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# SPUR DIFFUSION MODEL FOR THE RADIOLYSIS OF AQUEOUS SOLUTIONS

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Eileen W. Ruppel

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## ABSTRACT

A computer model which simulates the simultaneous reaction and diffusion of chemical species resulting from the radiolysis of aqueous solutions was updated and improved. This model numerically solves the deterministic rate equations for the deaerated Fricke dosimeter (dilute ferrous sulfate in sulfuric acid). Based on a review of the literature, the model results were compared to other models and experimental data.

The model was improved by the addition of an algorithm to determine the optimum timestep. This decreased the execution time of the model significantly with less than a 5% difference in the yield results.

It was determined that the model does not correctly describe scavenger reactions and only accurately reflects experimental results during the period of spur reactions (1 ps to 200 ns).

The model results for long term yields of $Fe^{+3}$ and $H_2$ were within 10% of experimental values. The G values, the number of species produced per 100 eV of energy absorbed, determined from the model were 8.6 for $Fe^{+3}$ and 4.1 for $H_2$. Agreement with experimental data can be improved by adjusting several parameters in the model.

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## LIST OF SYMBOLS

Roman

| | |
|---|---|
| $C_i$ | concentration of specie i, number/$cm^3$ |
| $C_i(r,t)$ | concentration of specie i at distance r and time t, number/$cm^3$ |
| $D_i$ | diffusion constant of specie i, $cm^2/s$ |
| $G^0_i$ | initial G value of specie i, number/100 eV |
| $G_i$ | primary G value of specie i, number/100 eV |
| G(i) | long term G value of specie i, number/100 eV |
| $k_{ij}$ | rate constant for the reaction of specie i and specie j, l/(mole*s) |
| M | number of molecular products |
| m | spatial node number, m=1 at center of spur, mlast is last node |
| $N_i$ | number of species of i |
| $N_i(t)$ | number of species i at time t |
| No | number of initial radical pairs |
| r | distance from center of spur, cm |
| $r^0_i$ | initial unit spur radius of specie i, Å |
| $r_i$ | initial spur radius of specie i, Å |
| $\Delta r$ | distance between nodes, cm |
| t | time, s |
| $\Delta t$ | time increment, s |
| W | energy required to form a radical pair, eV |
| $X_i$ | specie i, moles |

## LIST OF SYMBOLS (continued)

Greek

| | |
|---|---|
| $\nabla^2$ | three dimensional Laplacian operator |
| $\Phi_i$ | probability density per specie i, number/$cm^3$ |
| $\Omega_i$ | equivalent conductance of specie i, specific conductance/(concentration in equivalents/$cm^3$) |

# 1. INTRODUCTION

Radiation chemistry is the study of the chemical effects produced in a system by the absorption of ionizing radiation (Spinks and Woods, 1976). Fundamental studies in radiation chemistry are the identification of species formed, the physical processes by which they are formed, the quantities formed, and the mechanisms of the species' reactions with themselves and other compounds (O'Donnell and Sangster, 1970). This work involves improving and updating a model for the simultaneous diffusion and reaction of the chemical species resulting from the irradiation of aqueous solutions and comparing results with experimental data.

The irradiation of aqueous solutions results in the excitation and ionization of the molecules in solution. The species formed from the excitation, ionization and subsequent reactions are concentrated in small clusters along the track of the ionizing particle. The geometry and initial distance between clusters depends on the energy deposited. The small clusters are classified as spurs (low energy - glancing collisions), blobs (intermediate energy), and tracks (high energy - knock-on collisions) (Chatterjee, 1987). Spurs are spherical volume elements which do not overlap and can be treated individually. The average spur contains two radical pairs and has a diameter on the order

of 20 Å with a spacing between the spurs on the order of $10^4$ Å (Spinks and Woods, 1976). Tracks consist of overlapping volume elements which can be represented as cylinders.

Radiation is characterized by its linear energy transfer (LET) which is the amount of energy lost to the solution divided by the distance traveled. LET depends on the medium irradiated and the radiation type. In aqueous solutions, gamma and beta radiation and x-rays are considered low LET while alpha and other heavy particles are high LET. The development of pulse radiolysis, short pulses of high intensity ionizing radiation, has led to major advances in identification and evaluation of transient species in water radiolysis (Spinks and Woods, 1976).

The radiolysis of aqueous solutions is divided into three stages - physical, physicochemical and chemical. The physical stage lasts about to about .1 fs after irradiation and involves the initial dissipation of energy in the ionization and excitation of water. Thermal equilibrium is established in the physicochemical stage. The electrons ejected in the physical stage are solvated to form hydrated electrons ($e^-_{aq}$). The hydrated electron is an electron which is trapped by a small group of water molecules which have become suitably oriented as a consequence of the electron's presence (Spinks and Woods, 1976). The positive

ion $H_2O^+$ formed by the water ionization reacts with water to form OH and $H_3O^+$ and excited water dissociates to H and OH during the physiochemical stage. The duration of the physicochemical stage is on the order of 1 ps (Buxton, 1987).

The simultaneous spur diffusion and reaction of the species formed in the previous stages occurs in the chemical stage. The chemical stage lasts until approximately 100 ns seconds at which time spur expansion is complete. Reactions in the chemical stage include reduction by the H radical, oxidation by the OH radical, and recombination reactions.

Radical species which don't react in the spur and molecular products from the radical reactions escape into the bulk solution and become homogeneously distributed throughout the medium. At low solute concentration only the radicals which diffuse out of the spur into the bulk are scavenged by any solutes in the medium (Buxton, 1987).

The species present in spurs of aqueous solutions at the end of the physicochemical stage are called primary species. The primary species for deaerated aqueous solutions are H, $H^+$, OH, and $e^-_{aq}$. In the presence of oxygen there are two additional primary species, $HO_2$ and $O_2^-$. $HO_2$ is also present for high LET radiolysis of deaerated solutions. In acidic solutions, the hydrated electron is rapidly converted to H.

Solutes such as $Fe^{+2}$ and $H^{+}$ are used as scavengers to determine the yields of reaction intermediates of water radiolysis. The yields are calculated as G values (number of species produced per 100 eV of energy absorbed). Initial yields are yields at the beginning of the chemical stage. Yields at the end of spur reactions or the end of the chemical stage are called primary yields and yields at the end of scavenger reactions are called long term yields.

The following characteristics have been observed from aqueous solution radiolysis experiments (Buxton, 1987):

1. Radicals are scavenged by low concentrations of solute in yields independent of solute concentration. Molecular products are formed in constant yield.
2. At solute concentrations above .001 M, yields of scavenged radicals increase, and molecular products are formed in constant yield.
3. As LET increases, the yields of radical products decrease and yields of molecular products increase.

These results indicate the existence of spurs and can be explained by spur diffusion theory. Only radicals which diffuse out of the spur are scavenged by solutes at low concentration. At high concentration of solutes, radicals react with the scavengers within the spur,increasing the yield of scavenged radicals. A solution that has been

irradiated with low LET radiation contains mostly non-overlapping spurs but some blobs and tracks are formed when secondary electrons escape. As LET increases, more tracks are formed. The primary species are closer together in tracks causing more radical recombination, increasing the molecular yield and decreasing the radical yield of products.

This work is concerned with modifying a computer program to simulate the diffusion and reaction in spurs during the chemical stage of low LET radiolysis and to calculate the yields of reaction products. Simultaneous diffusion and reaction is a problem in chemical kinetics in which the rate of reaction depends on the rate of supply of one of the reactants by diffusion (Crank, 1956). There are two basic approaches to modeling diffusion and reaction in spurs. The deterministic method, used in this work, is based on deterministic rate equations. A newer method utilizes a stochastic approach.

# 2. DETERMINISTIC MODEL

## 2.1 Description and Assumptions

The generalized reaction mechanism for reactions in spurs for the deterministic model can be written as (Kuppermann and Belford, 1962 I.) :

1. Reaction of specie i with specie j

$$X_i + X_j \xrightarrow{k_{ij}} \text{Product} \qquad (2.1)$$

2. Reaction of specie i with solute s

$$X_i + X_s \xrightarrow{k_{is}} \text{Product} \qquad (2.2)$$

3. Formation of specie i by reaction of species b and d

$$X_b + X_d \xrightarrow{k_{bd}} X_i. \qquad (2.3)$$

The equation which describes simultaneous diffusion and reaction based on this generalized reaction mechanism is (Kuppermann and Belford, 1962 I.):

$$\delta C_i(r,t)/\delta t = D_i \nabla^2 C_i - \Sigma K_{ij} C_i C_j + \Sigma(1-.5\delta bd) K_{bd} C_b C_d - \Sigma K_{is} C_i C_s. \qquad (2.4)$$

$\delta bd$ is the Kronecker delta which equals 1 when b=d and 0 otherwise. This is because when b=d the rate of appearance of specie i is one-half the rate of disappearance of specie b.

There is an equation similar to equation 2.4 for each reactive specie in the system. The problem of modeling the

diffusion and reaction in spurs becomes one of solving a system of simultaneous non-linear partial differential equations.

The conventional concept of concentration is invalid for the small size of the spurs and the small number of particles in each spur. It has been shown that equation 2.4 is still valid if the concentration is expressed as the average probability density (Kuppermann and Belford, 1962 I.).

The initial amounts and distribution of the primary species must be known to solve the model. A Gaussian distribution has been used most often (mostly for mathematical expediency) and the width is dependent on the mechanism assumed for the formation of the primary species.

Several assumptions were used in developing the deterministic model of spur diffusion (Kuppermann and Belford, 1962 I.). The first of these is that the primary reactive species are in thermal equilibrium with the medium at the beginning of the chemical stage. This eliminates any overlap of the physicochemical and chemical stages. The second assumption of the spur diffusion model is that diffusion is not affected by charged species. The third assumption is that Fick's macroscopic diffusion law is obeyed by species in spurs. The final assumption is that reaction rate laws which govern reactions in macroscopic homogeneous systems can be used to model reactions in

spurs. This assumption neglects the correlation between particles. This is probably not true due to the small volume of the spur and the high local initial concentration of particles. The H and OH pair would tend to recombine more than indicated by homogeneous rate constants.

## 2.2 Prescribed Diffusion

The theory of spurs was first proposed by Lea (1955). He suggested that fast charged particles generated tracks of ionization, which lead to an inhomogeneous distribution for initial radiolysis products. Lea called these groups of ionizations clusters. He assumed that the primary species for water were H and OH and that these species were formed far apart. The ionization of water caused the formation of $H_2O^+$ which dissociated to OH and $H^+$. The H radical was formed from the thermalized electron becoming attached to a hydrogen ion or a water molecule. Any H and OH radicals formed by the direct decomposition of water were assumed to recombine. Based on Wilson cloud chamber experiments with positive and negative charged particles in gases, Lea assumed a cylindrical track with an initial Gaussian distribution with a radius of 150 Å for the H radical and an arbitrary radius of 20 Å for the OH radical.

In order to determine an analytical solution to the spur diffusion equations Lea introduced three assumptions. The first of these was a Gaussian initial distribution for

the primary species in the spur. Lea assumed that the distributions maintained a Gaussian form as the spur expands. He also assumed that the variation of the radius of the distributions was due only to diffusion only. The last two assumptions are called the "prescribed diffusion" approximation. Implicit in the prescribed diffusion approximation is the assumption that no solute molecules diffuse into the spur to replace those which react (Lea, 1955).

Samuel and Magee (1953) used a modified form of Lea's model to calculate yields for aqueous solution radiolysis. They proposed a different reaction mechanism in which electrons produced by the ionization were recaptured by the parent ion forming an excited water molecule which dissociated into H and OH. An equal number of these radicals were contained in small spheres or spurs with a radius of about 10 Å. The spurs were isolated for low LET radiations and overlapped to form a cylindrical track for high LET radiations. The distance between spurs was a function of the LET of the ionizing particle. The reaction mechanism only involved reactions of one specie of radicals. An initial Gaussian distribution and the prescribed diffusion approximation were also assumed.

The one-radical-no-solute reaction mechanism reduces equation 2.4 to:

$$\delta C_i/\delta t = D_i \nabla^2 - k_{ii} C_i^2. \qquad (2.5)$$

The probability density of finding two particles at a specific r and t was assumed to be $N_i(N_i-1)\Phi_i^2$ rather than $N_i^2\Phi_i^2$. This introduced a small amount of particle correlation. Equation 2.5 then becomes:

$$\delta C_i/\delta t = D_i\nabla^2 - (k_{ii}(N_i-1)/N_i)C_i^2. \qquad (2.6)$$

The equation which represents the initial Gaussian distribution is:

$$C_i(r,0) = N_i(0)/(4\pi D_i t)^{3/2}e^{-(r^2/4D_i t)} \qquad (2.7)$$

The initial spur radius squared was assumed to be equal to:

$$r_i^2 = 2D_i t \qquad (2.8)$$

Samuel and Magee's representation of the Gaussian distribution at any time t was:

$$C_i(r,t)= N_i(t)/(\pi^{3/2}(2r_i^2 + 4D_i t)^{3/2}) \; e^{-(r^2/(2r_i^2 + 4D_i t))} \qquad (2.9)$$

which is exact if there is no reaction. Substituting equation 2.9 into equation 2.6 and integrating gives an ordinary differential equation for $N_i(t)$.

Samuel and Magee also assumed that the initial radius was proportional to the cube root of $N_i(0)$ and used a spur size distribution based on cloud chamber data. Yields from this model were in reasonable agreement with experimental data.

Ganguly and Magee (1956) further modified Samuel and Magee's model. They assumed that the spurs, containing the same number of radicals, were randomly distributed along the path of the fast particle with the spacing between the

center of the spurs proportional to the local LET of the particle. Therefore overlap of the spurs was allowed. The mechanism they used included reactions between radicals and between radicals and solutes.

Mozumder and Magee proposed a model (1966 II.) which included spurs, short tracks, and blobs and a distribution for the initial number of radicals in the track entities for low energy radiation (100-5000 eV). Spurs, blobs and short tracks represented energy losses up to 100 eV, 100-500 eV, 500-5000 eV respectively. Blobs were larger and had a higher radical concentration than spurs. Short tracks were cylindrical regions of high LET in a long track due to ionization from low LET radiation. They developed an algorithm to determine the percent of spurs, blobs and short tracks based on the primary energy of the ionizing particle. A Monte Carlo technique was used to determine the energy distribution in the spur and the spur size distribution was inferred from this energy distribution. Comparison of this model with experimental data for the lowering of molecular yield with increase in scavenger concentration showed good agreement except at high scavenger concentration.

The model proposed by Ganguly and Magee was extended to a many radical system and solved numerically by Schwarz (1969). His model allowed for spur overlap and used the spur size distribution developed by Mozumder and Magee. A

correction factor was introduced to the prescribed diffusion hypothesis and time dependent rate constants were used.

Schwarz assumed there were initial hydrogen molecules in the spur formed by an unknown mechanism. He used Samuel and Magee's assumption that the initial radius of the spur was proportional to the number of dissociations in the spur and that OH and H radicals had the same initial distribution. The hydrated electron had a larger initial radius. Initial yields for $e^-_{aq}$, $H_2$, and H were assumed and the other yields calculated from charge and material balance equations. Results of Schwarz agreed well with experimental data for the yield of nitrogen gas in nitrous oxide solutions.

A recent addition to the prescribed diffusion model was proposed by Girija and Gopinathan (1980). They proposed that the size of a spur, for a given number of initial dissociations, varies as a Gaussian distribution instead of having only one value. In another modification, Yamaguchi (1987) proposed the use of interspur distances based on the average energy instead of the average distance based on all energies.

## 2.3 Numerical Solutions

Fricke and Flanders (1958) obtained the first numerical solution to the partial differential equations of

the deterministic spur diffusion model for a one-radical-one-solute reaction scheme without the prescribed diffusion approximation. The differential equations were cast into dimensionless form and then solved using the explicit finite difference method. The model was calculated for both spherical and cylindrical geometry. This model gave a larger fractional number of radicals combining with themselves and solutes than predicted by prescribed diffusion but were within 10%.

Kuppermann and Belford (1962 II.) also solved the one-radical-one-solute system for both spherical and cylindrical geometry using the explicit finite difference method. That was the most realistic reaction mechanism which could be solved due to the speed of the computers available. Comparison between Ganguly and Magee's prescribed diffusion results showed a small deviation occurring at times less than 100 ps. The model was used to examine the effect on the yields of parameters such as diffusion constants, rate constants, initial radii and initial number of radicals in spurs. Kuppermann showed that the Gaussian shape of the initial concentration was maintained quite well during the history of the spur and that an initial square distribution became Gaussian after about 1 ns.

Burns, Sims and Goodall (1984) developed a numerical solution to the deterministic model using the FACSIMILE

computer program for initial value problems. In the solution to this model, the reaction space was divided into spherical shells or zones which contain the primary species as required by the initial distribution. Reaction occurred in each zone according to concentrations and rate constants. The rate of change of each species was then adjusted to account for diffusion and reaction based on Fick's first law of diffusion. Simultaneous differential equations were solved using Gear's method in which the order of the predictor-corrector method is chosen to maximize step size. This model improved the values of early $G_{OH}$ and $G_{e^-_{aq}}$ over the predictions of the Schwarz model. Results of the FACSIMILE model with an initial Gaussian distribution showed a non-Gaussian distribution for the hydrated electron at 100 ps with a central minimum for cylindrical tracks.

A model for spur diffusion was developed using a skewed Gaussian (Central Minimum) initial distribution for the hydrated electron and overlap of spurs (Fanning et al., 1977 I.). This distribution was chosen to more accurately model experimental data for the decay of $e^-_{aq}$ which indicated a slower decay rate in the time range 10 ps to 1 ns than results of previous deterministic models (Jonah et al., 1976). It also conformed to the theory of Lea and Plaztmann that ejected electrons are hydrated at a distance from the parent ion. A similar distribution was suggested

(Burns et al., 1977) to correct discrepancies between experimental and model results for the decay of the hydrated electron in proton tracks.

Comparison of the central minimum and the Gaussian initial distributions for the hydrated electron indicated that the central minimum distribution was more accurate in simulating hydrated electron decay and less accurate in simulating the relative OH decay. Results for long term G values with scavengers present showed that the central minimum distribution gave low molecular product yields and high radical yields as compared to experimental values (Burns et al., 1984).

The central minimum model was later modified to divide the diffusion and reaction into a high LET fraction and a low LET fraction (Trumbore et al., 1978). Results of this model compared well with experimental data for 14 MeV electron pulse radiolysis but not for gamma radiolysis. It was suggested that these results imply that the model was underestimating the fraction of energy in the high energy region. The addition of regions of cylindrical geometry as was done by Schwarz (1969) may improve the gamma radiation model results (Trumbore and Youngblade, 1983).

# 3. STOCHASTIC MODELS

The deterministic model can be described as the generation of an average spur,in terms of initial spatial distributions of species, and following it's kinetics. The stochastic method of modeling involves following the kinetics of each individual spur and then averaging the results. Stochastic models are based on equations governing probability distributions for the number of reacting species as a function of time (Zaider and Brenner, 1984). Deterministic models are based on average specific rates of reactions with no correlation between particles.

Stochastic models eliminate the necessity for the deterministic assumption of point particles. This assumption neglects any reaction between adjacent radicals at zero-time. In a real spur there will be some reactions between adjacent particles at very short times which creates concentration gradients (Clifford et al., 1982 I.)

Deterministic models use rate constants based on diffusion controlled reaction rates which require a constant concentration. To account for concentration gradients in a spur some deterministic models have used time dependent rate constants (Clifford et al., 1982 I.).

The stochastic Monte-Carlo model can be thought of as random walks or jumps of species with reaction occurring if the species are within the reaction radii. Several

efficient approximations to the full Monte-Carlo method have been developed (Clifford et al., 1985). The Master Equation model was based on assumptions that pair distances are initially independent and that the rate of reaction was determined by the independent evolution of pair distances. The Random Reaction Time model used real initial particle distributions and the assumption of independent pair distance evolution. In this model, which accounted for all initial particle correlations, the minimum reaction time was found, and that pair was allowed to react and was then removed. The Master Equation model had several shortcomings compared to the Random Reaction Time model. The major one of these was that it did not account for competitiveness in the scavenging at high radical densities (Clifford et al., 1985). The Independent Reaction Time model was developed for multi-specie spurs. Zero time reaction was accounted for and then each pair distance between remaining particles was used to calculate an independent reaction time (Clifford et al., 1987).

Comparison of the Master Equation model and deterministic models in which the number of particles initially present was reduced to account for zero time reactions indicated that deterministic models overestimate the reaction in spurs and thus overestimate the molecular product yield. Agreement between the two models improved

as the number of initial particles in the spur increased (Green et al., 1984).

The Master Equation model showed non-Gaussian concentration profiles for the hydrated electron. The deviation increased as the number of initial particles increased. A central minimum similar to that proposed by Fanning et al. (1977, I.) occurred for seven or more particles (Green et al., 1984).

A different type of Monte-Carlo program to stochastically simulate the fast reactions of radiolysis products in water was developed in 1984. The model used the concept of proximity functions of radicals (PFR) which was defined as the point-pair distribution of distances between two different types of radicals. Comparison of the PFR for Monte Carlo and deterministic spurs showed that for a small number of species, deterministic models do not correctly reproduce the evolution in time of the number of species (Zaider and Brenner, 1984).

At the present time most stochastic models have been developed using only a few radical and solute species. In 1983, Turner et al. calculated yields using a Monte Carlo model for ferrous sulfate solution and the results compared well with experimental values (Turner et al., 1983).

A limitation of the stochastic technique is that cross sections in aqueous solutions are not available. Another disadvantage is the large number of tracks that must be

considered to determine the average spur (Chatterjee, 1987).

Comparison of stochastic simulations and experimental data is difficult because the stochastic models are developed using spur radii estimated from prescribed diffusion. For stochastic results to be similar to the experimental yields, a much smaller spur radii is required (Clifford et al., 1987).

## 4. REACTION MECHANISM

Much of the work on the spur diffusion model involves investigating the effect of different factors on yields and extracting a reaction mechanism that is consistent with the experimental findings (Anbar, 1968). The reaction mechanism used in this work is the classical diffusion model in which the primary species H,OH, $H^+$ and $e^-_{aq}$ react with themselves, each other and solutes such as $Fe^{+2}$ and $H^+$ to yield the radical and molecular products. Several new reaction mechanisms for the radiolysis of aqueous solutions have been proposed.

A reaction mechanism for the radiolysis of ferrous sulphate suggested by Matthews (1974) included a long lived excited water species ($H_2O^*$). He determined that the increase in the yield of $Fe^{+3}$ (deaerated) with ferrous concentration was due to a reaction between ferrous ion and $H_2O^*$:

$$H_2O^* + Fe^{+2} \longrightarrow Fe^{+3} + H_2O + H^\cdot \qquad (4.1)$$

$$H^\cdot + Fe^{+2} \xrightarrow{H^+} Fe^{+3} + H_2 \qquad (4.2)$$

He estimated the life of excited water was not less than 100 ns. Matthews proposed a new equation for the yield of $Fe^{+3}$ which included an excited water term:

$$G(Fe^{+3})\text{deaerated} = G^o + 2G(H_2O^*)/(1+.0135/C_{Fe}{}^{+2}) \qquad (4.3)$$

where $G^{\circ}$ is the value of $G(Fe^{+3})$ using the classical diffusion model mechanism.

Based on experimental results, Anbar (1968) postulated a new reaction mechanism for low LET radiolysis in which most of the reactions take place in separate events homogeneously distributed throughout the medium with only minor amount of reaction in spurs. This mechanism included the formation and dissociation of the superexcited water molecule and the excited water molecule. Molecular products were formed by a unimolecular process which involve the solvent molecules as second reagents. At high LET, the local density of radicals and excited water was large enough to make recombination processes dominate and the kinetic behavior of the system was predicted by the diffusion model.

A theoretical study on the effect of correlation between radical distributions (Naumann and Stiller, 1976) led to the conclusion that unimolecular reactions were important in the reaction mechanism. The study was done in terms of joint probabilities of radical pairs in a one-radical model. Combination and recombination processes in spurs were shown to be more effective than those predicted by classical diffusion models assuming independence of the distribution of reacting particles. They proposed that the discrepancies between classical diffusion models and their

model were due to the assumption that radical and molecular yields result from bimolecular diffusion-limited reactions of the primary species.

# 5. MODEL DEVELOPMENT

## 5.1 Model Description

This work modified an existing computer program to numerically solve the deterministic rate equations for low LET gamma radiolysis (Weber, 1982). The program now includes an algorithm to select an optimum time step and calculates material balance convergence. Updated rate and diffusion constants are used in the model.

The program simulates reaction and one dimensional diffusion in spherical non-overlapping spurs. Results of the model are concentration of reactive species and the number of species per spur for both the products and reactive species. A flow chart and listing for the program are given in Appendix A.

The model was applied to the deaerated Fricke dosimeter which is a solution of dilute (.001M) ferrous sulfate in .4 M sulfuric acid. A dosimetry solution is used to measure radiation dose. The amount of chemical reaction in the solution being studied is compared with a standard system for which the radiation yield has been determined by the use of physical standards (Allen, 1961). The deaerated Fricke dosimeter was chosen because it has a small number reactants compared to other dosimetry solutions.

The primary species in this model are $e^-_{aq}$, H, $H^+$, and OH. The reactive solutes are $H^+$ and $Fe^{+2}$ and the products include $H_2O_2$, $H_2$ and $Fe^{+3}$. A small amount of $H_2$ is assumed to be present initially (Schwarz, 1969). The reaction mechanism for these species and the rate constants are given in Table 1. Table 2 contains the diffusion constants used in the model.

The sulfuric acid and its anions are not included in the Fricke dosimeter mechanism although some hydroxyl radicals react with $HSO_4^-$ to give the $HSO_4$ radical and $OH^-$. This does not affect yields since $HSO_4$ behaves chemically like OH. A small amount of $HO_2$ is present in the system but it is neglected in this work. In the mechanism presented in Table 1, ferrous and ferric ions are represented as $Fe^{+2}$ and $Fe^{+3}$ instead of complexes with water and sulfuric acid anions (Spinks and Woods, 1976).

From the reaction mechanism, an equation for each species in the form of Equation 2.4 is developed (Appendix B). These are solved using the finite difference method.

Initial G values for the primary species are those used by Schwarz (1969) based on the relations:

$$2G^0H_2 + G^0H + G^0e^-_{aq} = G^0OH \qquad (5.1)$$

$$G^0H^+ = G^0e^-_{aq}. \qquad (5.2)$$

Initial G values used in the model are 4.78 for the hydrated electron, .62 for H, and .15 for $H_2$.

Table 1. Reactions of the Deaerated Fricke Dosimeter.

| Reaction | K ($10^{10}$ 1/(mole*s)) | Reference |
|---|---|---|
| 1. $e^-_{aq} + H^+ \rightarrow H$ | 2.3 | Anbar et al., 1973 |
| 2. $H + Fe^{+2} \rightarrow FeH^{+2}$ | 0.002 | Anbar et al., 1975 |
| 3. $H^+ + FeH^{+2} \rightarrow Fe^{+3} + H_2$ | 0.00075 | Anbar et al., 1975 |
| 4. $H_2O_2 + Fe^{+2} \rightarrow Fe^{+3} + OH^- + OH$ | $6.2 \times 10^{-9}$ | Keene, 1964 |
| 5. $OH + Fe^{+2} \rightarrow Fe^{+3} + OH^-$ | 0.023 | Farhataziz and Ross, 1977 |
| 6. $2e^-_{aq} + 2H_2O \rightarrow H_2 + 2OH^-$ | 0.50 | Anbar et al., 1973 |
| 7. $e^-_{aq} + H + H_2O \rightarrow H_2 + OH^-$ | 2.5 | Anbar et al., 1973 |
| 8. $e^-_{aq} + OH \rightarrow OH^-$ | 3.0 | Anbar et al., 1973 |
| 9. $e^-_{aq} + H_2O_2 \rightarrow OH + OH^-$ | 1.23 | Kuppermann, 1974 |
| 10. $H + H \rightarrow H_2$ | 1.3 | Kuppermann, 1974 |
| 11. $H + OH \rightarrow H_2O$ | 3.2 | Buxton, 1987 |
| 12. $H + H_2O_2 \rightarrow H_2O + OH$ | 0.009 | Anbar et al., 1975 |
| 13. $H^+ + OH^- \rightarrow H_2O$ | 14.3 | Buxton, 1987 |
| 14. $OH + OH \rightarrow H_2O_2$ | 0.60 | Farhataziz and Ross, 1977 |

Table 2. Diffusion Constants.

| Specie | D ($10^{-5}cm^2/s$) | Reference |
|---|---|---|
| $e^-_{aq}$ | 5.0 | Schmidt, 1972 |
| H | 7.0 | Schwarz, 1969 |
| $H^+$ | 9.0 | Schwarz, 1969 |
| OH | 2.3 | Farhataziz and Ross, 1972 |
| $OH^-$ | 5.0 | Schwarz, 1969 |
| $H_2O_2$ | 2.2 | Schwarz, 1969 |
| $FeH^{+2}$ | 1.4 | See Note 1 |
| $Fe^{+2}$ | 1.4 | See Note 2 |

Note 1: Assumed equal to Diffusion Constant for $Fe^{+2}$

Note 2: Calculated from the method of Naleway et al.(1972)

$$D_{Fe+2} = D_{e-aq}(\Omega_{Fe+2}/\Omega_{e-aq})$$

Value for $\Omega_{e-aq}$ from Schmidt (1972)

Value for $\Omega_{Fe+2}$ from Milazza (1963)

The model uses the assumptions of Samuel and Magee (1953) for the initial distributions of primary species. The initial spur radius of the hydroxyl radical is assumed to be equal to the product of the initial unit spur radii and the cube root of the number of dissociations in the spur:

$$r_{OH} = r^{0}_{OH} No^{1/3}. \tag{5.3}$$

Hydrogen ions and radicals are assumed to have the same initial distributions as the hydroxyl radical. The electron is hydrated further away from the center of the spur, and is assumed (Schwarz, 1969) to have a initial radius of:

$$r_{e^-_{aq}} = ((r^{0}_{e^-_{aq}})^2 - (r^{0}_{OH})^2 + (r_{OH})^2)^{1/2}. \tag{5.4}$$

The width of the unit spurs are 7.5 Å for the hydroxyl radical and 23 Å for the hydrated electron (Schwarz, 1969). The primary species are assumed to have an initial Gaussian distribution dependent on the initial spur radius:

$$C_i(0,0)=N_i(0)/(2\pi^{3/2} r_i^{\,3}) \tag{5.5}$$

$$C_i(r,0)=C_i(0,0)e^{-(r^2/2(r_i)^2)}. \tag{5.6}$$

The total number of reactive species is found by integrating the concentration over the spur volume:

$$N_i(t) = \int 4\pi r^2 C_i dr \tag{5.7}$$

This is calculated by Simpson's method using the concentration at each node:

$$N_i(t)=4\pi[(0\Delta r)^2C_i(1,t) + 4(1\Delta r)^2C_i(2,t) + 2(2\Delta r)^2C_i(3,t) + \ldots + ((mlast-1)\Delta r)^2C_i(mlast,t)] \quad (5.8)$$

where distance in the r direction is $(m-1)\Delta r$. The total number of molecular products is found by integrating $N_i(t)$ with respect to time:

$$N_i(t) = \iint 4\pi r^2 C_i dr dt. \quad (5.9)$$

The time integral is approximated by the rectangle under the curve:

$$N_i(t) = 4\pi\Delta t \int r^2 C_i dr + N_i(t-1). \quad (5.10)$$

An algorithm to determine the optimum time step was developed to decrease the computation time. The $\Delta t$ is doubled every five time steps until the percent difference in the material balance closure between time steps is greater than a specified value. When the material balance does not close the concentrations of reactants and total numbers of products are reset to the values from the last converging iteration and $\Delta t$ is halved. Material balance closure between initial conditions and the current time is used to check for round off error.

Initially the spur is divided into 99 equally spaced grid points in the r direction. The number of nodes is increased when the difference between time steps in the concentrations at the next to last node is above 1%. The maximum number of grid points is 1000. Based on a Gaussian distribution, the initial concentration of primary species

is very small or zero at the edge of the spur. The boundary condition sets the concentration of primary species at the last node equal to zero. As the radicals diffuse, concentration will increase in the r direction. At the next to last grid point, a concentration difference between time steps indicates that species may be diffusing out of the spur size considered. The spur size or number of nodes is then increased to include these species and simulate spur expansion. Increasing the spur size as needed improved the speed of the model compared to using the maximum spur size for all the finite difference calculations. Neglecting the very small number of species which diffuse out of the spur before the size is increased introduces only slight error in the yields. This is demonstrated by closure of the material balance between time steps.

The model is run for spur sizes of one to six initial radical pairs. Results for an average spur are determined by weighing these yields with the spur size distribution of Mozumder and Magee (1966,II.). Table 3 contains the normalized spur size and energy distributions.

## 5.2 Finite Difference Calculation

Before solving the partial differential equations they must be cast into a dimensionless form. This is necessary to avoid numerical errors due to the orders of magnitude

Table 3. Spur Size and Energy Distribution.

| No - Number of Initial Radical Pairs | Fraction of Spurs with No Radical Pairs | Fraction of Energy for No Radical Pair Spur |
|---|---|---|
| 1 | 0.486 | 0.273 |
| 2 | 0.351 | 0.393 |
| 3 | 0.097 | 0.164 |
| 4 | 0.035 | 0.079 |
| 5 | 0.019 | 0.054 |
| 6 | 0.011 | 0.037 |

Note: From Mozumder and Magee (1966 II).
Energy distribution calculated assuming 6 radical pairs formed for 100 eV or 16.6 eV per pair.

difference between $\Delta r$ ($10^{-7}$) and $\Delta t$ ($10^{-12}$) (Kuppermann and Belford, 1962 I.). $D^*$, $r^*$, and $C^*$ are chosen as constants having dimensions of diffusion coefficient, length, and probability density respectively. These constants are set to the values of $D_H$, $r^0_H$, and $C_{OH}(0,0)$. The dimensionless variables $r'$, $t'$, $C_i'$, $D_i'$, and $k_{ij}'$ are given by:

$$r' = r/r^* \tag{5.11}$$

$$t' = t/(r^{*2}/D^*) \tag{5.12}$$

$$C_i'(r',t') = C_i(r,t)/C^* \tag{5.13}$$

$$D_i' = D_i/D^* \tag{5.14}$$

$$k_{ij}' = k_{ij}/(D^*/(r^{*2}C^*)) \tag{5.15}$$

These variables are used to determine a dimensionless version of equation 2.4 for each specie.

The derivation of the finite difference equations used in the model is described in Appendix B. The finite difference equations used to solve the differential equations are developed from a control volume set up around a grid point. The differential equations are integrated over the time variable using a fully implicit finite difference solution method. In this method, the concentration is equal to the value at the new time step. This method requires iterations over a time step but it has been shown to be stable over all $\Delta r$ and $\Delta t$ (Weber, 1982). The equations are integrated over r using a central difference scheme.

In deriving the finite difference equations, the reaction terms in Table 1 on page 25 are divided into two terms for each specie to increase the stability of the finite difference equations (Weber, 1982). One term is independent of the concentration of specie i and the other is directly proportional to the concentration of specie i such that:

$$\text{Reaction term} = \text{Constant} + \text{Center} * C_i(r,t) \qquad (5.16)$$

where Constant and Center depend on all other concentrations. The Center term must be negative to prevent the reaction term from exploding as $C_i(r,t)$ increases.

Two boundary conditions are required to solve the partial differential equations. The boundary conditions used in this model are:

1. At infinity (a sufficiently large distance from the center of the spur) the concentration of the primary and secondary species are zero and the solute concentrations are the initial values.
2. The center of the spur is a point of symmetry.

The second boundary condition, which is represented as $\delta C_i/\delta r = 0$ at $r = 0$ for all i, is input into the model as described in Appendix B.

An initial condition is necessary to solve the model. The initial concentration at any distance from the center

of the spur is zero for secondary species and the initial value for primary species and solutes.

After integration of the finite difference equations, equation 2.4 becomes of the form:

$$AC_i(m,t) = BC_i(m+1,t) + DC_i(m-1,t) + E \qquad (5.17)$$

where A, B, D, and E are constants depending on the rate and diffusion constants and E depends on the concentrations of the other species.

For an grid of N points there will be N-2 simultaneous equations in the form of equation 5.17 which can be arranged into a tri-diagonal matrix. There is one tri-diagonal matrix for each reactive specie. Now it is only necessary to solve the eight tri-diagonal matrices.

An iterative procedure is used to solve the matrices for $C_i(r,t)$. The Gauss-Seidel method was used. In this method, approximations are replaced by new values as soon as they are calculated. This method was chosen over the Jacobi method since the Gauss-Seidel method converges faster (Noble and Daniel, 1977).

# 6. MODEL STUDIES

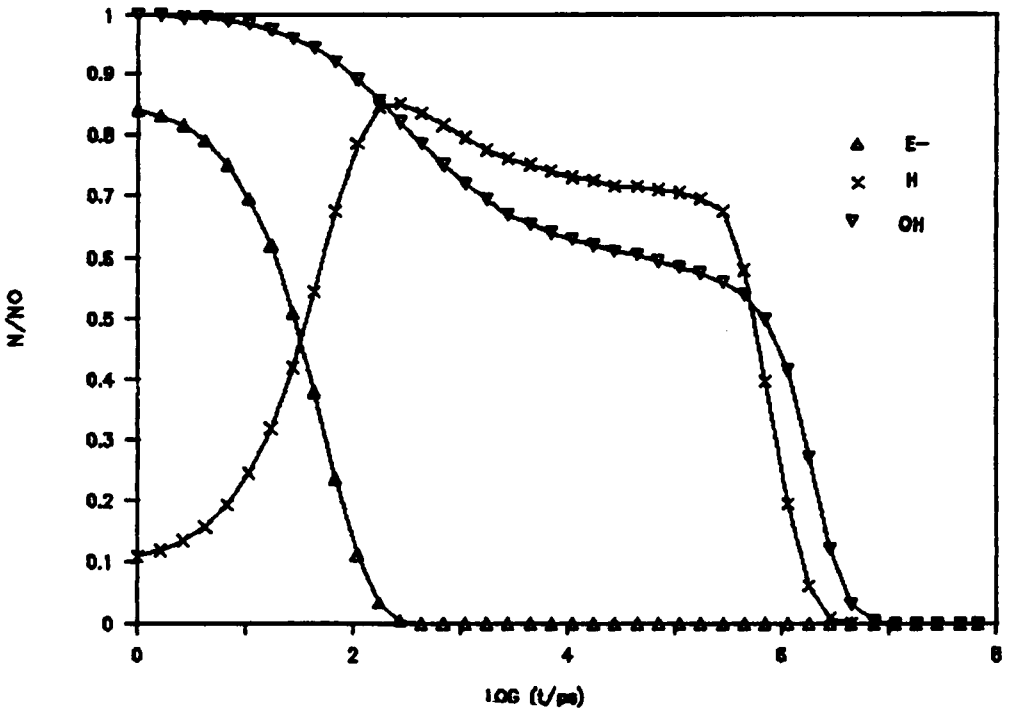
## 6.1 Time Step Optimization Algorithm

The time step optimization modification developed in this work was compared to the original model of Weber (1982) which increased the change in time based only on the iteration number. Both models were run with the most recent literature values for rate and diffusion constants. Figure 1 shows the variation of reactants with time for both models for an initial spur size of two radical pairs. The variation of the products with time is shown in Figure 2. Reactant and product yields are similar for both models with a difference of 1% at 100 ns and 5% at 10 μsec.

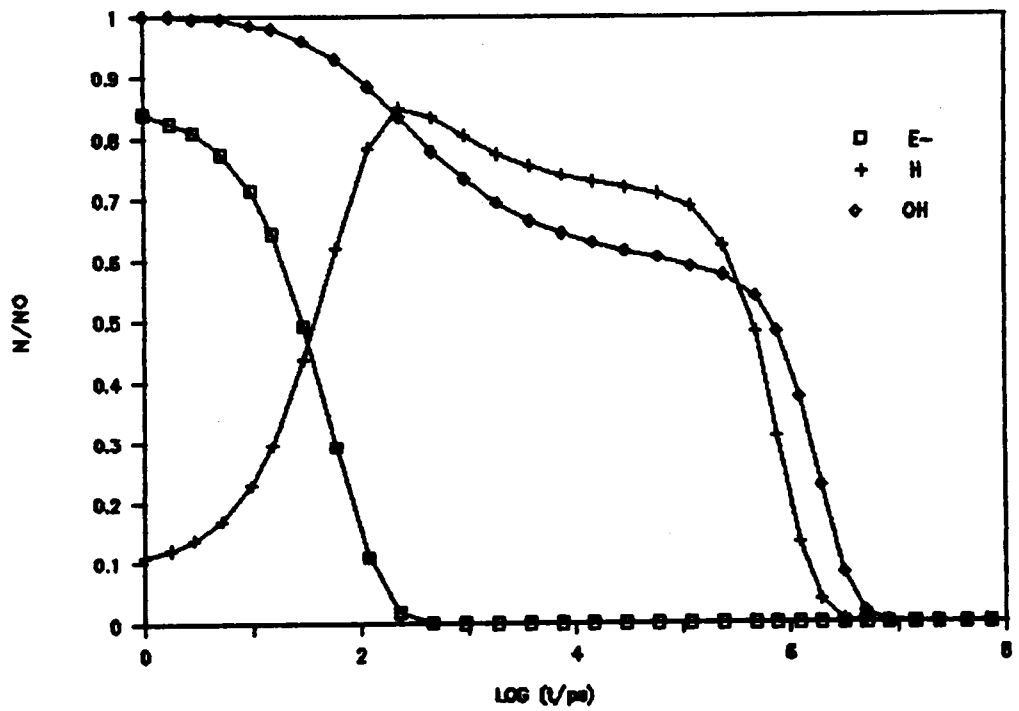
The addition of the optimum time step algorithm greatly reduced the computing time thereby reducing the cost of running the model. The Weber model required 10,000 time steps to reach 60 μs while this work needed only 395 time steps. Both models were run on the DEC VAX. The model with the time step optimization algorithm was about 15 times faster than the original model with negligible differences in the results. The CPU time for the Weber model was about 54 minutes and the CPU time for the time step optimization algorithm was 3 minutes and 48 seconds.

## 6.2 Comparison with Experimental Data

Several quantities from the model can be compared to experimental data. The G values are determined from:

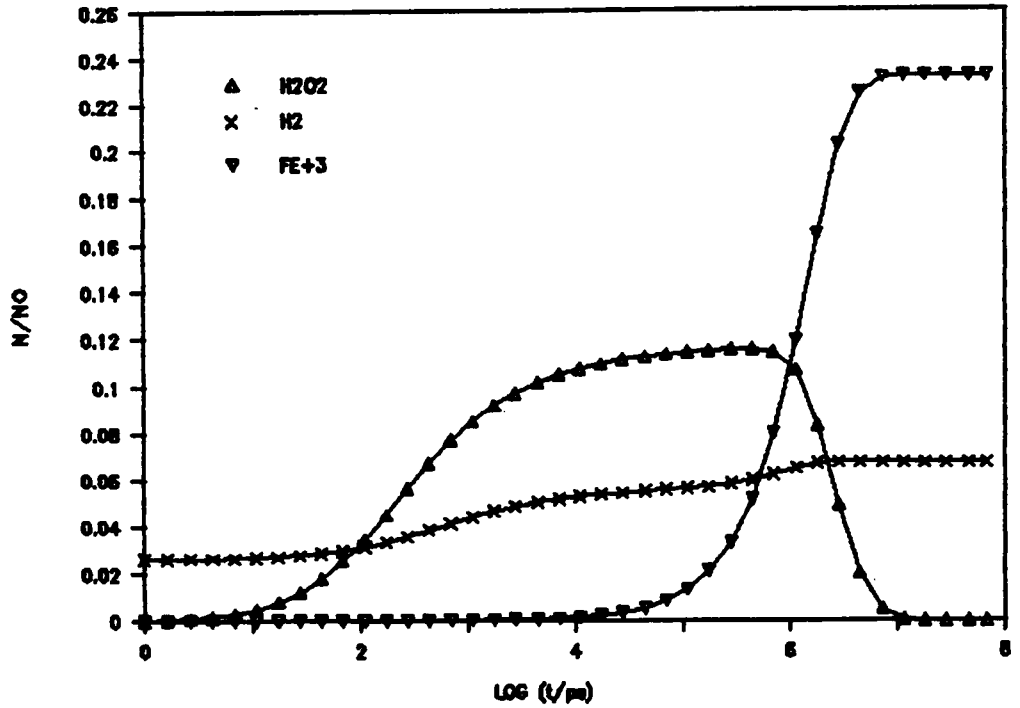



(a) Weber Model

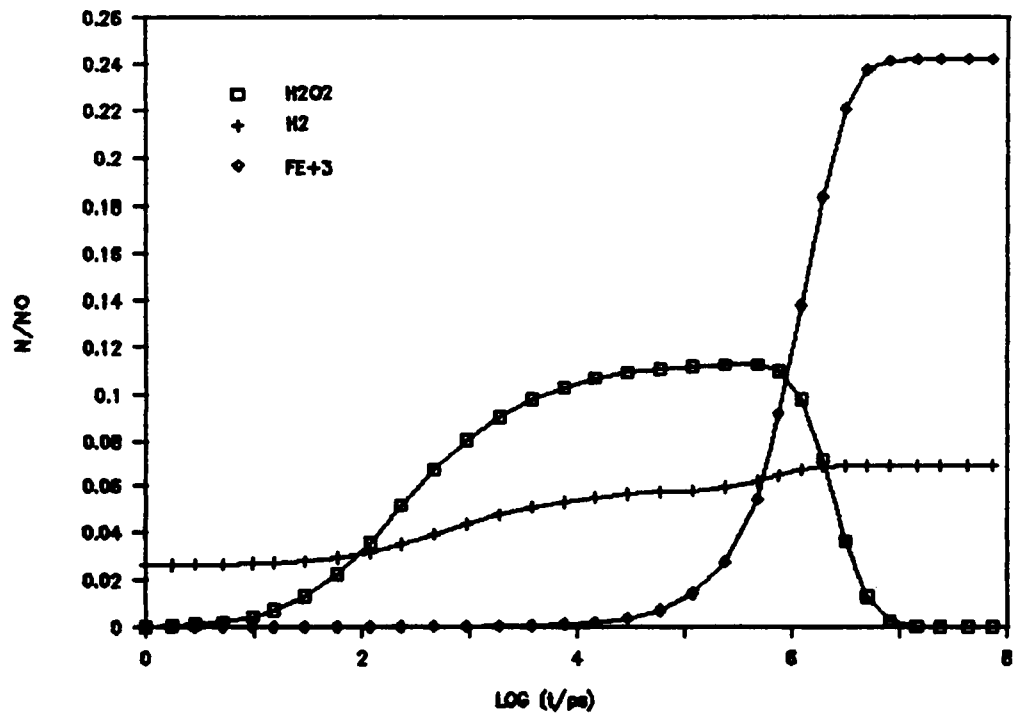



(b) Time Step Optimization Model

Figure 1. Comparison of Model Results - Reactants.




(a) Weber Model




(b) Time Step Optimization Model

Figure 2. Comparison of Model Results - Products.

$$G=M/No \times 100\ eV/W \qquad (6.1)$$

The value for W, the energy required to form a radical pair, is not known for aqueous solutions (Spinks and Woods, 1976). Chatterjee and Magee (1987) used a value of 17 eV for W. W can also be estimated from the $G^0$ values of the primary species. Using the $G^0$ values from Schwarz (1969) for OH, H, and $e^-_{aq}$, the average W was calculated to be 17.9 eV. Table 4 lists experimentally determined yields for the deaerated Fricke dosimeter.

The model does not accurately represent experimental results at long times. The long term yields of $Fe^{+3}$ and $H_2$ are much lower than experimental values. As shown in Figures 1 and 2, the radicals and $H_2O_2$ which react to form $Fe^{+3}$ and $H_2$ have gone to zero by 10 μs so the product yields should be their final long term value at this time. Values from Figure 2 give a $G(Fe^{+3})$ of 1.3 and a $G(H_2)$ of .33 which are significantly lower than experimental values in Table 4.

Another inconsistency with experimental data is that the model predicts that the number of hydrogen peroxide molecules go to zero before 10 μs. This should not happen because all the species which react with hydrogen peroxide except $Fe^{+2}$ have gone to zero before 10 μs. The reaction of $Fe^{+2}$ with hydrogen peroxide is very slow requiring 20 minutes for completion (Spinks and Woods,1976). The number of hydrogen peroxide molecules goes to zero even if all the

Table 4. Primary and Long Term G Values.

| PRIMARY G VALUES | | | | LONG TERM G VALUES | | |
|---|---|---|---|---|---|---|
| $G_{OH}$ | $G_{H}$ | $G_{H2}$ | $G_{H2O2}$ | $G(Fe^{+3})$ | $G(H_2)$ | REFERENCE |
| 2.78 | 3.68 | .28 | .72 | 7.92 | 3.92 | Weber, 1982 |
| 2.90 | 3.65 | .40 | .78 | 8.10 | 4.05 | Spinks and Woods, 1976 |
| 2.90 | 3.65 | .45 | .71 | 7.97 | 4.10 | Buxton, 1968 |
| 2.95 | 3.65 | .45 | .80 | 8.20 | 4.10 | Anbar, 1968 |

rate constants for the reactions which consume hydrogen peroxide are set to zero.

The model was first modified by keeping the $\Delta t$ small and increasing the number of nodes for the same size spur to determine if the problem described above was caused by numerical error. The hydrogen peroxide yields still went to zero and the long terms remained low, so the spatial and time grids were not the problem. The problem with the model was then thought to be due species diffusing out of the space domain. The size of the spur was increased to see if this improved the results. Increasing the grid from 1000 to 4000 nodes caused the hydrogen peroxide to remain constant until 10 μs. The hydrogen peroxide went to zero by 100 μs and H and OH went to zero by 60 μs. Final $Fe^{+3}$ and $H_2$ yields from this model were still much lower and the ratio of the yields of $Fe^{+3}$ to $H_2$ was much higher than experimental results.

Increasing the spur size violated the assumption that spurs do not overlap. The separation between spurs was calculated to be 4000 Å for a LET of .02 eV/Å (Magee and Chatterjee,1983). Spinks and Woods (1976) suggested a spacing of $10^4$Å. Using the smaller value of spur spacing and the distance between grid points of the model, spurs begin to overlap at 1000 grid points.

Since the model does not correctly represent scavenger reactions and long term yields, model results at

the end of spur reactions were used to determine long term yields. Scavenger reactions listed in Table 1 on page 25 are used to determine equations for the long term yields using the primary yields. The long term yields are given by:

$$G(Fe^{+3}) = G_{H_2} + G_{OH} + 2G_{H_2O_2} \quad (6.2)$$

$$G(H_2) = G_{H_2} + G_{H}. \quad (6.3)$$

These equations assume that radical recombination reactions occur only in the spur and that at the end of intraspur reactions the expansion of the spur is terminated because the reactive species are uniformly distributed.

Values for the time at which spur reactions end and scavenger reactions start range from 100 ns (Buxton, 1987) to 1 μs (Turner et al., 1983) after the beginning of the spur. Chatterjee and Magee (1987) used the time of 300 ns as the end of spur reactions for the Fricke dosimeter. This model gives reasonable results using equations 6.2 and 6.3 and primary yields at times on the order of 100 ns. The model also gives reasonable results if, after 100 ns, diffusion terms are set to zero and radical recombination reactions are stopped and the model run to longer times. This modification requires more computer calculation with less than 8% difference in results compared to stopping the model at the end of intraspur reactions and calculating the long term yields from primary yields.

The time that spur reactions end can be estimated from Figures 1 and 2 on pages 35 and 36. Spur reactions terminate when the OH and H radicals start to decrease and the product yields of $Fe^{+3}$ start to increase. This occurs at about 100 - 300 ns. Another method for determining the end of spur reactions requires setting the lifetime of a spur equal to a specific decrease in radical recombination rate. The lifetime of the spur was chosen to be when the sum of the OH recombination reaction rates at each node was $(.01\%)^2$ of the initial value. The reaction rate is a function of the concentration squared so this represents a decrease in the concentration to .01% of its initial value. This method gave the end of spur reactions at 230 ns for two initial radical pairs and 180 ns for one radical pair. These values are in the range of the values proposed by other authors. The model was stopped when time reached a value greater than 200 ns, the average of the one and two ion pair spurs. This value was chosen since the average spur contains one to two ion pairs.

The optimum $\Delta t$ algorithm improved the speed of the model even if calculation is stopped at the end of spur reactions. The CPU time for the model run to 200 ns was close to 55 seconds. The CPU time for the Weber model run to this time was about 19 minutes. The spur expanded to 840 grid points when the model was run to 200 ns.

Figures 3 and 4 show the results of the spur diffusion model over time for the species of interest in the deaerated Fricke dosimeter. The weighted average of the results for each spur size, using the distribution of Table 3 on page 30, was used in developing Figures 3 and 4.

Using Figures 3 and 4, equations 6.2 and 6.3, and a W of 17.9 eV, the G values at 200 ns were determined to be 8.6 for $Fe^{+3}$ and 4.1 for $H_2$. The yield of $Fe^{+3}$ at 200 ns was added to the results of equation 6.2 to give the total $Fe^{+3}$ yield. The error for the $Fe^{+3}$ value was less than 10% when compared to the values of Table 4. The error for the $H_2$ value was less than 5% when compared to experimental values. According to the model, the ratio of $Fe^{+3}$ to $H_2$ at 200 ns was 2.10. Comparison of this value with ratios determined from Table 4 gave an error of about 5%.

Figures 5-10 show the variations with spur size for each specie. With a higher number of radical pairs in the spur there are more radicals to react and form molecular products. As Figures 5 and 6 show, the number of radicals decrease with increasing spur size. Correspondingly, the number of molecular products increase with increasing spur size as shown in Figure 7 and 8. According to Figure 9, the hydrated electron does not show any variation with spur size. The hydrated electron reacts with $H^+$ by about 100 ps and at this early time other species do not show any variation with spur size either. As shown in Figure 10,

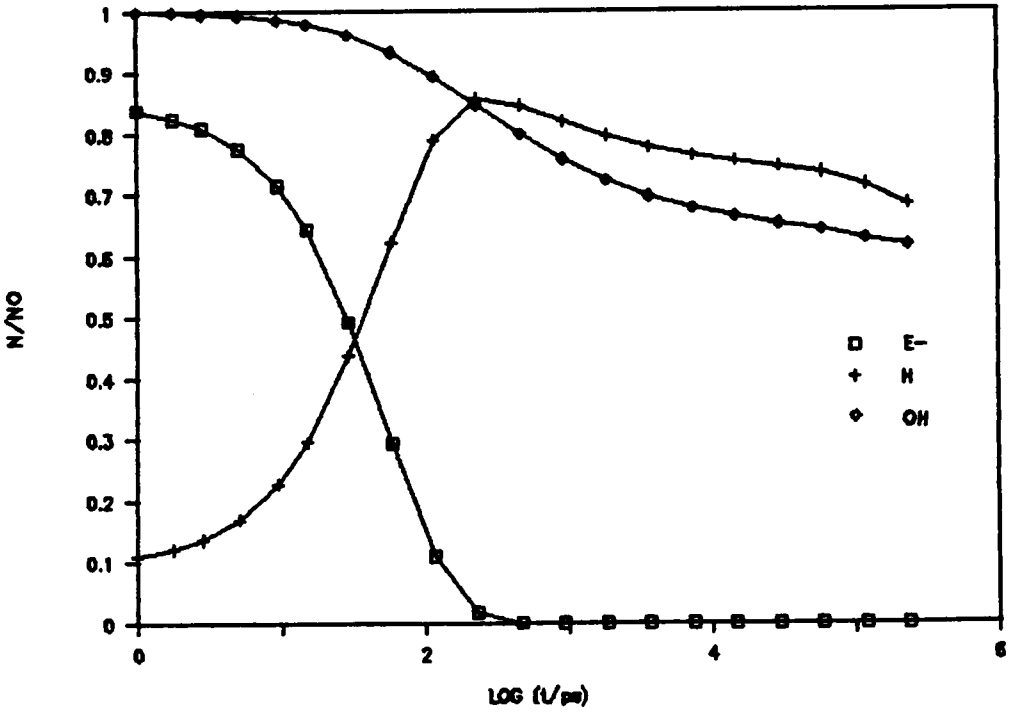



Figure 3. Weighted Average Yields - Reactants.

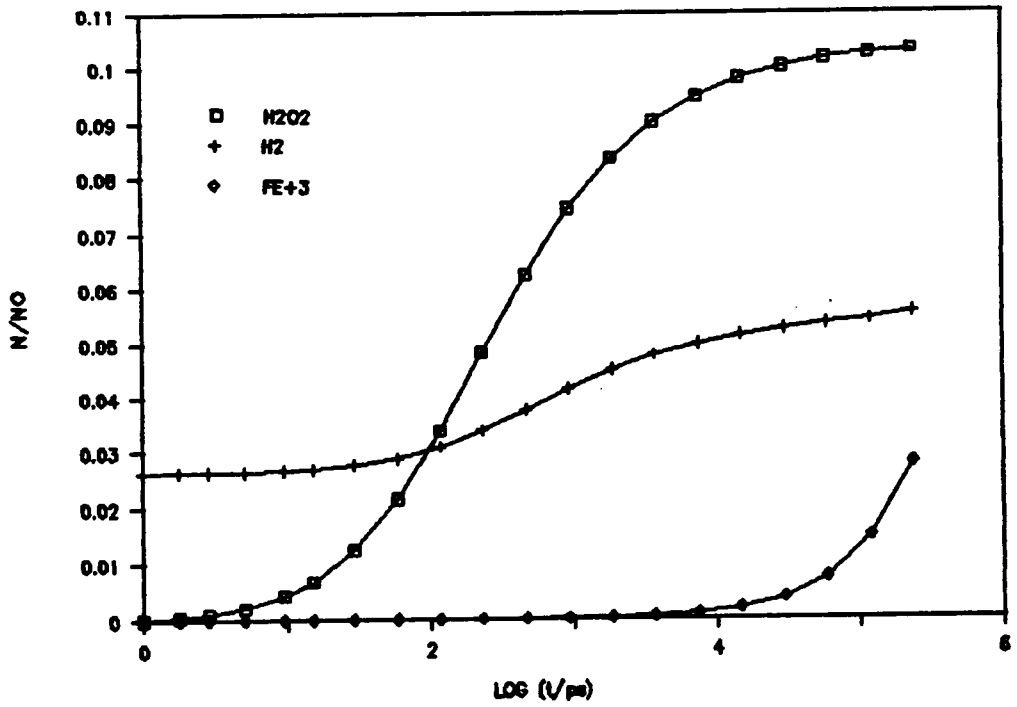



Figure 4. Weighted Average Yields - Products.

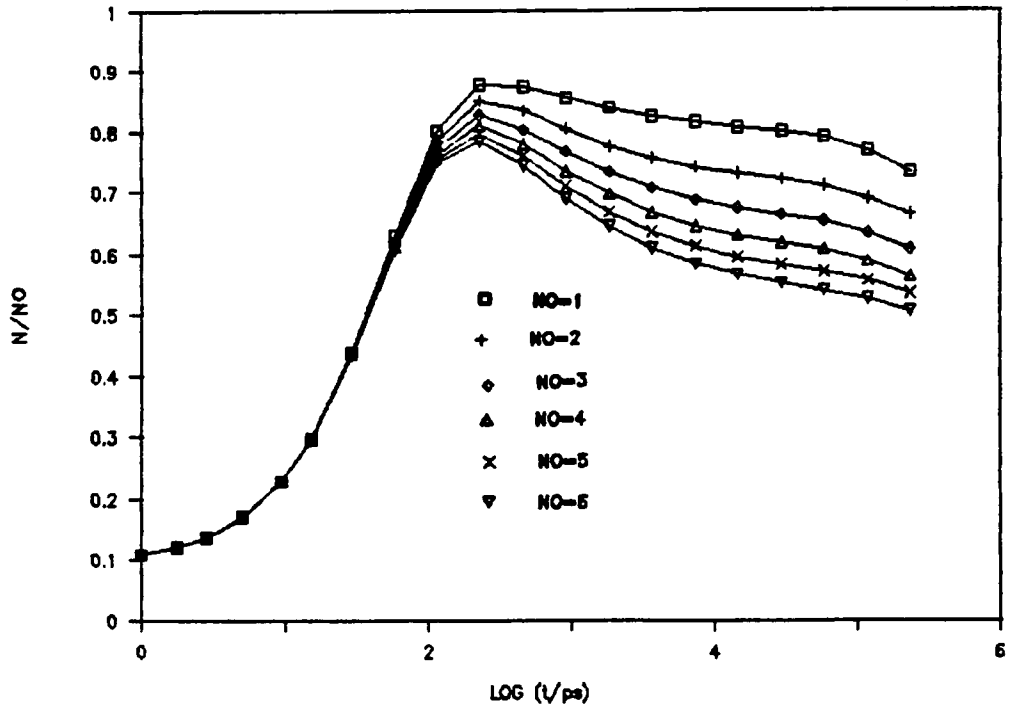



Figure 5. H Variation with Spur Size.

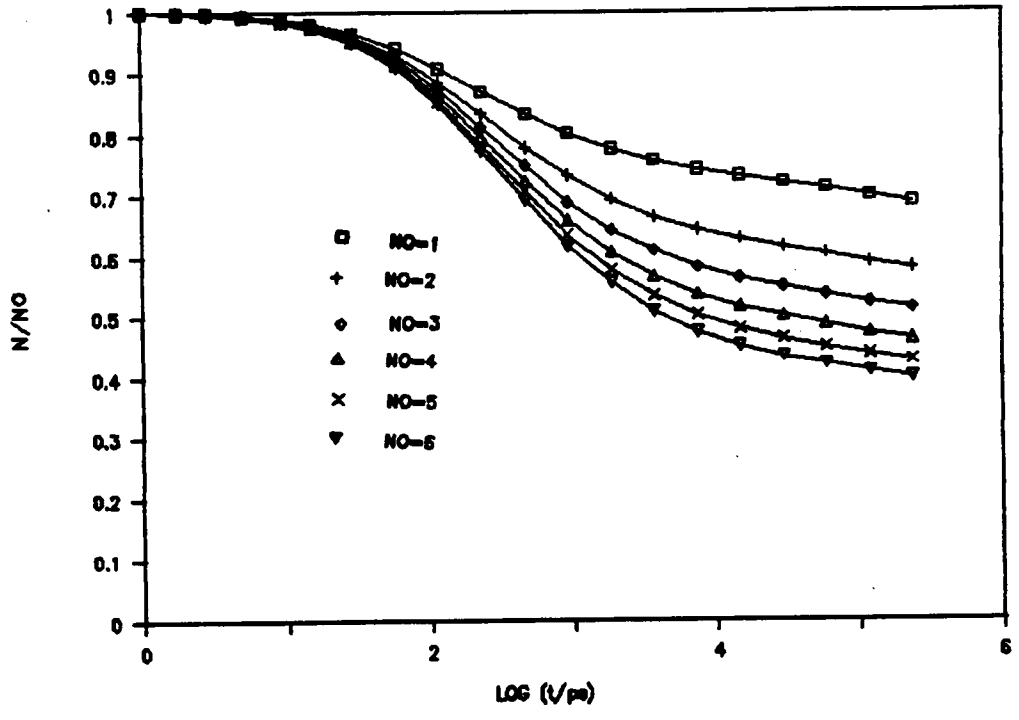



Figure 6. OH Variation with Spur Size.

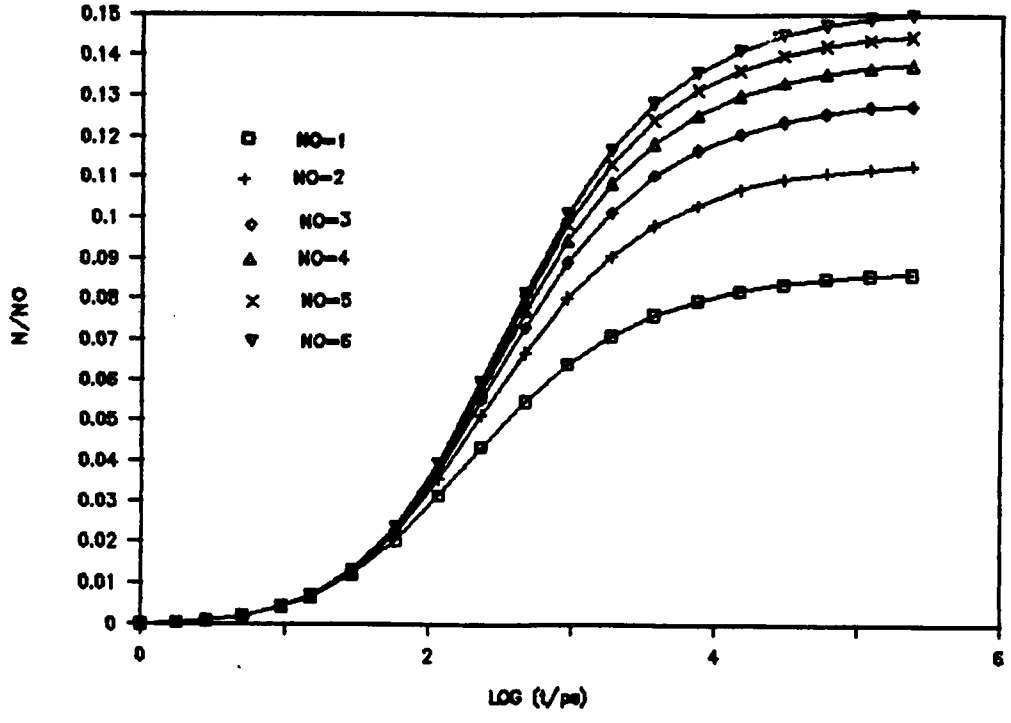



Figure 7. $H_2O_2$ Variation with Spur Size.

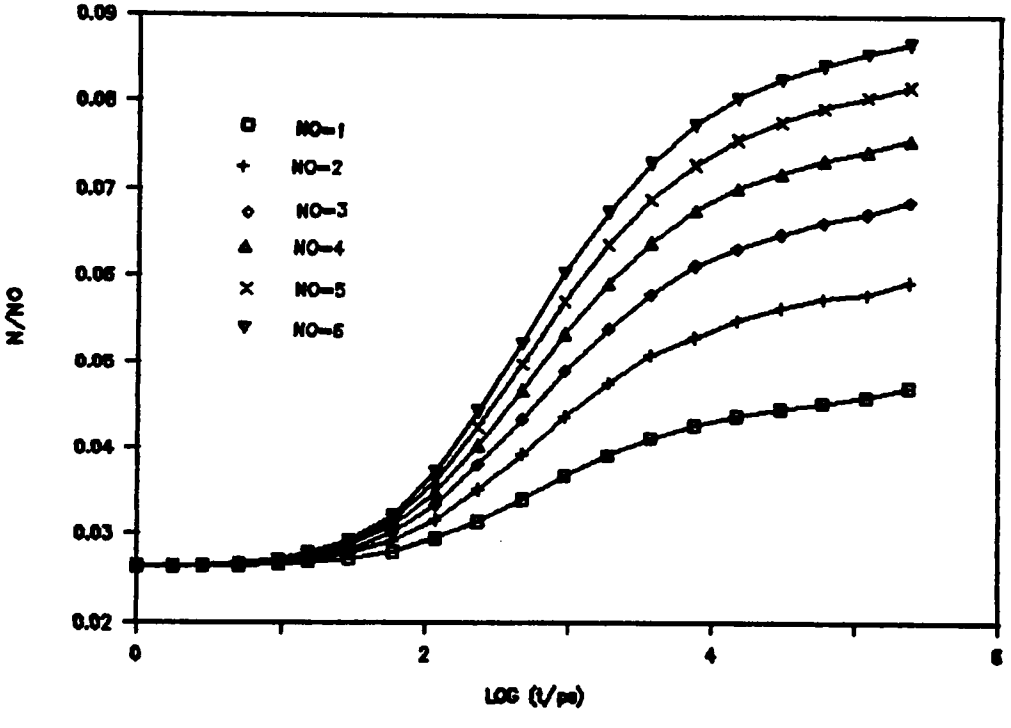



Figure 8. $H_2$ Variation with Spur Size.

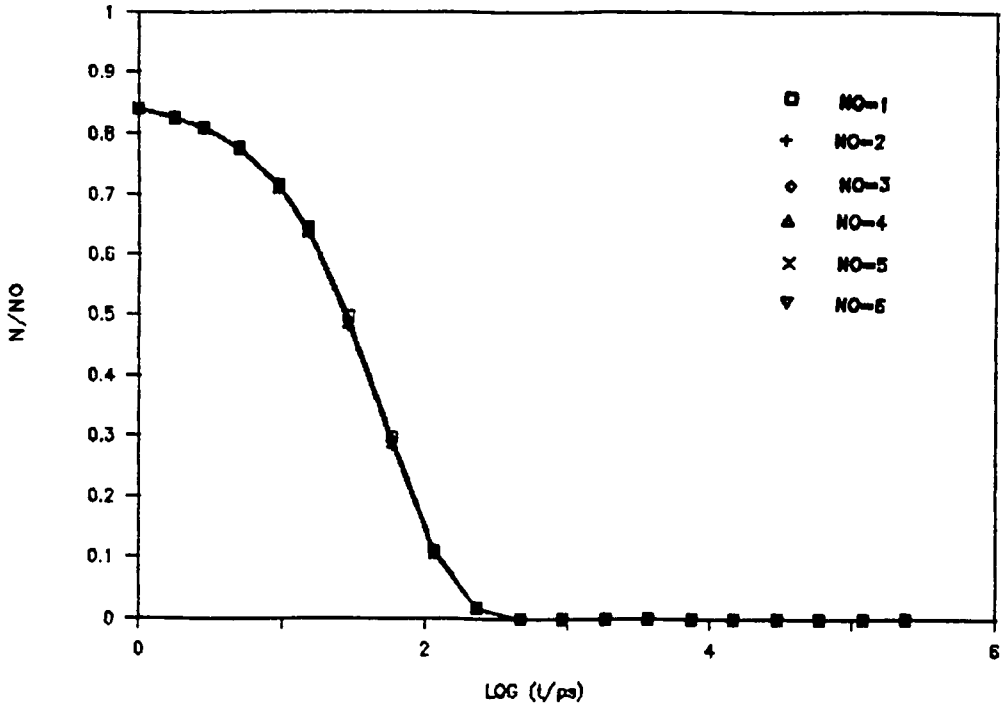



Figure 9. Hydrated Electron Variation with Spur Size.

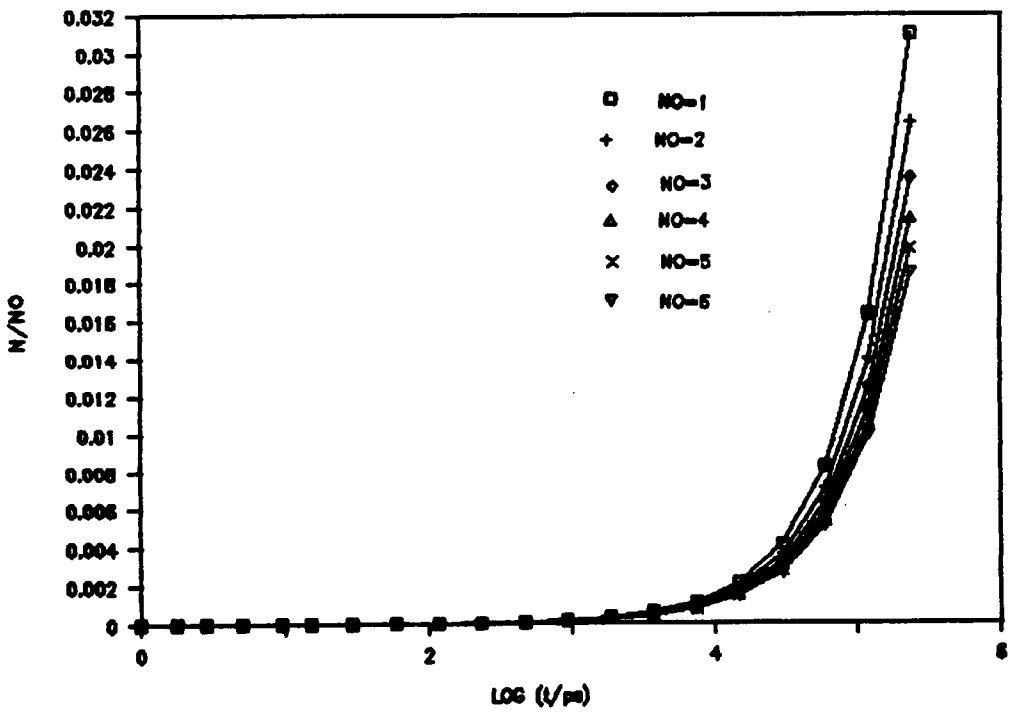



Figure 10. $Fe^{+3}$ Variation with Spur Size.

the ferric ions decrease with increasing spur size because the number of radicals which react to form ferric ions decreases as the spur size increases.

Model results show that concentration distributions of the reacting species maintain a Gaussian form except for the hydrated electron. This indicates that the prescribed diffusion approximation of the distribution remaining Gaussian is a good assumption. Figure 11 shows the initial dimensionless concentration distribution for the hydrated electron, OH and H radical for a spur of 2 initial radical pairs. The final concentration distributions at 200 ns for H and OH are shown in Figure 12. At 100 ps, the concentration of the hydrated electron becomes non-Gaussian as seen by Burns et al. (1984). As shown in Figure 13, the concentration shows a slight central minimum at 100 ps. This time is very close to the time when all the hydrated electron has reacted.

## 6.3 Effect of Parameters

The sensitivity of the model to various parameters was studied. As expected, varying the material balance convergence tolerance in the time step optimization algorithm had the greatest effect on the execution time. Decreasing the allowable error from 1% to .1% increased the number of time steps from 373 to 2459 and increased the execution time from 3:42 to 28:47 for the model run to

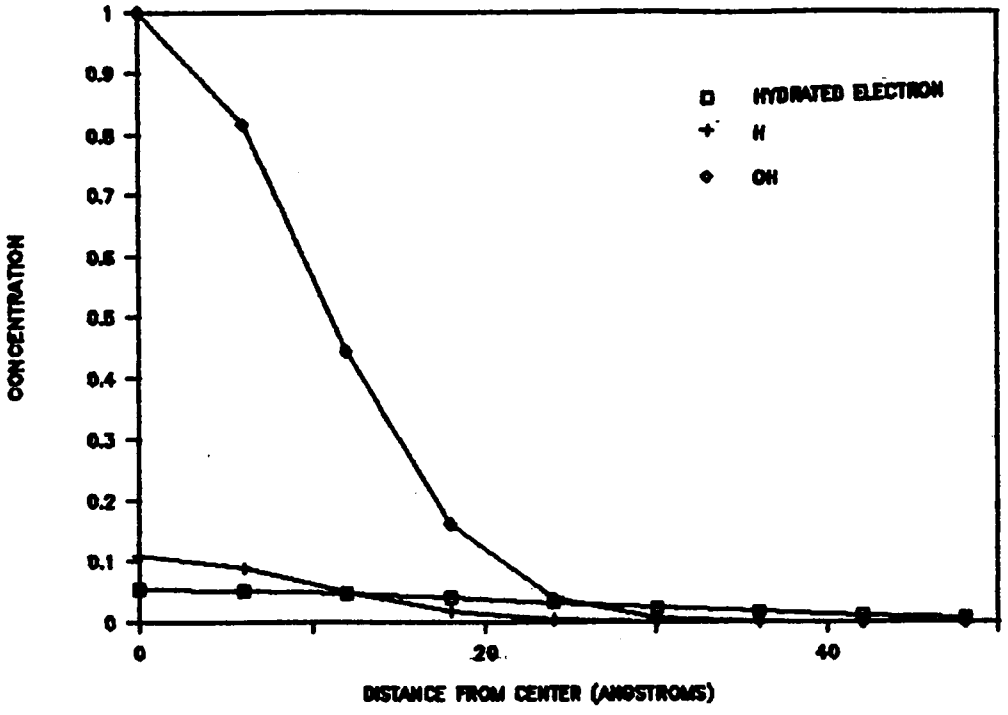



Figure 11. Initial Concentration Distributions.

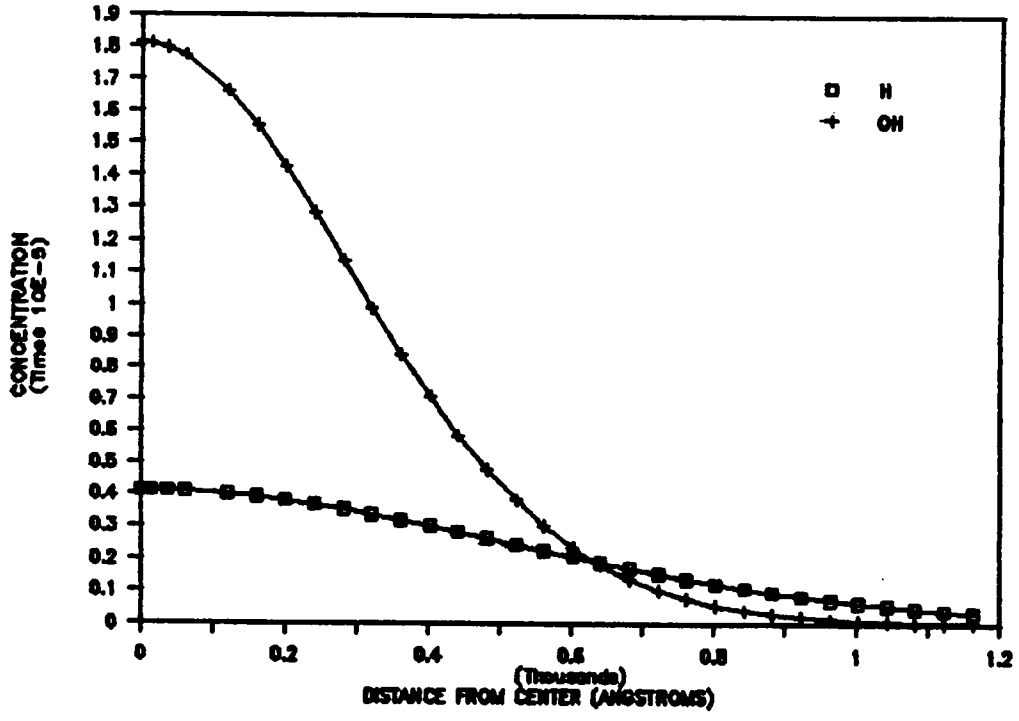



Figure 12. Final Concentration Distributions.

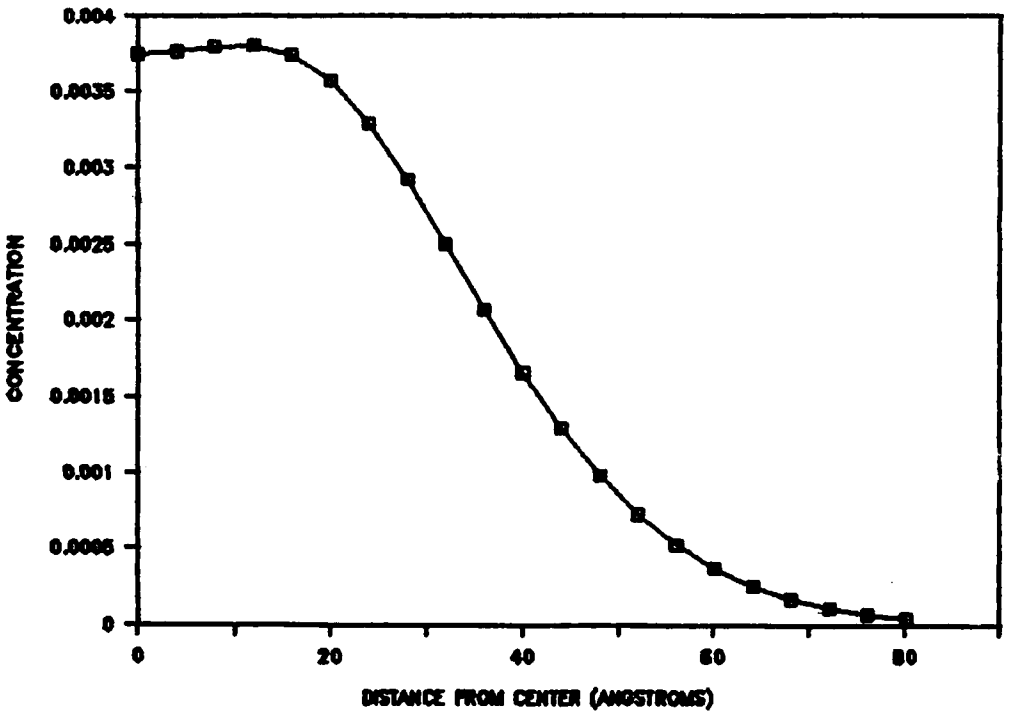



Figure 13. Hydrated Electron Concentration Distribution at 100 ps.

10 μs. The yields resulting from this change were within 1% of the original yields. The tighter convergence parameter only slightly affected the computation time and model results for times less than 100 ns.

Varying MMax, the parameter which sets how often the time step optimization algorithm is to be activated, had a slight effect on the model results. Increasing MMax from 5 to 9 time steps changed the product amounts by 2.5% and increased the number of time steps from 373 to 466. There were only slight differences in yields and computation times for times less than 100 ns.

Tightening the convergence between iterations in the finite difference calculation from .1% to .005% did not change model results or execution time. The model was also not affected by a change in the tolerance for the addition of grid points from 1% to .05%.

The model was slightly sensitive to changes in rate constants but was not affected by changes in diffusion constants. A 20% increase in the rate constants increased the product amounts by about 10% and decreased the reactants accordingly but gave only a 1% difference in long term yields.

The primary and long term G values are affected by the parameters of W, the initial spur radii, the initial G values, and the time chosen for the end of spur reactions. These parameters have not been experimentally determined

and therefore their values are adjustable. The trends caused by varying these parameters was studied.

Table 5 shows a comparison of experimental values and model results for primary and long term yields for varying the values of parameters. The model results were for a spur of two initial radical pairs.

As W increases, the primary and long term yields decrease as seen in runs 1,2, and 3 in Table 5. Ratios of the yields are constant with changes in W. Using a value of 18.5 eV for W, the $G(Fe^{+3})$ is closer to the experimental value but $G(H_2)$ and the primary yields are farther from experimental values compared to the results for W equal to 17.9 eV. The optimum value is between 18.5 eV and 17.9 eV.

Comparisons of runs 1, 4 and 5 show that as the time chosen for the end of spur reactions increases, the long term G values and primary radical G values decrease and the primary molecular yields increase. The results for the end of spur reactions at 200 ns are the best fit with the experimental data.

As shown in runs 1,6,and 7, as the unit spur radii are increased the long term and primary radical yields are increased and the primary molecular yields are decreased. The results using the smaller unit spur radii of 6.0 Å for the hydroxyl radical and 18.4 Å for the hydrated electron fit the experimental data best. All of the yields agree

Table 5. Model Results with Varying Parameters.

| RUN | PRIMARY G VALUES | | | | | LONG TERM G VALUES | |
|---|---|---|---|---|---|---|---|
| | OH | H | $H_2O_2$ | $H_2$ | $Fe^{+3}$ | $Fe^{+3}$ | $H_2$ |
| EXP | 2.88 | 3.66 | .75 | .40 | | 8.05 | 4.04 |
| 1 | 3.25 | 3.71 | .63 | .33 | .15 | 8.37 | 4.04 |
| 2 | 3.14 | 3.58 | .60 | .32 | .14 | 8.06 | 3.90 |
| 3 | 3.42 | 3.91 | .66 | .35 | .16 | 8.81 | 4.26 |
| 4 | 3.31 | 3.87 | .63 | .33 | .08 | 8.52 | 4.20 |
| 5 | 3.16 | 3.39 | .63 | .34 | .21 | 8.02 | 3.73 |
| 6 | 2.95 | 3.52 | .72 | .36 | .13 | 8.04 | 3.88 |
| 7 | 3.48 | 3.86 | .56 | .31 | .16 | 8.62 | 4.17 |
| 8 | 3.21 | 3.91 | .62 | .20 | .15 | 8.51 | 4.11 |
| 9 | 3.27 | 3.59 | .63 | .41 | .15 | 8.27 | 4.00 |
| 10 | 3.00 | 3.66 | .71 | .35 | .07 | 8.15 | 4.01 |

Note:

EXP - Average of experimental results from Table 4 on page 38

Run 1 - Model results with original parameters, W = 17.9, end of spur reactions at 200 ns, $r^0_{OH}$ = 7.5 Å, $r^0_{e\text{-}aq}$ = 23 Å, $G^0H_2$ = .15

Run 2 - Original parameters with W = 18.5 eV

Run 3 - Original parameters with W = 17 eV

Run 4 - Original parameters with end of spur reactions at 100 ns

Run 5 - Original parameters with end of spur reactions at 300 ns

Run 6 - Original parameters with $r^0_{OH}$ = 6.0 Å, $r^0_{e\text{-}aq}$ = 18.4 Å

Run 7 - Original parameters with $r^0_{OH}$ = 9.0 Å, $r^0_{e\text{-}aq}$ = 27.6 Å

Run 8 - Original parameters with $G^0H_2$ = 0.0

Run 9 - Original parameters with $G^0H_2$ = .25

Run 10 - Parameters of runs 4 and 6

well with experimental data except for the long term $H_2$ yield.

There are several other values for initial radii in the literature besides the values of Schwarz used in this work. It was postulated by Clifford et al.(1987) that in an acidic solution hydrogen and hydroxyl radicals would have different initial radii since the majority of hydrogen radicals are formed as the result of fast reactions between trapped electrons and the homogeneously distributed protons of the acid. Electron trapping distances are larger than those of other water fragments. He suggested an initial unit spur radius of 23 Å for the hydrogen radicals. When the model was run with an initial unit spur radius of 23 Å for the hydrogen radical, the primary G value for $H_2$ and the long term G values for $Fe^{+3}$ and $H_2$ were higher than experimental and higher than the results with the original parameters. Trumbore and Youngblade (1983) used larger spur radii than the values used in this work.

The initial yield of $H_2$ was varied and OH initial yield was adjusted according to equation 5.1. As shown in runs 1,8, and 9, increasing the initial $H_2$ caused decreases in the long term yields and the primary yield of H and an increase in the primary yield of $H_2$. The yields of OH and $H_2O_2$ were not affected by varying the initial $H_2$ yield. Unlike this model, the Trumbore model did not vary the initial OH yield with changes in initial $H_2$ yield. The

results of Trumbore's model were insensitive to $G^0H_2$ between 0 and .25 (Trumbore and Youngblade, 1983). The long term yields fit the experimental data best for an initial $H_2$ yield of .25 which gives an initial OH yield of 5.9. These values are similar to the yields used in the model of Trumbore and Youngblade (1983). The higher OH initial yield agrees with the experimental value at 100 ps of 5.9 for the hydroxyl radical (Jonah et al.,1977). The initial yield of 4.78 for the hydrated electron is close to the experimentally determined G value of 4.8 at 30 ps (Sumiyoshi and Katayama, 1982).

Run 10 is the best fit with the experimental values for a spur of two initial radical pairs. This run uses the smaller unit spur radii and a time for the end of spur reactions of 100 ns. The long term $H_2$ yield is improved compared to the results for 200 ns as the end of spur reactions. The long term $Fe^{+3}$ yield is higher than experimental results but the ratio of $G(Fe^{+3})$ to $G(H_2)$ is closer to the experimental value.

The weighted average long term yields for one to six initial radical pairs are higher than the yields for a two initial radical pair spur. The yields for a one radical spur are high bringing the weighted average higher than the results for a two radical pair spur. Values of parameters which give lower long term yields for a two radical pair

spur, such as the values used in run 6, should give the best fit with experimental data for the average spur.

## 6.4 Excited Water Mechanism

The model was modified according to equation 4.3 to account for reactions of excited water. Using the values of Matthews (1974), at an $Fe^{+2}$ concentration of .001M, the correction factor to add to the yield of $Fe^{+3}$ for the dearated Fricke dosimeter was .067. This is not a significant amount and does not improve the model results since they were already larger. At higher scavenger concentrations the factor is significant. For example, at an $Fe^{+2}$ concentration of .01M the factor is .265.

The experimental results of Matthews showed a much lower value for $G(Fe^{+3})$. The values increased with increasing scavenger concentration. His value for $G(Fe^{+3})$ at an $Fe^{+2}$ concentration of .002M was 7.88 and in the absence of scavengers the value was 7.68. When the model developed in this work was run in the absence of $Fe^{+2}$ the G value was not changed compared to the G value determined with the scavenger present. The G value with scavenger present would increase if the correction factor was added and this would cause the $G(Fe^{+3})$ in the absence of scavengers to be less than the value in the presence of scavengers.

## 6.5 Comparison with Other Models

The model was modified so it could be compared to a study of various models for the hydrogen and hydrogen peroxide yields from the radiolysis of water (Clifford et al. 1987). The initial species considered were H and OH and the products were $H_2$, $H_2O_2$, and water. The rate constants, diffusion constants, initial radii, and spur size distribution used in the model were from Clifford.

Figures 14 and 15 show the G values for the products and reactants for the number average spur. The yields from this work followed the same trends and were in the range of Clifford's deterministic models. The product yields for this model were approximately 20% below the values of Clifford's deterministic models. Ratios of yields were similar to Clifford's results. The difference in yields may be due to the value of W used. The G values were calculated using a W which was determined to be 16.65 eV from the initial N/No values and initial G values used by Clifford. G values at 100 ns for the various models and experimental data are given in Table 6.

Results of Clifford's stochastic models showed smaller yields for $H_2$ and $H_2O_2$ than the deterministic models. The experimental data gives a higher yield for $H_2O_2$ than determined by any of the models. The experimental values were determined from the radiolysis of water in which the initial yield of OH is higher than H, causing a greater

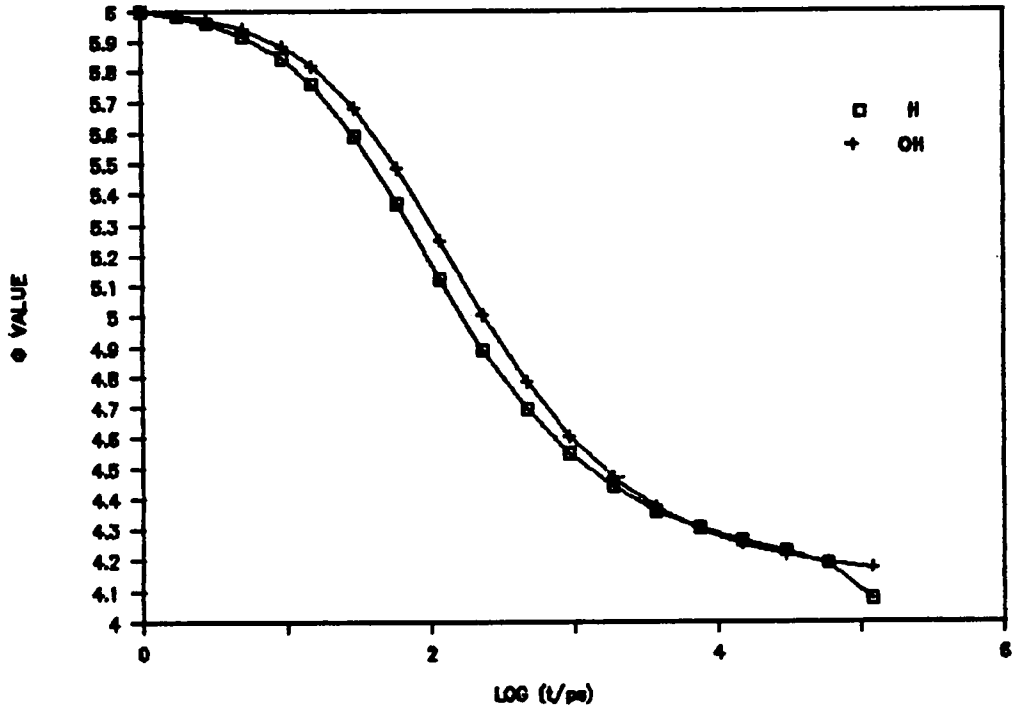



Figure 14. G Values for Reactants - Simplified Mechanism.

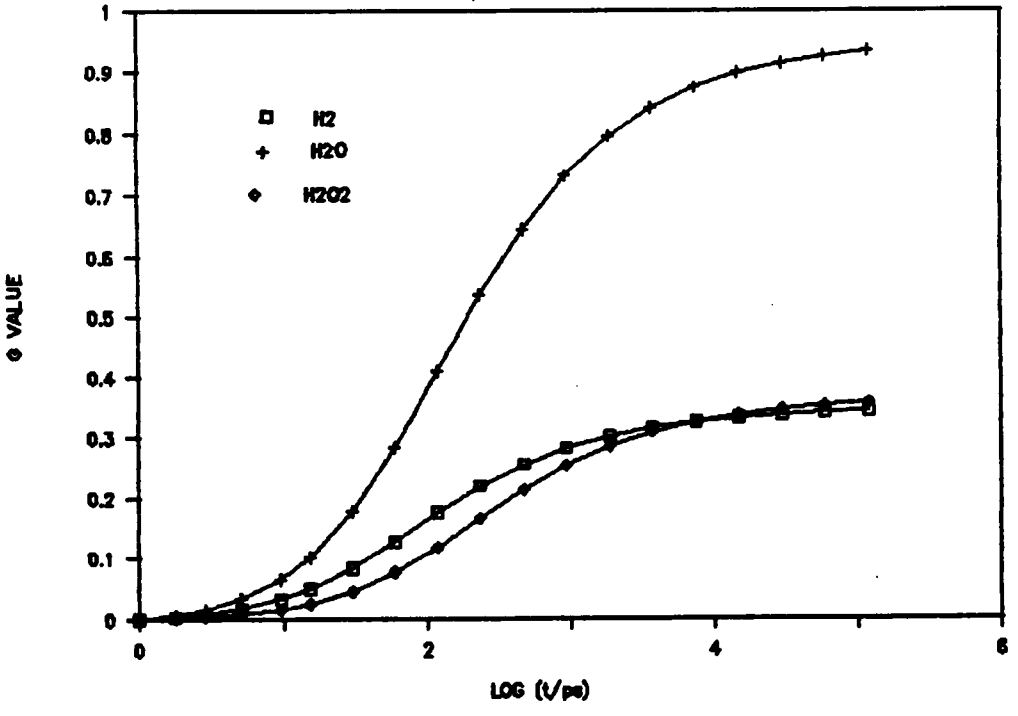



Figure 15. G Values for Products - Simplified Mechanism.

Table 6. G Values at 100 ns.

| Model | $H_2$ | $H_2O$ | $H_2O_2$ |
|---|---|---|---|
| Prescribed Diffusion[1] | .4386 | 1.2997 | .4680 |
| FACSIMILE[2] | .4327 | 1.2002 | .4502 |
| ME solution[3] | .2424 | 1.4375 | .2481 |
| IRT solution[4] | .2469 | 1.4866 | .2541 |
| Experimental[5] | .45 | | .80 |
| This Work[2] | .34 | .93 | .36 |

Note:
[1]Schwarz model averaged over spur size distribution
[2]Numerical solution averaged over spur size distribution
[3]Master Equation stochastic model assumes pair distances evolve independently
[4]Independent Reaction Times stochastic model assumes that pair reaction times are independent
[5]From Anbar (1968)

$H_2O_2$ yield. The simplified mechanism models used equal initial yields for H and OH which results in more equivalent yields of $H_2$ and $H_2O_2$. The stochastic models did not correspond to the experimental data or the deterministic models. This was because the stochastic model uses the spur radii estimated using prescribed diffusion. Much smaller spur radii were required by the stochastic model for the results to match experimental values. Clifford did not propose that these small radii are correct because there are other assumptions in the models. According to Clifford, since these deterministic models overestimate molecular yields they should not be used to interpret experimental yields and that spur parameters inferred from these models are probably invalid (Clifford et al., 1987).

# 7. CONCLUSIONS AND RECOMMENDATIONS

The model developed in this work adequately describes the diffusion and reactions in spurs to the time of 200 ns. The time step optimization algorithm improved the computing speed of the model significantly. Comparison of model results with experimental data for the long term G values for $H_2$ and $Fe^{+3}$ gave errors of less than 10%. These values were calculated from yields at the end of spur reactions, which was estimated to be about 200 ns. Comparison of primary and molecular yields with experimental values gave errors of up to 25%.

The model does not adequately represent the scavenger reactions after spur reactions have ended. The model shows too much diffusion and radical recombination reaction and not enough scavenger reactions.

One of the criticisms of the deterministic model is that it includes adjustable parameters which can be varied until the model agrees with experiment. This criticism is relevant to this model also. Trends of these adjustable parameters were studied to determine the optimum values. Rate and diffusion constants have been measured experimentally or good estimates are available so these parameters are not adjustable. The adjustable parameters in the model are the initial spur radii, initial G values, value for W, and the time chosen for the end of spur

reactions. Model results improved when the initial yield of $H_2$ was increased, W was increased, unit spur radii were decreased and the time to end spur reactions was kept at the original value. Smaller unit spur radii have been suggested by results of stochastic models (Clifford et al., 1987). An increase in the initial $H_2$ yield brings the initial OH yield closer to the experimental value.

The best fit with experimental data for a spur of two initial radical pair spur occurred with smaller unit spur radii, 6.0 Å for the OH radical and 18.4 Å for the hydrated electron, and a time to end spur reactions of 100 ns. The W value used was 17.9 eV and the initial $H_2$ yield was .15.

It is recommended that this model be simplified by removing scavengers in low concentration since the model doesn't accurately simulate the bulk reactions after the intraspur reactions are completed. This was done by Chatterjee and Magee (1987) and Turner et al.(1983). Since the long term G values can be calculated from the primary yields it is not necessary to model the reactions after the intraspur reactions are completed.

Although stochastic models of spur reaction and diffusion may be more correct, the deterministic models can still be useful. The model used in this work as well as other deterministic models are much simpler to develop and use and can describe more complex systems. The deterministic models are useful in the quantitative

comparisons of the effect of initial yields and distributions, spur parameters, and reaction mechanisms on the primary and long term yields. As developments occur in stochastic modeling, findings should be incorporated into deterministic models. Continued experimental work is needed to determine values for the adjustable parameters in spur diffusion models.

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# APPENDIXES

# APPENDIX A

# SPUR DIFFUSION MODEL

# COMPUTER PROGRAM

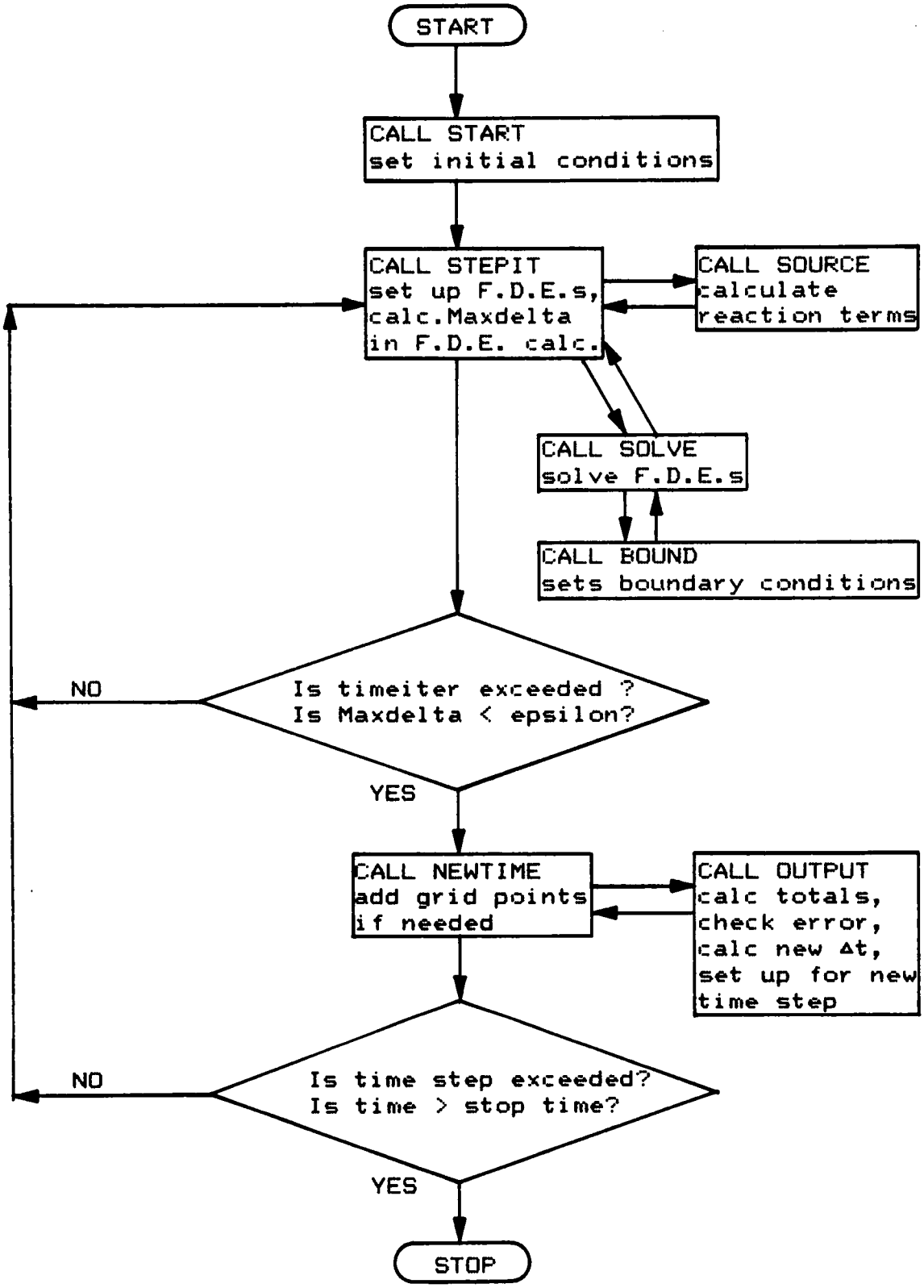


Figure 16. Flow Chart for Spur Diffusion Model Program

# Program Listing for Spur Diffusion Model

```
      PROGRAM SDM
C     PROGRAM FOR THE SPUR DIFFUSION MODEL

      INCLUDE 'SDMCOMMO.FOR'

      CALL START
  10  IF(.NOT.StopAll) THEN
        WRITE(*,200) dtime
  20    IF(.NOT.Ntime) THEN
          CALL STEPIT
          TimeIter=TimeIter+1
          IF(MaxDelta.LT.ConvEps.OR.TimeIter.EQ.MaxSteps) THEN
            Ntime=.TRUE.
          END IF
          GOTO 20
        END IF
        CALL NEWTIME
        GOTO 10
      END IF

 200  FORMAT(' Current simulation time = ',1PG11.5)
      END


C-----------------------------------------------------------------------

      SUBROUTINE START


      INCLUDE 'SDMCOMMO.FOR'

C     This subroutine initializes the problem.

C     Create data files and print headings.
      OPEN(UNIT=12,FILE='SDMTotals',STATUS='NEW')
      WRITE(12,250)
 250  FORMAT (7X,'Time',9X,'e-',10X,'H',9X,'H+',9X,'OH',8X,
     +           'OH-',7X,'H2O2',6X,'FeH+2',7X,'Fe+2',9X,
     +           'H2',7X,'Fe+3',8X,'H2O')
      CLOSE(UNIT=12)
      OPEN(UNIT=11,FILE='SDMErrors',STATUS='NEW')
      CLOSE(UNIT=11)
      OPEN(UNIT=14,FILE='SDMConcs',STATUS='NEW')
      WRITE(14,260)
 260  FORMAT  (8X,'Time',6X,'Radius',10X,'e-',11X,'H',10X,'H+',
     +           10X,'OH',9X,'OH-',8X,'H2O2',7X,'FeH+2',
     +           8X,'Fe+2')
      CLOSE(UNIT=14)
      OPEN(UNIT=10,FILE='SDMResults',STATUS='NEW')
      CLOSE(UNIT=10)

C     Species for the Dearated Fricke Dosimeter
C        1 = e-, 2 = H, 3 = H+, 4 = OH, 5 = OH-, 6= H2O2, 7 = FeH+2, 8 = Fe+2,
C        9 = H2, 10 = Fe+3, 11 = H2O
```

```
C     Calculate initial spur parameters
C      N0 is the initial number of radicals in spur/2 = initial radical pairs
C      InitialN(Specie) = G(Specie)/G(OH) x InitialN(OH)


      N0=2.D0
      InitialN(4)=N0
      InitialN(2)=0.109D0*InitialN(4)
      InitialN(1)=0.839D0*InitialN(4)
      InitialN(3)=InitialN(1)
      InitialR(4)=(7.5D-8)*InitialN(4)**(1.D+00/3.D+00)
      InitialR(1)=((23.D-8)**2-(7.5D-8)**2+InitialR(4)**2)**0.5D+00
      InitialR(3)=InitialR(4)
      InitialR(2)=InitialR(4)


C     Set dimensionalization quantities

      DD=7.D-5
      RD=7.5D-8
      CD=1.D0/(RD**3*(2.D0*3.141597D0)**1.5D+00)
      KD=DD/(RD**2*CD)
      TD=RD**2/DD

C     pi is 4/3 times pi
      pi=4.18879207D0

C     Set number of reactive species

      NSpecie=8

C     Set size parameters and the number of grid points in R
C     direction.  X1 must be odd for Simpson's rule to work

      X1=999
      dt=5.D-14
      RLength=2.D-5

C     Initialize the iteration parameters.

      ConvEps=0.001D+00
      REps=0.0005D+00
      MBEps=0.01D+00
      Time=1.D-12
      LastIter=300
      MaxSteps=15
      Ntime=.FALSE.
      StopAll=.FALSE.
      DeltaPrn=0.2D+00
      TimeIter=0
      TimeStep=0
      NextPrn=10**(DLOG10(Time)+DeltaPrn)
      NextPrn=NextPrn/TD
      M=0
      MMax=5
      GEPS=.01D0
      MM=0
      NP=0
      NC=0
```

```
C     Set rate constants
C       Rate constants obtained by multiplying k in l/(mole*s) by
C        10^3cm^3/l*mole/(6.02 x 10^23molecules) to give units of
C        cm^3/(s*molecules). Divide by KD to make dimensionless

      K(1)=3.82D-11/KD
      K(2)=3.32D-14/KD
      K(3)=1.24D-14/KD
      K(4)=1.03D-19/KD
      K(5)=3.82D-13/KD
      K(6)=8.31D-12/KD
      K(7)=4.15D-11/KD
      K(8)=4.98D-11/KD
      K(9)=2.04D-11/KD
      K(10)=2.16D-11/KD
      K(11)=5.32D-11/KD
      K(12)=1.50D-13/KD
      K(13)=2.37D-10/KD
      K(14)=9.97D-12/KD

C     Set the Diffusion coefficients
C        Units of cm^2/s made dimensionless by  dividing by DD

      D(1)=4.96D-5/DD
      D(2)=7.0D-5/DD
      D(3)=9.0D-5/DD
      D(4)=2.3D-5/DD
      D(5)=5.0D-5/DD
      D(6)=2.2D-5/DD
      D(7)=1.4D-5/DD
      D(8)=1.4D-5/DD

C     Set initial Concentrations of solute (radicals/cm^3)

      InitialC(3)=4.816D20/CD
      InitialC(5)=7.529D6/CD
      InitialC(8)=6.023D17/CD


C     Construct the grid

      Time=Time/TD
      dtime=Time*TD
      dt=dt/TD
      RLength=RLength/RD
      dR=RLength/DBLE(X1-1)
      X1=99
      X2=X1-1
      X3=X2-1


C     Set up initial Gaussian Concentration profiles

      DO 9 Specie=1,4
        DO 10 I=2,X1
        C(I,Specie)=DEXP(-DBLE(I-1)*DBLE(I-1)*dR*dR*RD*RD/
     +              (2.D0*InitialR(Specie)**2))
   10   CONTINUE
        C(1,Specie)=1.D0
    9 CONTINUE
```

```
C     Normalize the concentration profiles to the total number

      DO 2 Specie=1,4
        Sum=0.D+00
        DO 3 I=2,X2
          P=DBLE(I-1)
          ASum=P*P*C(I,Specie)
          IF(0.5D+00*DBLE(I)-INT(0.5D+00*DBLE(I)).LT..01D+00) THEN
            Sum=Sum+ASum
          END IF
          Sum=Sum+ASum
    3   CONTINUE
        Sum=2.D+00*Sum+X2*X2*C(X1,Specie)
        N(Specie)=Sum*pi*dR**3*CD*RD*RD*RD
        Denom=InitialN(Specie)/N(Specie)
        DO 4 I=1,X1
          C(I,Specie)=C(I,Specie)*Denom
    4   CONTINUE
    2 CONTINUE

C     Set initial values of species for total number of grid points

      DO 6 I=1,X1
        C(I,3)=C(I,3)+InitialC(3)
        C(I,5)=InitialC(5)
        C(I,6)=0.D+00
        C(I,7)=0.D+00
        C(I,8)=InitialC(8)
    6 CONTINUE

      DO 151 Specie=1,NSpecie
        DO 150 I=100,999
          C(I,Specie)=0.D+00
  150   CONTINUE
  151 CONTINUE

      DO 152 I=100,999
        C(I,3)=InitialC(3)
        C(I,5)=InitialC(5)
        C(I,8)=InitialC(8)
  152 CONTINUE


C     Calculate totals of species for spur (grid points 1-999)

      DO 26 Specie=1,NSpecie
        Sum=0.D+00
        DO 25 I=2,998
          P=DBLE(I-1)
          ASum=P*P*C(I,Specie)
          IF(0.5D+00*DBLE(I)-INT(0.5D+00*DBLE(I)).LT..01D+00) THEN
            Sum=Sum+ASum
          END IF
          Sum=Sum+ASum
   25   CONTINUE
       Sum=2.D+00*Sum+998.D0**2*C(999,Specie)
        N(Specie)=Sum*pi*dR**3*CD*RD*RD*RD
  LastC(Specie)=C(X2,Specie)
   26 CONTINUE

C       Set initial values of products
C       N(9) is calculated as G(9)/G(4)*InitialN(4)

      N(9)=0.02631D0*InitialN(4)
      N(10)=0.D+00
      N(11)=0.D+00
```

```
C     Determine totals of charge,H species,Fe species,O species

      TotalC=-N(1)+N(3)-N(5)+2.D+00*N(7)+2.D+00*N(8)+3.D+00*N(10)
      TotalH=N(2)+N(3)+N(4)+N(5)+2.D+00*N(6)+N(7)+2.D+00*N(9)
     +    +2.D+00*N(11)
      TotalO=N(4)+N(5)+2.D+00*N(6)+N(11)
      TotalFe=N(7)+N(8)+N(10)

C     Save initial totals for use in calculation of error of numerical method
      ITotalC=TotalC
      ITotalH=TotalH
      ITotalO=TotalO
      ITotalFe=TotalFe

C      Calculate initial reaction rate for OH recombination.
C      Calculate reaction rate at end of spur reactions as percentage of
C      initial reaction rate.

C      RROH=0.D0
C      DO 400 I=1,X1
C      RROH=RROH+2.D0*K(14)*C(I,4)**2
C 400  CONTINUE
C      RROH=1.D-8*RROH

C     Store the Concentrations at the beginning of each iteration
C     over a time step

      DO 39 Specie=1,NSpecie
        DO 35 I=1,999
          SavedC(I,Specie)=C(I,Specie)
  35    CONTINUE
  39  CONTINUE



C     Print the initial amount of each specie for later plotting.

      OPEN(UNIT=12,FILE='SDMTotals',STATUS='OLD',
     +      ACCESS='APPEND')
        WRITE(12,200) dtime,N(1),N(2),N(3),N(4),
     +              N(5),N(6),N(7),N(8),
     +              N(9),N(10),N(11)
      CLOSE(UNIT=12)

 200   FORMAT(12E11.3)

C     Print the initial concentration of each specie for later plotting.

      OPEN(UNIT=14,FILE='SDMConcs',STATUS='OLD',
     +     ACCESS='APPEND')
      DO 44 I=1,24,3
        Place=DBLE(I-1)*dR*RD
        WRITE(14,210) dtime,Place,C(I,1),C(I,2),
     +    C(I,3),C(I,4),C(I,5),C(I,6),
     +    C(I,7),C(I,8)

  44  CONTINUE

      DO 46 I=25,X1,20
        Place=DBLE(I-1)*dR*RD
         WRITE(14,210) dtime,Place,C(I,1),C(I,2),
     +      C(I,3),C(I,4),C(I,5),C(I,6),
     +      C(I,7),C(I,8)

  46  CONTINUE
      CLOSE(UNIT=14)

 210   FORMAT (10E12.4)
```

```
C     Print the initial totals of each specie.

      OPEN(UNIT=10,FILE='SDMResults',STATUS='OLD',
     +     ACCESS='APPEND')
          WRITE(10,74) dtime
          WRITE(10,80) N(1)
          WRITE(10,81) N(2)
          WRITE(10,82) N(3)
          WRITE(10,83) N(4)
          WRITE(10,84) N(5)
          WRITE(10,85) N(6)
          WRITE(10,86) N(7)
          WRITE(10,87) N(8)
          WRITE(10,88) N(9)
          WRITE(10,89) N(10)
          WRITE(10,90) N(11)
          WRITE(10,91) TotalH
          WRITE(10,92) TotalO
          WRITE(10,93) TotalFe
          WRITE(10,94) TotalC
          WRITE(10,95)
      CLOSE(UNIT=10)

 74   FORMAT(' Current time = ',1PG11.5)
 80   FORMAT(' Number of electrons          = ',1D12.5)
 81   FORMAT(' Number of hydrogen radicals  = ',1D12.5)
 82   FORMAT(' Number of hydrogen ions      = ',1D12.5)
 83   FORMAT(' Number of hydroxyl radicals  = ',1D12.5)
 84   FORMAT(' Number of hydroxyl ions      = ',1D12.5)
 85   FORMAT(' Number of hydrogen peroxide  = ',1D12.5)
 86   FORMAT(' Number of FeH+2              = ',1D12.5)
 87   FORMAT(' Number of Fe+2               = ',1D12.5)
 88   FORMAT(' Number of hydrogen molecules = ',1D12.5)
 89   FORMAT(' Number of Fe+3               = ',1D12.5)
 90   FORMAT(' Number of water molecules    = ',1D12.5)
 91   FORMAT('  Total Hydrogen =',1D12.5)
 92   FORMAT('  Total Oxygen   =',1D12.5)
 93   FORMAT('  Total Iron     =',1D12.5)
 94   FORMAT('  Net Charge     =',1D12.5)
 95   FORMAT(//)
      RETURN
      END
```

```
      SUBROUTINE NEWTIME

      INCLUDE 'SDMCOMMO.FOR'
      LOGICAL AddPts
      DOUBLE PRECISION MaxFrac

C     This subroutine does housekeeping chores at the beginning of a new
C     time step.

C     Print warning if previous time step did not converge.

      IF(TimeIter.GE.MaxSteps) THEN
        OPEN(UNIT=11,FILE='SDMErrors',STATUS='OLD',
     +           ACCESS='APPEND')
        WRITE(11,*) '** Error **'
        WRITE(11,200) dtime
        WRITE(11,*) '    The maximum change in concentration',
     +           ' between iterations was ',MaxDelta,'.'
        WRITE(11,*)
        CLOSE(UNIT=11)
      END IF

C     See if need to add X-grid points.

      AddPts=.FALSE.
      MaxFrac=0.D0
      IF(X1.LT.980) THEN
        DO 50 Specie=1,NSpecie
   IF(C(X2,Specie).GT.1.D-10) THEN
          Fraction=DABS(LastC(Specie)-C(X2,Specie))
     Fraction=Fraction/C(X2,Specie)
   ELSE
     Fraction=0.D0
        END IF
        IF(Fraction.GT.REps) THEN
     AddPts=.TRUE.
     IF(MaxFrac.LT.Fraction) MaxFrac=Fraction
   END IF
        LastC(Specie)=C(X2,Specie)
  50    CONTINUE
      END IF

      IF(AddPts) THEN
        X1OLD=X1
        X1=X1+20
        X2=X2+20
        X3=X3+20


C       Print message that new grid points were added.

        OPEN(UNIT=11,FILE='SDMErrors',STATUS='OLD',
     +           ACCESS='APPEND')
        WRITE(11,*) '-- Note --'
        WRITE(11,201) dtime
        WRITE(11,*) '    There are now',X1,' grid points.'
        WRITE(11,202) MaxFrac
        WRITE(11,*)
        CLOSE(UNIT=11)
      END IF
```

```
C     Store the two previous concentrations at the beginning of
C     each iteration over a time step. Two previous values used if
C     have material balance nonconvergence, one otherwise.

      DO 8 Specie=1,Nspecie
        DO 7 I=1,X1
          StoreC(I,Specie)=SavedC(I,Specie)
          SavedC(I,Specie)=C(I,Specie)
  7     CONTINUE
  8   CONTINUE

C     Calculate totals and update variables to refect the new time step

      CALL OUTPUT

      TimeIter=0

C     Stop calculation if number of iterations is exceeded or time limit
C     is reached or if reaction rate for OH recombination is decreased to
C     .01% of it's initial value.

C      RR=0.D0
C      DO 400 I=1,X1
C      RR=RR+2.D0*K(14)*C(I,4)**2
C 400  CONTINUE

      IF(dtime.GT.2.1D-7) StopAll=.TRUE.
      IF(TimeStep.GE.LastIter) StopAll=.TRUE.
C      IF(RR.LT.RROH) StopAll=.TRUE.

      Ntime=.FALSE.

C    Print the final amounts of each specie

        IF(StopAll) THEN

          OPEN(UNIT=10,FILE='SDMResults',STATUS='OLD',
     +            ACCESS='APPEND')


          WRITE(10,74) dtime
          WRITE(10,73) TimeStep
          WRITE(10,98) X1
          WRITE(10,99) NC
          WRITE(10,80) N(1)
          WRITE(10,81) N(2)
          WRITE(10,82) N(3)
          WRITE(10,83) N(4)
          WRITE(10,84) N(5)
          WRITE(10,85) N(6)
          WRITE(10,86) N(7)
          WRITE(10,87) N(8)
          WRITE(10,88) N(9)
          WRITE(10,89) N(10)
          WRITE(10,90) N(11)
          WRITE(10,91) TotalH
          WRITE(10,92) TotalO
          WRITE(10,93) TotalFe
          WRITE(10,94) TotalC

          WRITE(10,95)


          CLOSE(UNIT=10)
```

```
C        Print the total amounts of each specie in a format that
C        Lotus can read for later plotting.

         OPEN(UNIT=12,FILE='SDMTotals',STATUS='OLD',
     +           ACCESS='APPEND')
          WRITE(12,203) dtime,N(1),N(2),N(3),
     +             N(4),N(5),N(6),N(7),
     +             N(8),N(9),N(10),N(11)
         CLOSE(UNIT=12)

 203     FORMAT (12E11.3)

C        Print the concentration distribution of each specie in a
C        format that Lotus can read for later plotting.

         OPEN(UNIT=14,FILE='SDMConcs',STATUS='OLD',
     +           ACCESS='APPEND')
          DO 44 I=1,40,2
            Place=DBLE(I-1)*dR*RD
            WRITE(14,210) dtime,Place,C(I,1),C(I,2),
     +      C(I,3),C(I,4),C(I,5),C(I,6),
     +      C(I,7),C(I,8)

  44      CONTINUE
          DO 46 I=41,X1,20
            Place=DBLE(I-1)*dR*RD
            WRITE(14,210) dtime,Place,C(I,1),C(I,2),
     +       C(I,3),C(I,4),C(I,5),C(I,6),
     +       C(I,7),C(I,8)

  46      CONTINUE
         CLOSE(UNIT=14)

 210     FORMAT (10E12.4)
 73    FORMAT(' TimeStep = ',I5)
 74    FORMAT(' Current time = ',1PG11.5)
 80    FORMAT(' Number of electrons          = ',1D12.5)
 81    FORMAT(' Number of hydrogen radicals  = ',1D12.5)
 82    FORMAT(' Number of hydrogen ions      = ',1D12.5)
 83    FORMAT(' Number of hydroxyl radicals  = ',1D12.5)
 84    FORMAT(' Number of hydroxyl ions      = ',1D12.5)
 85    FORMAT(' Number of hydrogen peroxide  = ',1D12.5)
 86    FORMAT(' Number of FeH+2              = ',1D12.5)
 87    FORMAT(' Number of Fe+2               = ',1D12.5)
 88    FORMAT(' Number of hydrogen molecules = ',1D12.5)
 89    FORMAT(' Number of Fe+3               = ',1D12.5)
 90    FORMAT(' Number of water molecules    = ',1D12.5)
 91    FORMAT('  Total Hydrogen =',1D12.5)
 92    FORMAT('  Total Oxygen   =',1D12.5)
 93    FORMAT('  Total Iron     =',1D12.5)
 94    FORMAT('  Net Charge     =',1D12.5)
 95    FORMAT(//)
 98    FORMAT('   Number of Grid Points =',I5)
 99    FORMAT('   Total Nonconvergences =',I5)
       END IF

 200   FORMAT('   At time =',1PG11.5,'the iterations over a',
     +       ' time step did not converge.')
 201   FORMAT('   At time =',1PG11.5,' 20 new grid points',
     +       'were added.')
 202   FORMAT('    Maximum fractional change in concentration',
     +       /,'between time steps =',G11.5,'.')
       RETURN
       END
```

```
      SUBROUTINE STEPIT

      INCLUDE 'SDMCOMMO.FOR'
      DOUBLE PRECISION COld(1000)

C     This subroutine sets up and solves the finite difference
C     equations.

      MaxDelta=0.D0

C     Calculate the reaction source terms.

      DO 600 Specie=1,NSpecie
        CALL SOURCE

C       Calculate the finite difference coefficients for the main
C       grid points.

        Gamma=dt*D(Specie)/(dR*dR)
        DO 610 I=2,X2
          P=1.D0/DBLE(I-1)
          Center(I)=1.D0+2.D0*Gamma-dt*Center(I)
          Right(I)=Gamma*(1.D0+P)
          Left(I)=Gamma*(1.D0-P)
          Constant(I)=SavedC(I,Specie)+Constant(I)*dt
          COld(I)=C(I,Specie)
 610    CONTINUE
        COld(1)=C(1,Specie)

C       Solve the finite difference equations.

        CALL SOLVE
        IF(TimeStep.GT.0.OR.TimeIter.GT.0) THEN
          CALL BOUND
        END IF

C       Calculate the largest % change in concentration between
C       any two iterations.

        DO 625 I=1,X2
          IF(COld(I).GT.1.D-10) THEN
            Denom=1.D0/COld(I)
            DeltaC=DABS(COld(I)-C(I,Specie))*Denom
          END IF
          MaxDelta=DMAX1(MaxDelta,DeltaC)
 625    CONTINUE
 600  CONTINUE
      RETURN
      END
```

```
      SUBROUTINE Source

      INCLUDE 'SDMCOMMO.FOR'

C     This subroutine calculates the source reaction terms.

      IF(Specie.EQ.1) THEN
        DO 401 I=1,X2
          Center(I)=-2.D0*K(6)*C(I,1)-K(1)*C(I,3)-K(7)*C(I,2)
     +              -K(8)*C(I,4)-K(9)*C(I,6)
          Constant(I)=0.D0
  401   CONTINUE

      ELSEIF(Specie.EQ.2) THEN
        DO 402 I=1,X2
          Center(I)=-K(7)*C(I,1)-K(2)*C(I,8)-2.D0*K(10)*C(I,2)
     +              -K(11)*C(I,4)-K(12)*C(I,6)
          Constant(I)=K(1)*C(I,3)*C(I,1)
  402   CONTINUE

      ELSEIF(Specie.EQ.3) THEN
        DO 403 I=1,X2
          Center(I)=-K(1)*C(I,1)-K(13)*C(I,5)-K(3)*C(I,7)
          Constant(I)=0.D0
  403   CONTINUE

      ELSEIF(Specie.EQ.4) THEN
        DO 404 I=1,X2
          Center(I)=-K(8)*C(I,1)-K(11)*C(I,2)-K(5)*C(I,8)
     +              -2.D0*K(14)*C(I,4)
          Constant(I)=K(9)*C(I,1)*C(I,6)+K(12)*C(I,2)*C(I,6)
     +               +K(4)*C(I,6)*C(I,8)
  404   CONTINUE

      ELSEIF(Specie.EQ.5) THEN
        DO 405 I=1,X2
          Center(I)=-K(13)*C(I,3)
          Constant(I)=2.D0*K(6)*C(I,1)*C(I,1)+K(7)*C(I,1)*C(I,2)
     +              +K(8)*C(I,1)*C(I,4)+K(9)*C(I,1)*C(I,6)
     +              +K(4)*C(I,6)*C(I,8)+K(5)*C(I,4)*C(I,8)
  405   CONTINUE

      ELSEIF(Specie.EQ.6) THEN
        DO 406 I=1,X2
          Center(I)=-K(9)*C(I,1)-K(12)*C(I,2)-K(4)*C(I,8)
          Constant(I)=K(14)*C(I,4)*C(I,4)
  406   CONTINUE

      ELSEIF(Specie.EQ.7) THEN
        DO 407 I=1,X2
          Center(I)=-K(3)*C(I,3)
          Constant(I)=K(2)*C(I,8)*C(I,2)
  407   CONTINUE

      ELSE
        DO 408 I=1,X2
          Center(I)=-K(2)*C(I,2)-K(4)*C(I,6)-K(5)*C(I,4)
          Constant(I)=0.D0
  408   CONTINUE
      END IF
      RETURN
      END
```

```
      SUBROUTINE SOLVE

      INCLUDE 'SDMCOMMO.FOR'
      DOUBLE PRECISION PT(1000),QT(1000)

C     This subroutine solves the finite difference equations
C     created in STEPIT

      Denom=1.D0/Center(2)
      PT(2)=Right(2)*Denom
      QT(2)=(Constant(2)+Left(2)*C(1,Specie))*Denom
      DO 100 I=3,X2
        IMinus1=I-1
        Denom=Center(I)-PT(IMinus1)*Left(I)
        Denom=1.D0/Denom
        PT(I)=Right(I)*Denom
        QT(I)=(Constant(I)+Left(I)*QT(IMinus1))*Denom
  100 CONTINUE
      DO 150 I=X2,2,-1
        C(I,Specie)=C(I+1,Specie)*PT(I)+QT(I)
  150 CONTINUE

      RETURN
      END

C-------------------------------------------------------------

      SUBROUTINE BOUND

      INCLUDE 'SDMCOMMO.FOR'

C     This subroutine sets the boundary values

      Gamma=dt/(dR*dR)
      Denom=1.D0+6.D0*D(Specie)*Gamma-Center(1)*dt
      Denom=1.D0/Denom
      C(1,Specie)=(6.D0*Gamma*D(Specie)*C(2,Specie)+SavedC(1,Specie)
     +             +dt*Constant(1))*Denom
      C(X1,Specie)=0.D0
      C(X1,3)=InitialC(3)
      C(X1,5)=InitialC(5)
      C(X1,8)=InitialC(8)
      RETURN
      END
```

```
      SUBROUTINE OUTPUT

      INCLUDE 'SDMCOMMO.FOR'

C     This subroutine calculates and prints the total amounts of
C     each specie at the end of a time step. Material balance convergence
C     is calculated, dt changed and variables updated for new time step.


C     Simpsons rule to calculate totals for products
      ASum9=0.D0
      ASum10=0.D0
      ASum11=0.D0
      DO 37 I=2,X2
        P=DBLE(I-1)**2
        Sum9=K(6)*C(I,1)*C(I,1)+K(7)*C(I,2)*C(I,1)
     +        +K(10)*C(I,2)*C(I,2)+K(3)*C(I,7)*C(I,3)
        Sum10=K(5)*C(I,4)*C(I,8)+K(3)*C(I,7)*C(I,3)
     +       +K(4)*C(I,6)*C(I,8)
        Sum11=-2.D0*K(6)*C(I,1)*C(I,1)-K(7)*C(I,1)*C(I,2)
     +         +K(11)*C(I,2)*C(I,4)+K(12)*C(I,2)*C(I,6)
     +         +K(13)*C(I,3)*C(I,5)
        IF(0.5D0*DBLE(I)-INT(0.5D0*DBLE(I)).LT..01D0) THEN
          ASum9=ASum9+Sum9*P
          ASum10=ASum10+Sum10*P
          ASum11=ASum11+Sum11*P
        END IF
        ASum9=ASum9+Sum9*P
        ASum10=ASum10+Sum10*P
        ASum11=ASum11+Sum11*P
 37   CONTINUE
      ASum9=2.D0*ASum9+X2*X2*(K(6)*C(X1,1)*C(X1,1)
     +       +K(7)*C(X1,2)*C(X1,1)+K(10)*C(X1,2)*C(X1,2)
     +       +K(3)*C(X1,7)*C(X1,3))
      ASum10=2.D0*ASum10+X2*X2*(K(5)*C(X1,4)*C(X1,8)
     +       +K(3)*C(X1,7)*C(X1,3)+K(4)*C(X1,6)*C(X1,8))
      ASum11=2.D0*ASum11+X2*X2*(-2.D0*K(6)*C(X1,1)*C(X1,1)
     +       -K(7)*C(X1,1)*C(X1,2)+K(11)*C(X1,2)*C(X1,4)
     +        +K(12)*C(X1,2)*C(X1,6)+K(13)*C(X1,3)*C(X1,5))

      Q=pi*dR**3*dt*TD/3.D0*CD*KD*RD*RD*RD*CD


C     Add to total for even timesteps
      IF(0.5D0*DBLE(TimeStep)-INT(0.5D0*DBLE(TimeStep)).LT..01D0) THEN
        N(9)=N(9)+Q*ASum9
        N(10)=N(10)+Q*ASum10
        N(11)=N(11)+Q*ASum11
      END IF



C       Calculate totals, check material balance convergence, print results
C       for even timesteps.

        I=DBLE(TimeStep)
        IF(DBLE(I)-2.D0*INT(0.5D0*DBLE(I)).LT..01D0) THEN
```

```
C       Calculate the amounts of Species 1 -- 8

        DO 27 Specie=1,NSpecie
          Sum=0.D00
          DO 28 I=2,998
            P=DBLE(I-1)
            ASum=P*P*C(I,Specie)
            IF(0.5D0*DBLE(I)-INT(0.5D0*DBLE(I)).LT..01D0) THEN
              Sum=Sum+ASum
            END IF
            Sum=Sum+ASum
 28       CONTINUE
          Sum=2.D0*Sum+998.D0**2*C(999,Specie)
          N(Specie)=Sum*pi*dR***3*CD*RD*RD*RD
 27     CONTINUE


        STotalC=TotalC
        STotalH=TotalH
        STotalO=TotalO
        STotalFe=TotalFe
        TotalC=-N(1)+N(3)-N(5)+2.D0*N(7)+2.*N(8)+3.*N(10)
        TotalH=N(2)+N(3)+N(4)+N(5)+2.*N(6)+N(7)+2.*N(9)+2.D0*N(11)
        TotalO=N(4)+N(5)+2.D0*N(6)+N(11)
        TotalFe=N(7)+N(8)+N(10)

C       check for mass balance closure

        OPEN(UNIT=11,FILE='SDMErrors',STATUS='OLD',
     +          ACCESS='APPEND')
        CloseC=DABS(STotalC-TotalC)/TotalC
        IF(CloseC.GT.MBEps) THEN
          WRITE(11,*) '** Warning **'
          WRITE(11,75) dtime
          WRITE(11,*) '       closure =',CloseC
          WRITE(11,*)
        END IF


        CloseH=DABS(STotalH-TotalH)/TotalH
        IF(CloseH.GT.MBEps) THEN
          WRITE(11,*) '** Warning **'
          WRITE(11,77) dtime
          WRITE(11,*) '       closure =',CloseH
          WRITE(11,*)
        END IF


        CloseO=DABS(STotalO-TotalO)/TotalO
        IF(CloseO.GT.MBEps) THEN
          WRITE(11,*) '** Warning **'
          WRITE(11,78) dtime
          WRITE(11,*) '       closure =',CloseO
          WRITE(11,*)
         END IF


          CloseF=DABS(STotalFe-TotalFe)/TotalFe
          IF(CloseF.GT.MBEps) THEN
          WRITE(11,*) '** Warning **'

          WRITE(11,79) dtime
          WRITE(11,*) '       closure =',CloseF
          WRITE(11,*)
         END IF
         CLOSE(UNIT=11)

        IF((CloseC.GT.MBEPS).OR.(CloseH.GT.MBEPS).OR.(CloseO.GT.MBEPS)
     +  .OR.(CloseF.GT.MBEPS)) GO TO 50
```

```
C       Calculate error of numerical method and
C           print results at specified intervals

          IF(Time.GT.NextPrn) THEN
           NextPrn=(10**(DLOG10(Time*TD)+DeltaPRN))/TD

C       Calculate error of material balance from initial amounts
        OPEN(UNIT=11,FILE='SDMErrors',STATUS='OLD',
     +       ACCESS='APPEND')

          GErrC=Dabs(TotalC-ITotalC)/ITotalC
          IF (GErrC.GT.GEPS) THEN
          WRITE (11,*) ' ** ERROR **'
          WRITE (11,75) dtime
          WRITE (11,*) '     Total error C=',GErrC
          WRITE (11,*)
          END IF

          GErrH=Dabs(TotalH-ITotalH)/ITotalH
          IF (GErrH.GT.GEPS) THEN
          WRITE (11,*) ' ** ERROR **'
          WRITE (11,77) dtime
          WRITE (11,*) '     Total error H=',GErrH
          WRITE (11,*)
          END IF

          GErrO=Dabs(TotalO-ITotalO)/ITotalO
          IF (GErrO.GT.GEPS) THEN
          WRITE (11,*) ' ** ERROR **'
          WRITE (11,78) dtime
          WRITE (11,*) '     Total error O=',GErrO
          WRITE (11,*)
          END IF

          GErrFe=Dabs(TotalFe-ITotalFe)/ITotalFe
          IF (GErrFe.GT.GEPS) THEN
          WRITE (11,*) ' ** ERROR **'
          WRITE (11,79) dtime
          WRITE (11,*) '     Total error Fe=',GErrFe
          WRITE (11,*)
          END IF
         CLOSE(UNIT=11)

C         Print the total amounts of each specie

          OPEN(UNIT=10,FILE='SDMResults',STATUS='OLD',
     +           ACCESS='APPEND')

          WRITE(10,74) dtime
          WRITE(10,73) TimeStep
          WRITE(10,98) X1
          WRITE(10,99) NC
          WRITE(10,80) N(1)
          WRITE(10,81) N(2)
          WRITE(10,82) N(3)
          WRITE(10,83) N(4)
          WRITE(10,84) N(5)
          WRITE(10,85) N(6)
          WRITE(10,86) N(7)
          WRITE(10,87) N(8)
          WRITE(10,88) N(9)
          WRITE(10,89) N(10)
          WRITE(10,90) N(11)
          WRITE(10,91) TotalH
          WRITE(10,92) TotalO
          WRITE(10,93) TotalFe
          WRITE(10,94) TotalC
          WRITE(10,95)
          CLOSE(UNIT=10)
```

```
C        Print the total amounts of each specie in a format that
C        Lotus can read for later plotting.

         OPEN(UNIT=12,FILE='SDMTotals',STATUS='OLD',
     +           ACCESS='APPEND')
         WRITE(12,200) dtime,N(1),N(2),N(3),
     +             N(4),N(5),N(6),N(7),
     +             N(8),N(9),N(10),N(11)
         CLOSE(UNIT=12)

 200     FORMAT (12E11.3)

C        Print the concentration distribution of each specie in a
C        format that Lotus can read for later plotting.
C           NP is counter for printing at intervals

         IF (NP.GT.3) THEN
         OPEN(UNIT=14,FILE='SDMConcs',STATUS='OLD',
     +           ACCESS='APPEND')
          DO 44 I=1,40,2
            Place=DBLE(I-1)*dR*RD
            WRITE(14,210) dtime,Place,C(I,1),C(I,2),
     +      C(I,3),C(I,4),C(I,5),C(I,6),
     +      C(I,7),C(I,8)

  44      CONTINUE
          DO 46 I=41,X1,20
            Place=DBLE(I-1)*dR*RD
            WRITE(14,210) dtime,Place,C(I,1),C(I,2),
     +       C(I,3),C(I,4),C(I,5),C(I,6),
     +       C(I,7),C(I,8)

  46      CONTINUE
         CLOSE(UNIT=14)

 210     FORMAT (10E12.4)
          NP=0
        END IF
         NP=NP+1

       END IF

       END IF

C      End if time is greater than end time

       IF(dtime.GT.2.1D-7) GO TO 55

C         Increase dt and update variables to reflect new time step
C          M is counter to increase dt on intervals of MMax

          M=M+1
          Olddt=dt
          IF (M.LE.MMax) GO TO 40

         dt=2.D0*DT
           M=0

          OPEN(UNIT=11,FILE='SDMErrors',STATUS='OLD',
     +           ACCESS='APPEND')
         WRITE(11,76) dtime,dt
         CLOSE(UNIT=11)
  40      Time=Time+dt
          Timestep=Timestep+1
          dtime=Time*TD
```

```
C     If not last time step, set up integrals for N(I) for Simpson's rule
C       for next time step (i.e. end in 4*ASUM or 2*ASUM).

      IF(TimeStep.NE.LastIter) THEN
        IF(Olddt.EQ.dt) THEN
          Temp=DBLE(TimeStep)
          IF(Temp-2.D0*INT(0.5D0*Temp).GT..01D0) THEN
            Factor=3.D0
          ELSE
            Factor=1.D0
          END IF
        ELSE
          Factor=dt/Olddt
        END IF
        N(9)=N(9)+Factor*Q*ASum9
        N(10)=N(10)+Factor*Q*ASum10
        N(11)=N(11)+Factor*Q*ASum11
      END IF

C     Save values for odd timesteps to use for reintialization
C       in case of nonconvergence

      IF(Temp-2.D0*INT(0.5D0*Temp).GT..01D0) THEN
        OldN(9)=N(9)
        OldN(10)=N(10)
        OldN(11)=N(11)
        TimeO=TIME-dt
        PX1=X1
      END IF

      MM=0

   73 FORMAT(' TimeStep = ',I5)
   74 FORMAT(' Current time = ',1PG11.5)
   75 FORMAT('   At time = ',1PG11.5,' the charge balance',
     +       ' did not converge.')
   76 FORMAT('    At time = ',1PG11.5,' dt was increased to ',
     +        1PG11.5)
   77 FORMAT('   At time = ',1PG11.5,' the hydrogen balance',
     +       ' did not converge.')
   78 FORMAT('   At time = ',1PG11.5,' the oxygen balance',
     +       ' did not converge.')
   79 FORMAT('   At time = ',1PG11.5,' the iron balance',
     +       ' did not converge.')
   80 FORMAT(' Number of electrons          = ',1D12.5)
   81 FORMAT(' Number of hydrogen radicals  = ',1D12.5)
   82 FORMAT(' Number of hydrogen ions      = ',1D12.5)
   83 FORMAT(' Number of hydroxyl radicals  = ',1D12.5)
   84 FORMAT(' Number of hydroxyl ions      = ',1D12.5)
   85 FORMAT(' Number of hydrogen peroxide  = ',1D12.5)
   86 FORMAT(' Number of FeH+2              = ',1D12.5)
   87 FORMAT(' Number of Fe+2               = ',1D12.5)
   88 FORMAT(' Number of hydrogen molecules = ',1D12.5)
   89 FORMAT(' Number of Fe+3               = ',1D12.5)
   90 FORMAT(' Number of water molecules    = ',1D12.5)
   91 FORMAT('  Total Hydrogen =',1D12.5)
   92 FORMAT('  Total Oxygen   =',1D12.5)
   93 FORMAT('  Total Iron     =',1D12.5)
   94 FORMAT('  Net Charge     =',1D12.5)
   95 FORMAT(//)
   96 FORMAT('         At time = ',1PG11.5,' dt was decreased to ',
     +        1PG11.5)
   98 FORMAT('  Number of Grid Points =',I5)
   99 FORMAT('  Total Nonconvergences =',I5)

C     If converging timestep go to the end of this subroutine
      GO TO 55
```

```
C    Decrease dt because of nonconvergence and reinitalize variables for
C       last converging  timestep.
  50  Olddt=dt
      dt=.5D0*dt
       OPEN(UNIT=11,FILE='SDMErrors',STATUS='OLD',
     +            ACCESS='APPEND')
       WRITE(11,96) dtime,dt
       CLOSE(UNIT=11)

       X1=PX1
       X2=X1-1
       X3=X1-2


      DO 52 Specie=1,NSpecie
        DO 51 I=1,X1
          SavedC(I,Specie)=StoreC(I,Specie)
          C(I,Specie)=StoreC(I,Specie)
  51    CONTINUE
      LastC(Specie)=StoreC(X2,Specie)
  52  CONTINUE

      N(9)=OldN(9)
      N(10)=OLDN(10)
      N(11)=OldN(11)

      TotalC=STotalC
      TotalH=STotalH
      TotalO=STotalO
      TotalFe=STotalFe

      Time=Time0+dt
      dtime=Time*TD
      M=0
      NC=NC+1

C     MM is counter of nonconvergences in sequence
C     Calculation stopped if MM is greater than 6
C     NC is counter of total number of nonconvergences.

      MM=MM+1
      IF(MM.GT.6) THEN
      StopAll=.TRUE.
      WRITE(*,300)
 300  FORMAT(3X,'CONVERGENCE FAILURE, PROGRAM STOPPED')
      END IF


  55  RETURN

      END
```

```
C      PROGRAM SDMCOMMO.FOR
C      Common and dimension statements for Program SDM


       DOUBLE PRECISION MaxDelta,MBEps,NextPrn,Left(1000),K(14),KD,N(14)
       DOUBLE PRECISION RROH,RR
       DOUBLE PRECISION InitialC(8),InitialN(4),InitialR(4),InitC(8)
       DOUBLE PRECISION LastC(8),CD,C(1000,8),DeltaC,Time,TotalH,TotalC
       DOUBLE PRECISION TotalFe,TotalO,Right(1000),Center(1000)
       DOUBLE PRECISION ITotalO,ITotalFe,ITotalH,ITotalC,Constant(1000)
       DOUBLE PRECISION SavedC(1000,8),StoreC(1000,8),CMAX
       DOUBLE PRECISION STotalC,STotalO,STotalH,STotalFe,SUM,ASUM
       DOUBLE PRECISION OldN(11),TimeO,BackC(1000,8)
       DOUBLE PRECISION OTotalO,OTotalH,OTotalC,OTotalFe
       DOUBLE PRECISION Gamma,Denom,pi
       CHARACTER Tab*1
       LOGICAL StopAll,Ntime
       INTEGER TimeStep,TimeIter,X1,X2,X3,Specie,PX1
       COMMON/TIME/Month,Day,Year,IVAL
       COMMON/INDEX/Specie,NSpecie,TimeStep,TimeIter,LastIter,
      +             MaxSteps,NextPrn,DeltaPrn,NP,NC
       COMMON/GRID/dt,dtime,dR,RLength,X1,X2,X3
       COMMON/CNTL/StopAll,Ntime
       COMMON/COEF/Constant,Right,Left,Center
       COMMON/CONV/ConvEps,REps,MBEps,MaxDelta,M,MMax,GEPS
       COMMON/CONC/C,SavedC,N,Time,StoreC,
      +           TotalC,TotalH,TotalO,TotalFe,LastC
       COMMON/TOTAL/ITotalH,ITotalO,ITotalFe,ITotalC,
      +              OldN,Olddt,TimeO,BackC,RROH,
      +              OTotalC,OTotalH,OTotalFe,OTotalO
       COMMON/CONST/K,D(8),pi,InitialC,InitialN,InitialR,Tab
       COMMON/DMSN/KD,CD,TD,DD,RD,PX1
```

# APPENDIX B

# FINITE DIFFERENCE CALCULATION

System of Partial Differential Equations for the Dearated Fricke Dosimeter to be solved by Finite Difference and Equations for Product Totals

$$dC_1/dt = D_1\nabla^2 C_1 - k_1C_1C_3 - 2k_6C_1^2 - k_7C_1C_2 - k_8C_1C_4 - k_9C_1C_6 \quad (B.1)$$

$$dC_2/dt = D_2\nabla^2 C_2 - k_2C_2C_8 - k_7C_2C_1 - 2k_{10}C_2^2 - k_{11}C_2C_4 - k_{12}C_2C_6 + k_1C_1C_3 \quad (B.2)$$

$$dC_3/dt = D_3\nabla^2 - k_1C_3C_1 - k_3C_3C_7 - k_{13}C_3C_5 \quad (B.3)$$

$$dC_4/dt = D_4\nabla^2 - k_5C_4C_8 - k_8C_4C_1 - k_{11}C_4C_2 - 2k_{14}C_4^2 + k_4C_6C_8 + k_9C_1C_6 + k_{12}C_2C_6 \quad (B.4)$$

$$dC_5/dt = D_5\nabla^2 - k_{13}C_5C_3 + k_4C_6C_8 + k_5C_4C_8 + 2k_6C_1^2 + k_7C_1C_2 + k_8C_1C_4 + k_9C_1C_6 \quad (B.5)$$

$$dC6/dt = D_6\nabla^2 - k_4C_6C_8 - k_9C_6C_1 - k_{12}C_6C_2 + 2k_{14}C_4^2 \quad (B.6)$$

$$dC_7/dt = D_7\nabla^2 - k_3C_7C_3 + k_2C_2C_8 \quad (B.7)$$

$$dC_8/dt = D_8\nabla^2 - k_2C_8C_2 - k_4C_6C_8 - k_5C_4C_8 \quad (B.8)$$

$$\text{Total } N_9 = \iint 4\pi r^2(k_6C_1^2 + k_7C_1C_2 + k_{10}C_2^2 + k_3C_7C_3)drdt \quad (B.9)$$

$$\text{Total } N_{10} = \iint 4\pi r^2(k_5C_4C_8 + k_3C_7C_3 + k_4C_6C_8)drdt \quad (B.10)$$

$$\text{Total } N_{11} = \iint 4\pi r^2(k_8C_1^2 + k_{11}C_2C_4 + k_{12}C_2C_6 + k_{13}C_3C_5 - k_7C_1C_2)drdt \quad (B.11)$$

Note: 1 = $e^-_{aq}$, 2 = H, 3 = $H^+$, 4 = OH, 5 = $OH^-$, 6 = $H_2O_2$, 7 = $FeH^+$, 8 = $Fe^{+2}$, 9 = $H_2$, 10 = $Fe^{+3}$, 11 = $H_2O$

## Finite Difference Calculation

$$\delta C_i/\delta t = D_i \nabla^2 C_i - \Sigma K_{i,j} C_i C_j + \Sigma (1-.5\delta bd) K_{bd} C_b C_d \quad \text{(B.12)}$$

where:

$$\nabla^2 C_i = \delta C_i^2/\delta r^2 + (\alpha/r)\delta C_i/\delta r \quad \text{(B.13)}$$

$\alpha = 1$ for cylindrical geometry

$\alpha = 2$ for spherical geometry

$r = (m-1)\Delta r$

$$\delta C_i^2/\delta r = (C_i(m+1,t) - 2C_i(m,t) + C_i(m-1,t))/\Delta r^2 \quad \text{(B.14)}$$

$$\delta C_i/\delta r = (C_i(m+1,t) - C_i(m-1,t))/2\Delta r \quad \text{(B.15)}$$

$$\delta C_i/\delta t = (C_i(m,t) - C_i(m,t-1))/\Delta t \quad \text{(B.16)}$$

$$-\Sigma K_{i,j} C_i C_j = \text{Center}(m) \text{ from reaction terms} * C_i(m,t) \quad \text{(B.17)}$$

$$\Sigma (1-.5\delta bd) K_{bd} C_b C_d = \text{Constant}(m) \text{ from reaction terms} \quad \text{(B.18)}$$

Substituting equations B.13-B.18 into equation B.12 gives:

$$(C_i(m,t) - C_i(m,t-1))/\Delta t = D_i[(C_i(m+1,t) - 2C_i(m,t) + C_i(m-1,t))/\Delta r^2] + 2D_i/((m-1)\Delta r)[(C_i(m+1,t) - C_i(m-1,t))/2\Delta r] + \text{Center}(m) C_i(m,t) + \text{Constant}(m) \quad \text{(B.19)}$$

Equation B.19 can be rearranged to give:

$$C_i(m,t)[1 + 2D_i\Delta t/\Delta r^2 - \text{Center}(m)\Delta t] = C_i(m+1,t)[D_i\Delta t/\Delta r^2 + D_i\Delta t/((m-1)\Delta r^2] + C_i(m-1,t)[D_i\Delta t/\Delta r^2 - D_i\Delta t/((m-1)\Delta r^2] + C_i(m,t-1) + \text{Constant}(m)\Delta t \quad \text{(B.20)}$$

Substituting $\tau = D_i \Delta t / \Delta r^2$ into equation B.20 gives:

$$C_i(m,t)[1+2\tau-\text{Center}(m)\Delta t] = C_i(m+1,t)[\tau+\tau/(m-1)] + C_i(m-1,t)[\tau-\tau/(m-1)]+C_i(m,t-1)+\text{Constant}(m)\Delta t \quad \text{(B.21)}$$

From notation in the computer program;

$$\text{Center}(m) = 1 + 2\tau - \text{Center}(m)\Delta t \quad \text{(B.22)}$$

$$C_i(m,t-1) = \text{Saved}C_i(m) \quad \text{(B.23)}$$

$$\text{Constant}(m) = \text{Saved}C_i(m,t) + \text{Constant}(m)\Delta t \quad \text{(B.24)}$$

$$\text{Right}(m) = \tau(1+1/(m-1)) \quad \text{(B.25)}$$

$$\text{Left}(m) = \tau(1-1/(m-1) \quad \text{(B.26)}$$

Substituting equations B.22-B.26 into Equation B.21 and rearranging gives:

$$C_i(m,t) = C_i(m+1,t)\text{Right}(m)/\text{Center}(m) +(\text{Constant}(m)+ C_i(m-1,t)\text{Left}(m))/\text{Center}(m) \quad \text{(B.27)}$$

Boundary Condition at Center of Spur

$\delta C_i/\delta r = 0$ at $r = 0$ and $m = 1$ (center of the spur)

MacLaurin's Expansion of $\delta C_i(r,t)/\delta r$ gives;

$$\delta C_i(r,t)/\delta r = \delta C_i(1,t)/\delta r + r\,\delta^2 C_i(1,t)/\delta r^2 + 1/2r^2\,\delta^3 C_i(1,t)/\delta r^3 + \ldots \quad \text{(B.28)}$$

For the boundary condition of $\delta C_i(1,t)/\delta r = 0$ the limiting value of $1/r\ \delta C_i(r,t)/\delta r$ as r goes to zero is:

$$1/r\ \delta C_i(r\text{-->}0,t)/\delta r = \delta^2 C_i(1,t)/\delta r^2. \quad \text{(B.29)}$$

This is substituted in to equation B.12 and B.13 to give:

$$\delta C_i/\delta t = 3D_i\delta^2 C_i/\delta r^2 + \Sigma K_{i,j}C_iC_j - \Sigma(1-.5\delta_{bd})K_{bd}C_dC_b. \quad \text{(B.30)}$$

Using equations B.14 - B.18 this can be written as:

$$(C_i(1,t)-C_i(1,t-1))/\Delta t = 3D_i(C_i(2,t)-2C_i(1,t)+C_i(0,t))/\Delta r^2 + \text{Center}(1)C_i(1,t) + \text{Constant}(1). \quad \text{(B.31)}$$

Based on spherical symmetry around $C_i(1,t)$:

$$C_i(2,t)=C_i(0,t). \quad \text{(B.32)}$$

Using equation B.32 in equation B.31 gives:

$$C_i(1,t) = [(6D_iC_i(2,t)\Delta t)/\Delta r^2 + \text{Constant}(1)\Delta t + C_i(1,t-1)]/[1+6D_i\Delta t/\Delta r^2-\text{Center}(1)\Delta t]. \quad \text{(B.33)}$$

# VITA

Eileen W. Ruppel was born on February 19, 1959 in Stamford, Connecticut. In June 1977, she graduated from Ramapo Regional High School in Franklin Lakes, New Jersey. She attended Lehigh University in Bethlehem, Pennsylvania where she graduated with a Bachelor of Science degree in Chemical Engineering in May 1981. She began her graduate studies at the West Virginia College of Graduate Studies in 1981 and enrolled in the Graduate School of the University of Tennessee, Knoxville in 1984.

Eileen started working as a process engineer with Union Carbide Corporation at the South Charleston Technical Center in 1981. In 1984 she began work as an engineer for the United States Department of Energy in Oak Ridge, Tennessee. Since 1987, she has stayed home with her daughter.

Eileen is a member of Tau Beta Pi and plays in the Knoxville Women's Soccer League.