C             POINT IS WITHIN 0.0001 DIMENSIONLESS CONCENTRATION
C             UNIT OF THE BOUNDARY CONDITION. -------
C
C
      IF((1.-Y(1,5)).LT.0.0001) GO TO 90
C
C     ------- IF THE TEST FAILS, THE SPLINE POINT IS INCREASED,IE,
C             MOVED FURTHER INTO THE SOLUTION. -------
C
```

```
      CALL CHANGE(ZS,DZS,COEF3,COEF4,COEF5,FACTOR,DTAU,DTAUMI,DTAUMA,
     1             JSTART)
C
C
C     ------- EVALUATE THE CONCENTRATIONS OF NITRATE AND HYDROXY
C             IONS AT THE COLLOCATION POINTS AT THE NEW COORDINATE
C             DUE TO THE INCREASE OF THE SPLINE POINT. -------
C
C
      CALL EXPAND(Y,ROOT,DIF1,FACTOR,ND)
C
C
C     ------- INTEGRATE EQUATIONS (48) AND (49) USING THE CONCENTRATIONS
C             AT THE COLLOCATION POINTS AT THIS TIME TO OBTAIN THE
C             CONCENTRATIONS AT THE SUCCESSIVE TIME -------
C
C
   90 CALL DIFSUB(NER,TAU,Y,SAVE,DTAU,DTAUMI,DTAUMA,EPS,MF,YMAX,
     1             ERROR,KFLAG,JSTART,MAXDER,PW)
      IF(KFLAG.LT.0) GO TO 190
      DTAUMI=.001*DTAU
      DTAUMA=2.0*DTAU
     IF(I.GE.2) GO TO 93
     IF(Y(1,1).GT.1..OR.Y(1,2).GT.1..OR.Y(1,3).GT.1..OR.Y(1,4).GT.1.
    1  .OR.DABS(Y(1,5)-1.).GT.0.0004) GO TO 90
     GO TO 95
  93 M1=I/IC
     M2=M1*IC
     IF(I.EQ.M2.OR.TAU.GE.TAUMAX) GO TO 95
     GO TO 85
C
C     ------- CALCULATE THE SURFACE CONCENTRATIONS -------
C
  95 OLDXS2=XS(2)
     XX(1)=Y(1,1)
     ITERN=500
     CALL ZSYSTM(AUX2,EP,NSIG,NEZ,XX,ITERN,WA,BAR,IER)
      XS(1)=XX(1)
      XS(2)=-3.*COEF1*(A(1,1)*XX(1)+A(1,NT)*1.0)/A(1,1)-A(1,NT)/A(1,1)
    1        *COEF2
      DO 150 J=1,N
       XS(2)=XS(2)-3.*COEF1*A(1,J+1)*Y(1,J)/A(1,1)-A(1,J+1)
    1          *Y(1,J+N)/A(1,1)
 150  CONTINUE
     IF(XS(2).LT.OLDXS2) ISTOP=1
     GO TO 60
 190 WRITE(6,240) DK,SDTAU,NK,DTAU,DTIME,DMAX,AL,BE,ZS,EPS,KFLAG,
    1             EP,NSIG
     WRITE(6,245) BETA,GAMA,CON1,CON2,SMALLK
C
C     ------- FORMATS FOR INPUT AND OUTPUT STATEMENTS -------
C
 230 FORMAT(/,25X,'NO3-',1X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4
    1       /30X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4
```

```
     2         /30X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4)
 240 FORMAT(//,5X,'X INTERVAL=',D12.4,32X,'INITIAL TAU STEP SIZE='
     1         ,D12.4/5X,'NO OF POINTS IN X DIR= ',I3,29X,
     2         'LAST TAU STEP SIZE=  ',D12.4/5X,'REAL TIME INTERVAL=  '
     3         ,D10.4,24X,'DIFUSION LENGTH= ',D10.4//5X,'AL=  ',F7.2,30X,
     4         'BE=  ',F7.2,25X,'ZS=  ',F7.4//5X,'EPS=  ',D10.2,27X,
     5         'KFLAG=  ',I3//5X,'EP =  ',D10.2,27X,'NSIG=   ',I3)
 245 FORMAT(//,5X,'REACTION ORDER OF NO3- ION  =',F7.2,25X,
     1         'REACTION ORDER OF OH- ION  =',F7.2//5X,'1ST CONSTANT ='
     2         ,D12.4,25X,'2ND CONSTANT  =',D12.4
     3         //5X,'REACTION RATE CONSTANT=  ',D12.4)
 250 FORMAT(/,25X,'OH-',2X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4
     1         /30X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4
     2         /30X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4/30X,9D11.4)
 310 FORMAT(4I3,2F5.1,2D10.2,I5,F8.4)
 320 FORMAT(4D11.4,I7,F7.4)
 330 FORMAT(2F7.2,3D12.4)
 340 FORMAT(2I5,D12.4)
 350 FORMAT(15X,10F10.6)
 360 FORMAT(//,D12.4,1X,D12.4,2X,2D30.10,2I5,F20.7)
 370 FORMAT(/,2X,6F20.6/2X,6F20.6)
 380 FORMAT(2X,'COLLOCATION POINTS: ')
 390 FORMAT(//,3X,'TIME',12X,'CURRENT',45X,'ION CONCENTRATION')
 700 FORMAT(30X,10F10.5/30X,10F10.5)
     STOP
     END


     SUBROUTINE DIFFUN(T,YY,DYY)
     IMPLICIT REAL*8(A-H,O-Z)
     DIMENSION DYY(20),YY(8,20),A(20,20),B(20,20),C(20),XX(1),WA(3),
    1          QAR(20)

C*********************************************************************C
C                                                                     C
C   SUBROUTINE CALLED BY DIFSUB EVALUATES THE DERIVATIVES OF          C
C   DEPENDENT VARIABLES STORED IN YY(1,I),I=1,2*N, AND STORES         C
C   THE DERIVATIVES IN THE ARRAY DYY. T IS THE INDEPENDENT            C
C   VARIABLE.                                                         C
C                                                                     C
C*********************************************************************C

     EXTERNAL AUX1
     COMMON/L1/COEF1,COEF5
     COMMON/L2/COEF2
     COMMON/L3/N,NT
     COMMON/L4/A,B
     COMMON/L7/NSIG,NEQ,EP
     COMMON/L10/DBIGK,DKSP
     II=2*N
     DO 30 I=1,II
      QAR(I)=YY(1,I)
  30 CONTINUE
C
```

```
C    ------- CALCULATE THE VALUES ON THE SURFACE (X=0) -------
C
      XX(1)=YY(1,1)
      ITERN=500
      CALL ZSYSTM(AUX1,EP,NSIG,NEZ,XX,ITERN,WA,QAR,IER)
      CT=-3.*COEF1*(A(1,1)*XX(1)+A(1,NT)*1.)/A(1,1)-A(1,NT)/A(1,1)*COEF2
      DO 45 I=1,N
       C(I)=B(I+1,1)*CT+B(I+1,NT)*COEF2
   45 CONTINUE
C
C    ------- STORE THE DERIVATIVES IN ARRAY DYY -------
C
      DO 120 J=1,N
       DYY(J)=B(J+1,1)*XX(1)+B(J+1,NT)*1.
       DYY(J+N)=C(J)
        DO 110 K=1,N
         DYY(J)=DYY(J)+B(J+1,K+1)*YY(1,K)
  110    DYY(J+N)=DYY(J+N)-3.*B(J+1,1)*COEF1*A(1,K+1)*YY(1,K)/A(1,1)
     1              +(B(J+1,K+1)-B(J+1,1)*A(1,K+1)/A(1,1))*YY(1,K+N)
       DYY(J)=COEF1*COEF5*DYY(J)
       DYY(J+N)=DYY(J+N)*COEF5
       SUPER=2.*DBIGK*(0.5*(YY(1,J)+YY(1,J+N))-DKSP/YY(1,J+N)/YY(1,J+N))
       IF(SUPER.GT.0.) DYY(J+N)=DYY(J+N)-SUPER
  120 CONTINUE
      RETURN
      END


      SUBROUTINE PEDERV(T,Y,PW,N3)
      IMPLICIT REAL*8(A-H,Q-Z)
      DIMENSION  Y(8,20),PW(400),A(20,20),B(20,20)
C*****************************************************************C
C                                                                 C
C   SUBROUTINE CALLED BY DIFSUB STORES THE PARTIAL                C
C   DERIVATIVES OF THE DIFFERENIAL EQUATIONS PROVIDED IN          C
C   SUBROUTINE DIFFUN. THE PARTIAL DERIVATIVES (THE JACOBIAN)     C
C   WERE EVALUATED IN THE LAST SECTION IN CHAPTER 5.              C
C                                                                 C
C*****************************************************************C

      COMMON/L1/COEF1,COEF5
      COMMON/L3/N,NT
      COMMON/L4/A,B
      COMMON/L10/DBIGK,DKSP
      DO 10 KK=1,N
       DO 20 II=1,N
       PW(II+(2*KK-2)*N)=COEF1*COEF5*B(II+1,KK+1)
       PW(II+(2*KK-1)*N)=-COEF5*3.*B(II+1,1)*COEF1*A(1,KK+1)/A(1,1)
       IF(II.EQ.KK) GO TO 30
       GO TO 40
   30  SUP=2.*DBIGK*(0.5*(Y(1,II)+Y(1,II+N))-DKSP/Y(1,II+N)/Y(1,II+N))
       IF(SUP.GT.0.) PW(II+(2*KK-1)*N)=PW(II+(2*KK-1)*N)-DBIGK
   40  PW(II+2*N*N+(2*KK-2)*N)=0.
```

```
      PW(II+2*N*N+(2*KK-1)*N)=(B(II+1,KK+1)-B(II+1,1)*A(1,KK+1)/A(1,1))
     1                          *COEF5
      IF(II.EQ.KK) GO TO 60
      GO TO 20
   60 IF(SUP.GT.0.) PW(II+2*N*N+(2*KK-1)*N)=PW(II+2*N*N+(2*KK-1)*N)-2.*
     1                                 DBIGK*(.5+2.*DRSP/Y(1,II+N)/
     2                                 Y(1,II+N)/Y(1,II+N))
   20 CONTINUE
   10 CONTINUE
      RETURN
      END

C*******************************************************************C
C                                                                   C
C   THE OTHER SUBROUTINES CALLED BY THIS PROGRAM STAY THE SAME     C
C   AS THOSE IN THE FIRST PROGRAM.                                  C
C                                                                   C
C*******************************************************************C
```

END

DATE
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