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Numerical Solution of Nonlinear STIFF Initial-Value Problems by Perturbed Functional Iterations

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Numerical Solution of Nonlinear STIFF Initial-Value Problems by Perturbed Functional Iterations

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NUMERICAL SOLUTION OF NONLINEAR STIFF INITIAL-VALUE PROBLEMS BY
PERTURBED FUNCTIONAL ITERATIONS

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Abstract

Numerical solution of nonlinear stiff initial-value problems by a perturbed functional iterative scheme are discussed. The algorithm does not fully linearize the system and requires only the diagonal terms of the Jacobian. Some examples are presented.

1. Introduction

Stiff ODE's (ordinary differential equations) are of special significance in chemical kinetics, where decay of one component of the solution could happen much faster than other components. For numerical solution of these problems, it is generally found that some transient components which are negligible in comparison with other components, restrict the step sizes of the explicit methods to be very small in order that stability of the numerical solution may be maintained. Also, in order to understand the proper nature of the solution, the transient effects of the fast decaying terms should be revealed by the numerical process. This poses a very difficult problem. During the last decade, extensive research has been performed by mathematicians, engineers, and chemists to reveal the mechanism of stiff systems both mathematically and computationally.

Most conventional explicit methods such as Euler's method, Runge-Kutta schemes, Adams-Bashforth schemes, etc., require very small step sizes so that the algorithm may remain stable. Although some attempts have been made to extend the stability properties of explicit methods for special types of ODE's [11] by far the most common technique for solving stiff systems numerically is the use of implicit methods which requires the solution of simultaneous equations. In nonlinear cases Newton-type methods also requires the evaluation of a Jacobian, a process that has a high arithmetic operation count. These requirements can be costly in both computer time and storage requirements.

Let us now pose the problem, and set up an implicit algorithm for the solution.

$$\frac{dx}{dt} = f(x,t) \quad (1)$$

where $x = (x_1 \ x_2 \ \dots \ x_m)^T$; $f = (f_1 \ f_2 \ \dots \ f_m)^T$; and $x(0) = x_0$.

Approximating dx/dt by a backward Euler scheme, we find

$$x^{n+1} - x^n = \Delta t f(x^{n+1}, t_{n+1})$$

or

$$x^{n+1} - x^n - \Delta t \cdot f(x^{n+1}, t_{n+1}) = 0 \quad (2)$$

This equation must be solved for x^{n+1} assuming that x^n the value of x at the previous time step is known. Then, we may represent this equation as

$$F(x^{n+1}) = 0 \quad (3)$$

If $X = x^{n+1}$, then it becomes

$$F(X) = 0 \quad (4)$$

which is a nonlinear system. After we have solved this system for X , we update the system by replacing x^n by the computed values of X and

again solve another nonlinear system of the form (4), etc. The process will continue until we reach the steady state which is here assumed to exist.

At present, there are several methods to solve nonlinear systems of the form (4). They may be arranged into two classes:

(i) Methods which require relatively small computer memory storage and operational counts per iteration but have slow rates of convergence (e.g., Point Jacobi, Point Gauss-Seidel).

(ii) Methods which require relatively large computer memory storage and large operational counts per iteration but demonstrate fast rates of convergence (e.g., Newton's method).

In [1] a functional iterative scheme has been developed to solve nonlinear systems. It is obtained by perturbing nonlinear Gauss-Seidel iterations. The perturbation parameters stabilize the algorithm, control the mode of convergence, and, in some cases, can greatly speed up the rate of convergence. These parameters are essentially corrective factors for the iterates. Thus as the iterations converge, the perturbation parameters are all damped out. The present method has been applied to solve several stiff nonlinear ODE's. The results seemed to be encouraging in comparison with those obtained by conventional explicit schemes. The primary objective in this article is to show the usefulness of this method with regard to the numerical solution of stiff ODEs. A brief discussion regarding the details of the algorithm and its convergence properties is also included.

2. The Algorithm

Given a differential equation

$$h(\dot{x}, x, t) = 0, \quad x(t_0) = x_0$$

where $\dot{x} = dx/dt$ and t is the independent variable, if a difference approximation is made, it is reduced to a nonlinear system of the form

$$F_j(x_1, x_2, \dots, x_n) = 0, \quad j = 1, 2, \dots, n \quad (5)$$

This may be expressed as $F(x) = 0$, $x = (x_1 \ x_2 \ \dots \ x_n)^T$. We assume that a solution exists. Let us express (5) as:

$$x = G_0(x) \quad (6)$$

$G_0: DCR^n \rightarrow D$ ($R^n =$ real n -dimensional space). Nonlinear Gauss-Seidel iterations to solve (6) may be expressed as:

$$x^{k+1} = G(x^{k+1}, x^k) \quad (7)$$

where $x^k = (x_1^k \ x_2^k \ \dots \ x_n^k)^T \in D$; $x_j^k =$ value of x_j at the k th level of iteration; $G: D \times DCR^n \times R^n \rightarrow D$.

Let us perturb (7) and write:

$$x^{k+1} = \omega^k + G(x^{k+1}, x^k) \quad (8)$$

where $\omega^k = (\omega_1^k \ \omega_2^k \ \dots \ \omega_n^k)^T \in R^n$ is the perturbation parameter.

If the method converges, $\lim_{k \rightarrow \infty} x^k = x^*$ and $G(x^*, x^*) = x^*$, which implies:

Theorem: 1 A necessary condition so that (8) may converge is that for some norm

$$\lim_{k \rightarrow \infty} \|\omega^k\| = 0 \quad (9)$$

In the element form (8) may be expressed as:

$$x_j^{k+1} = \omega_j^k + G_j^{k+1,k} \quad (10)$$

where

$$G_j^{k+1,k} = G_j \left(x_1^{k+1}, x_2^{k+1}, \dots, x_{j-1}^{k+1}, x_j^k, \dots, x_n^k \right) \quad (11)$$

The algorithm has been derived in details in [1] and ω_j^k is computed by using the following equation:

$$\omega_j^k = \frac{G_j(G_j^{k+1,k}) - G_j^{k+1,k}}{1 - \partial_j G_j^{k+1,k}} \quad (12)$$

where $G_j^{k+1,k}$ is computed using (11),

$$G_j(G_j^{k+1,k}) = G_j(x_1^{k+1}, x_2^{k+1}, \dots, x_{j-1}^{k+1}, G_j^{k+1,k}, x_{j+1}^k, \dots, x_n^k)$$

and

$$\partial_j G_j^{k+1,k} = \left. \frac{\partial G_j}{\partial x_j} \right|_{x_1^{k+1}, x_2^{k+1}, \dots, x_{j-1}^{k+1}, G_j^{k+1,k}, x_{j+1}^k, \dots, x_n^k}$$

Thus in (12), for x_j^{k+1} , ω_j^k is computed in terms of quantities known a priori. The criterion for convergence is, if at some k ,

$$\max_j |\omega_j^k| < \epsilon \quad (13)$$

where ϵ is positive and arbitrarily small.

3. Convergence Analysis

Given a sequence of scalars $\{a_k\}$, $k = 1, 2, \dots$, a_k is called a D-element iff

$$\lim_{k \rightarrow \infty} a_1 a_2 \dots a_k = 0 \quad (14)$$

It is obvious that if $\forall k > K, |a_k| \leq \alpha < 1$ equation (14) is satisfied.

Given a sequence of square matrices $\{A_k\}$ of the same type with variable elements, A_k is called a D-matrix iff

$$\lim_{k \rightarrow \infty} A_k A_{k-1} \dots A_1 = 0 \quad (15)$$

Obviously if $A_k = A \forall k$, A_k is a D-matrix iff A is a convergent matrix.
 A sufficient condition that A_k is a D-matrix is, for some norm

$$\|A_k\| \leq \alpha < 1 \quad (16)$$

The necessary and sufficient condition so that A_k is a D-matrix is

$$\max_{i,j} \left| a_{i,j}^{k,k-1, \dots, 1} \right| < \epsilon \quad (17)$$

where ϵ is positive and arbitrarily small and $a_{i,j}^{k,k-1, \dots, 1}$ = an element of the product matrix

$$A_k A_{k-1} \dots A_1$$

An Example: Let $A_1 = \text{diag} (\alpha_1, a_1, b_1)$

$$A_2 = \text{diag} (a_2, \alpha_2, b_2), \quad A_3 = \text{diag} (a_3, b_3, \alpha_3)$$

$$A_4 = \text{diag} (\alpha_4, a_4, b_4), \quad \text{etc.}$$

Let $|\alpha_j| \leq \alpha < 1 \forall j > N$ and a_j 's and b_j 's are bounded and chosen arbitrarily and a finite number of them are greater than 1 in absolute value. Then

$$\lim_{n \rightarrow \infty} A_n A_{n-1} \dots A_1 = 0 \quad (18)$$

Thus each A_j is a D-matrix, however none of these matrices is a convergent matrix.

Let us consider an iterative scheme

$$x^{k+1} = G(x^{k+1}, x^k), \quad k = 1, 2, \dots$$

Let for a given $x^* \in D$,

$$G(x^{k+1}, x^k) - G(x^*, x^*) = A_k (x^{k+1} - x^*) + B_k (x^k - x^*) \quad (19)$$

Both A_k and B_k are matrices with variable elements which change as k changes.

G is called a D-mapping on $D \times D$ iff $(I - A_k)^{-1}$ exists

$\forall k$ and $(I - A_k)^{-1}B_k$ is a D-matrix.

The following theorem may now be proved.

Theorem: 2 In (8) if G is a D-mapping and $x = x^* \in D$, then the scheme of iteration converges to x^* if $\lim_{k \rightarrow \infty} |\omega_k| = 0$. Furthermore, if

$\rho \left\{ |(I - A_k)^{-1}B_k| \right\} < 1, \forall k > K, x^*$ is the unique root in D ($\rho(A)$ = spectral radius of a matrix A).

Proof:

$$\begin{aligned} x^{k+1} - x^* &= \omega^k + G(x^{k+1}, x^k) - G(x^*, x^*) \\ &= \omega^k + A_k(x^{k+1} - x^*) + B_k(x^k - x^*) \end{aligned} \quad (20)$$

Let $C_k = (I - A_k)^{-1}$ and $E_k = (I - A_k)^{-1}B_k$. Then from (20)

$$\begin{aligned} x^{k+1} - x^* &= C_k \omega^k + E_k(x^k - x^*) \\ &= \sum E_k E_{k-1} \dots C_j \omega^j + E_k E_{k+1} \dots E_1 (x^0 - x^*) \\ &= (E_k E_{k-1} \dots E_{k_0+1}) \sum_{j=1}^{k_0} (E_{k_0} E_{k_0-1} \dots E_{j+1}) C_j \omega^j \\ &\quad + \sum_{j=k_0+1}^k (E_k E_{k-1} \dots E_{j+1}) C_j \omega^j + E_k E_{k-1} \dots E_1 (x^0 - x^*) \end{aligned}$$

Now $\lim_{k \rightarrow \infty} |\omega^k| = 0$ implies for some $k > k_0 + 1, |\omega^k| < \epsilon$ (ϵ is positive and arbitrarily small). Thus each element ω_j^k is arbitrarily small in absolute value. Also, E_k being a D-matrix

$$\lim_{k \rightarrow \infty} E_k E_{k-1} \dots E_1 = 0$$

and $\lim_{k \rightarrow \infty} E_k E_{k-1} \dots E_{k_0+1} = 0$. Hence, $|x^{k+1} - x^*| < \epsilon$ which establishes convergence.

To prove uniqueness we assume $y^* \in D$ is another root. Then

$$x^* - y^* = G(x^*, y^*) - G(y^*, y^*)$$

This gives

$$x^* - y^* = E_* (x^* - y^*)$$

where $\lim_{k \rightarrow \infty} E_k = E_*$. Thus, $(I - |E_*|) |x^* - y^*| \leq 0$. Since $\rho(|E_k|) < 1 \forall k > K$, $\rho(|E_*|) < 1$. Hence, by Neumann's lemma, $(I - |E_*|)^{-1}$ exists and is non-negative. Hence $|x^* - y^*| \leq 0$ which implies $x^* = y^*$.

More discussions on D-matrices and D-mappings are given in [15].

4. Some Comparison with Other Methods

Implicit methods for solving differential equations usually demonstrate better stability properties than most explicit algorithms. When a system of nonlinear differential equations is reduced to a nonlinear difference system, various iterative schemes are available for numerical solution. The simplest methods involve functional iterative schemes (Jacobi or Gauss-Seidel iterations) which have generally very slow rates of convergence. Newton's method has a quadratic rate of convergence which may be expressed as:

$$\|x^{k+1} - x^*\| = \alpha \|x^k - x^*\|^2$$

This immediately implies that even if $0 < \alpha < 1$, if $\|x^0 - x^*\| > 1$, the method could fail. Thus one basic requirement is that the initial guess x^0 should be sufficiently close to the actual root x^* . This implies $\|x^0 - x^*\| < 1$. For many initial-value problem this condition could be satisfied. However the main disadvantage is that at each k level of iteration and for each iterate x^k a unique Jacobian must be computed which is not quite practical and for large systems such computations are very expensive.

The present method may be expressed as a combination of nonlinear Gauss-Seidel iterations and Lieberstein's method as follows:

$$x_j^{k+1/2} = G_j(x_1^{k+1}, x_2^{k+1}, \dots, x_{j-1}^{k+1}, x_j^k, \dots, x_n^k)$$

$$x_j^{k+1} = x_j^{k+1/2} - \frac{f_j(x_1^{k+1}, x_2^{k+1}, \dots, x_{j-1}^{k+1}, x_j^{k+1/2}, x_{j+1}^k, \dots, x_n^k)}{[\partial f_j / \partial x_j]_{x_1^{k+1}, x_2^{k+1}, \dots, x_{j-1}^{k+1}, x_j^{k+1/2}, x_{j+1}^k, \dots, x_n^k}}$$

$j = 1, 2, \dots, n; k = 0, 1, 2, \dots$

Thus if r_1 is the rate of convergence of Gauss-Seidel iteration and r_2 is the rate of convergence of Lieberstein's method, the rate of convergence of the present scheme is $r_1 r_2$. Also, if at each level Lipschitz condition is satisfied, combining both steps it may be seen:

$$\|x^{k+1} - x^*\| = \beta^2 \|x^k - x^*\|$$

where $0 \leq \beta < 1$. Since β^2 goes to zero at a quadratic speed, the method converges even if $\|x^0 - x^*\| > 1$. For various nonlinear systems this global convergence property has been verified computationally [14].

Furthermore, whereas Newton's method requires $(n^2 + n)$ functionals to be computed at each iteration level, only $3n$ functionals are computed at each iteration level by the present method. Also, to compute a Jacobian ($n \times n$), n^2 elements must be stored and a total number of N arithmetic operations (addition, subtraction, multiplication) must be done where $N = n![2 + 1/2! + 1/3! + \dots + 1/(n-1)!]$. In comparison with this the present method computes and stores n -diagonal elements of the Jacobian.

There are certain interpolatory methods available to solve stiff ODE's [9]. These algorithms, developed by Certainé and Jain reduce differential equations into integral equations which were integrated by approximating the integrands by interpolation polynomials over the range of integration. Although both of these methods have high accuracy and are A-stable, for large systems they are not practical.

The present method, having a simple algorithm, is applicable to most nonlinear systems in general. It can be applied to nonlinear integral equations or integro-differential equations. Some applications with regard to this are given in [12].

5. Applications to Nonlinear Stiff ODE's

Ex: 1 $\dot{x} = 50/x - 50x$, $x(0) = \sqrt{2}$

The analytical solution is $x(t) = \sqrt{1 + \exp(-100t)}$. To solve this stiff ODE we approximate \dot{x} by a backward difference formula

$$x_j = x_{j-1} + \Delta t(50/x_j - 50x_j)$$

If we replace x_j by x and x_{j-1} by x_0 we get

$$x = \Delta t(50/x - 50x) + x_0$$

Then, $g(x) = \Delta t(50/x - 50x) + x_0$

Also,

$$g(x^k) - g(x^*) = -50 \Delta t \left(\frac{1}{x^k x^*} + 1 \right) (x^k - x^*)$$

where x^* = the value of the root and x^k = value of x at some kth iteration.

Writing $g(x^k) - g(x^*) = a_k(x^k - x^*)$, we note that a_k is a D-element if $\Delta t < 10^{-3}$. However, if we define a new

$$g(x) = x + \alpha((\Delta t(50/x - 50x) + x_0) - x)$$

Then,

$$a_k = (1 - \alpha) - 50 \alpha \Delta t \left(\frac{1}{x^* x^k} + 1 \right)$$

and a_k is a D-element if α is sufficiently small and positive.

Computationally, it has been found that for $\alpha = 1.0$ and $\Delta t = 10^{-1}$ the method failed, whereas for $\alpha = 10^{-6}$ and $\Delta t = 10^3$ it did not.

Ex: 2

$$\dot{x} = -10004 x + 10000 y^4$$

$$\dot{y} = -y + x - y^4$$

$$x(0) = y(0) = 1$$

This system of stiff ODE's is given in [3]. It has an approximate analytical solution given by

$$y = \left[\frac{10004 e^{-3t}}{10008 - 4 e^{-3t}} \right]^{1/3}$$

$$x = \frac{10000}{10004} y^4$$

Using backward Euler's difference scheme, this nonlinear system may be expressed as:

$$x_j = \Delta t(-10004 x_j + 10000 y_j^4) + x_{j-1}$$

$$y_j = \Delta t(-y_j + x_j - y_j^4) + y_{j-1}$$

$$x_0 = y_0 = 1$$

Replacing x_j by x , y_j by y , x_{j-1} by x_0 and y_{j-1} by y_0 , we get:

$$x = \Delta t(-10004 x + 10000 y^4) + x_0$$

$$y = \Delta t(-y + x - y^4) + y_0$$

Let us express the system as $x = F(x,y)$ and $y = G(x,y)$; where

$$F(x,y) = x + \alpha_1 \{ \Delta t(-10004 x + 10000 y^4) + x_0 - x \}$$

$$G(x,y) = y + \alpha_2 \{ \Delta t(-y + x - y^4) + y_0 - y \}$$

At some $(k+1)$ iteration level:

$$x^{k+1} - x^* = b_{11}(x^k - x^*) + b_{12}(y^k - y^*)$$

$$y^{k+1} - y^* = a_{21}(x^{k+1} - x^*) + b_{22}(y^k - y^*)$$

where

$$b_{11} = 1 - \alpha_1 - 10004 \Delta t \alpha_1$$

$$b_{12} = 10000 \Delta t \alpha_1 (y^2 + y^{*2})(y + y^*)$$

$$a_{21} = \Delta t \cdot \alpha_2$$

$$b_{22} = 1 - \alpha_2 - \Delta t \alpha_2 (y^2 + y^{*2})(y + y^*)$$

From (19),

$$A_k = \begin{bmatrix} 0 & 0 \\ a_{21} & 0 \end{bmatrix}, \quad B_k = \begin{bmatrix} b_{11} & b_{12} \\ 0 & b_{22} \end{bmatrix}$$

Here

$$E_k = (I - A_k)^{-1} B_k = \begin{bmatrix} b_{11} & b_{12} \\ -a_{21} b_{11} & -a_{21} b_{12} + b_{22} \end{bmatrix}$$

Case: 1 Transient solutions

Choosing $\alpha_1 = \alpha_2 = 0.1$ and $\Delta t = 0.005$ results obtained by using perturbed functionals have been presented in table 5.

Case: 2 Steady-State solution

If the objective is to compute solutions at the steady state, variable time steps may be used and Δt could be very large. Using a sequence of $\Delta t = 1, 10, 10^2, 10^3 \dots 10^8$ it has been found that after a total of 55 iterations steady state solutions were found using Radio Shack TRS-80 color microcomputer (16K). Computational time was about one minute with x's converging to zero faster than y's. Newton's method did not show this mode of convergence.

Chemical Kinetic Models.

Magee and Chatterjee [4] developed models on chemical kinetics and sought solutions of these problems which should be time-accurate. These models are nonlinear and consist of a sequence of stiff ODE's. Some of these chemical species grow from a concentration of 10^{-30} moles/liter at $t = 10^{-6}$ sec to 10^{-8} moles/liter at $t = 1.0$ sec; whereas by the same time certain other species which have values of the order 10^{-15} moles/liter at

$t = 10^{-6}$ sec grow up to 10^{-8} moles/liter at $t = 1.0$ and stay almost unchanged. Since the equations are stiff, in the transient process numerical effects of some components of the solution which decay much faster in comparison with other components are quite difficult to capture in a computational process. This leads to some inaccuracies in the solution which eventually causes instabilities. For example, if the concentration of a species is found to be -10^{-35} mole/liter but whose true concentration is 10^{-30} moles/liter, this causes severe instabilities. In such computations which are very "sensitive" with regard to small errors, principles of perturbations could be applied in order to stabilize the algorithm. Indeed this was the finding when two distinct chemical kinetics problems were solved by the method. Let us consider them, and discuss some of the very interesting computational findings verified by actual experiments.

Models representing irradiation of water with γ -rays have been considered. Two conditions for water were taken (i) Acid Water and (ii) Pure Water.

Ex 3: Irradiation of Acid Water

The γ -radiation energy is absorbed with the creation of molecular (H_2 , H_2O_2) and radical (H, OH) products which may be treated as if formed homogeneously in the system. The mechanisms related to formations of these species are described in [5,6]. Seven species created by the radiation participate in thermal reactions, summarized in Table 1. If the irradiation is continuous at the rate of 100 I's electron volts per liter per sec, the differential equations which describe the concentration changes are given in Table 2. These equations are stiff. Here creation terms give concentrations of created species in terms of moles per liter per second.

The system described in Table 2 may be expressed as:

$$\frac{dx}{dt} = f(x)$$

where $x = [(H) (OH) (H_2O) (H_2) (H_2O_2) (HO_2) (O_2)]^T$ and $f = [f_1 f_2 \dots f_7]^T$

where f_1 corresponds to the right side of the first equation, f_2 corresponds to the right side of the second equation, etc. Applying a backward Euler-difference scheme we get

$$x^{n+1} - x^n - hf(x^{n+1}) = 0, \quad h = \Delta t$$

This nonlinear system for x^{n+1} may now be expressed as:

$$F(X) = 0$$

where $X = x^{n+1}$ which could be put in the form as

$$X = G_o(X)$$

where $G_o(X) = X + \alpha \cdot F(X)$ and $\alpha = \text{diag}(\alpha_1, \alpha_2, \dots, \alpha_7)$. As discussed in the Ex: 1, 2, $0 < \alpha_j \leq 1$.

A numerical solution is found for continuous irradiation at constant rate which starts with the molecular concentrations of H_2 , H_2O_2 and O_2 equal to zero. For this case the radical concentrations approach "stationary values" very quickly and as known from the chemical nature of the system that H_2 and H_2O_2 are destroyed in a chain reaction, these concentrations which build up linearly at first, approach stationary values on a longer time scale. Computational results showed these behaviors of various concentrations of this complicated chemical process. Figures 1, 2, 3 show these results for various values of I . (More results on this project will be published from Lawrence Berkeley Lab.) From "zero" values, H and OH quickly approached 2×10^{-8} and 2.5×10^{-8} , respectively, in 0.2 sec and then slowly decreased attaining "stationary values" at time equal to 1 sec. However, H_2 , H_2O_2 , HO_2 and O_2 attain their stationary values after almost 15 sec.

Chatterjee and Magee [4] applied an implicit second-order Runge-Kutta method to solve this problem and recorded its failure.

Ex: 4 Irradiation of Pure Water

The treatment of pure water is somewhat more complicated simply because it involves more species. Here H^+ is so low in concentration that the hydrated electrons are not converted into H atoms before the track reactions occur and charged species must be treated explicitly. There are eleven equations giving the rates of change of concentrations of eleven species. In Table 3, the thermal reactions and in Table 4 the differential equations of the system are given. Continuous irradiation starting with zero decompositions for all concentrations of species excepting $H_2O = 55$ moles/liter, $H_3O^+ = 1.0E - 07$ moles/liter and $OH^- = 1.0E - 07$ moles/liter was done. At this stage, the ODE's were represented as integral equations which were approximated by trapezoidal rule. The method virtually failed when the derivatives were approximated by backward Euler's difference formula. In the code a very stringent convergence criterion, namely,

$$WMAX = \max_j |\omega_j^k| < 10^{-20}$$

was used. Since this should give a very high order of accuracy, it was felt that such a criterion is necessary in order to get an almost perfect "mass balance" and "charge balance" both of which should be (theoretically) equal to "zero" at all times. In submicroseconds, the radical species like H, OH, e_{Aq}^- etc. grow much more rapidly than the molecular species O_2 , O_2^- , H_2 , H_2O_2 . These have strong impact upon the mathematical model for the subsequent chemical yields. Thus $\Delta t = 10^{-8}$ was chosen initially. It was noticed that while all other species were growing, O_2 and O_2^- stayed zero up to 5×10^{-8} sec. Then O_2^- grew faster and $O_2^- > O_2$ at all time levels. These computational

properties of these species which possibly have some strong impact upon the solution as time increases, cannot be detected if a large time step is used.

In Fig. 4 we see the transient stages of the growths of some of the species up to 10^{-1} sec. Up to this stage H_3O^+ and OH^{-1} did not show any changes from their initial concentrations. However in Fig. 5 some noticeable changes of their values were found around $t = 1.0$ sec. The values of these concentrations seem to be in agreement with those known both theoretically and experimentally.

In Fig. 6 we see all the species reaching steady-state around $t = 30$ secs.

For a further checking of the validity of these computational results an additional computer-run was taken with an initial value of $\text{H}_2\text{O}_2 = 10^{-4}$. These should cause a faster growth of O_2 , one of the most sensitive species, and its steady-state-concentration should be identically the same as that of H_3O^+ . This vital aspect of the chemical reaction process is clearly depicted in Fig. 7. Also it was noticed that whereas O_2 should increase H_2O_2 must decrease and both should merge at a steady-state configuration. This result, as evidenced by experiment, was also found computationally.

6. Discussions

From equation (12) it is clear that if $\partial_j G_j^{k+1,k} = 1$, the method fails. It has been proved and demonstrated in [14], that the perturbation parameters ω_j^k stabilize the algorithm and speed up the rate of convergence provided the Jacobian of the matrix representation of the system has nonzero diagonal elements. When diagonal terms are null, artificially they are brought in and are damped out as convergence is approached. This may be called nonlinear scaling. However, if diagonal elements are zeros and nonlinear scaling is not performed the rate of convergence is significantly decreased and the

algorithm could even be destabilized. This was found with regard to solution of several problems. The essential strength of the method lies in having functionals with diagonal nonlinearity. Fortunately, the set of equations given in Table 2 and Table 4 fulfill these requirements.

By computer experimentation it has been found that for nonlinear systems having multiple roots, the present scheme is not quite effective.

Although on a trial basis this method can be applied to solve a nonlinear system, it may be useful to apply the properties of D-Mappings to the functionals G_j in order that the method may be applied successfully [8,15]. Such an analysis is generally quite complicated.

7. Concluding Remarks

This is a preliminary report. The objective with regard to the solution of the chemical kinetic problem was primarily to study the treatment growths of the species, not the final equilibrium values which were somewhat known to the chemists [4] through experimental data. With this regard, the present method served the purpose of the researchers very well.

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Suggestions received from Dr. Lomax and Dr. Vinokur for betterment of this article are acknowledged with thanks.

My ten-year-old son Charlie Dey wrote codes in TR580 color computers and worked with great dedication on the chemical kinetic problems.

The graphs were all drawn at Lawrence Berkeley Lab. Dr. Chatterjee and Dr. Magee of LBL explained the nature of the chemical reaction problems to me.

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Table 1: Reactions in Irradiated Water (Acid)

Reactions	Reaction rate constant, ℓ/(mol s)
A. Recombination of Primary Radicals	
1. $\text{H} + \text{H} \rightarrow \text{H}_2$	1×10^{10}
2. $\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$	2.4×10^{10}
3. $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$	4×10^9
B. Reactions of Radicals and Product Molecules	
4. $\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH}$	1×10^8
5. $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	5×10^7
6. $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	6×10^7
7. $\text{HO}_2 + \text{H} \rightarrow \text{H}_2\text{O}_2$	1×10^{10}
8. $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	1×10^{10}
9. $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	2×10^6
10. $\text{H} + \text{O}_2 \rightarrow \text{HO}_2$	1×10^{10}

Table 2: Differential Equations for Transient Species
and Radiation Products in Irradiated Water (Acid)

$$\frac{d}{dt} (\text{H}) = 3.71\text{I} - 2k_1(\text{H})^2 - k_2(\text{H})(\text{OH}) - k_4(\text{H})(\text{H}_2\text{O}_2) + k_6(\text{OH})(\text{H}_2) - k_7(\text{HO}_2)(\text{H}) - k_{10}(\text{H})(\text{O}_2)$$

$$\frac{d}{dt} (\text{OH}) = 2.95\text{I} - k_2(\text{H})(\text{OH}) - 2k_3(\text{OH})^2 + k_4(\text{H})(\text{H}_2\text{O}_2) - k_5(\text{OH})(\text{H}_2\text{O}_2) - k_6(\text{OH})(\text{H}_2) - k_8(\text{HO}_2)(\text{OH})$$

$$\frac{d}{dt} (\text{H}_2\text{O}) = -4.51\text{I} + k_2(\text{H})(\text{OH}) + k_4(\text{H})(\text{H}_2\text{O}_2) + k_5(\text{OH})(\text{H}_2\text{O}_2) + k_6(\text{OH})(\text{H}_2) + k_8(\text{HO}_2)(\text{OH})$$

$$\frac{d}{dt} (\text{H}_2) = 0.40\text{I} + k_1(\text{H})^2 - k_6(\text{OH})(\text{H}_2)$$

$$\frac{d}{dt} (\text{H}_2\text{O}_2) = 0.78\text{I} + k_3(\text{OH})^2 - k_4(\text{H})(\text{H}_2\text{O}_2) - k_5(\text{OH})(\text{H}_2\text{O}_2) + k_7(\text{HO}_2)(\text{H}) + k_9(\text{HO}_2)^2$$

$$\frac{d}{dt} (\text{HO}_2) = k_5(\text{OH})(\text{H}_2\text{O}_2) - k_7(\text{HO}_2)(\text{H}) - k_8(\text{HO}_2)(\text{OH}) - 2k_9(\text{HO}_2)^2 + k_{10}(\text{H})(\text{O}_2)$$

$$\frac{d}{dt} (\text{O}_2) = k_8(\text{HO}_2)(\text{OH}) + k_9(\text{HO}_2)^2 - k_{10}(\text{H})(\text{O}_2)$$

The range of integration is from 0 sec to 20 sec.

Table 3: Reactions in Irradiated Neutral Water

Reactions	Reaction rate constant $\lambda / (\text{mol s})$
A. Recombination of Primary Radicals	
1. $\text{H} + \text{H} \rightarrow \text{H}_2$	1×10^{10}
2. $e_{\text{Aq}}^- + \text{H} \rightarrow \text{H}_2 + \text{OH}^-$	2.5×10^{10}
3. $e_{\text{Aq}}^- + e_{\text{Aq}}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	6×10^9
4. $e_{\text{Aq}}^- + \text{OH} \rightarrow \text{OH}^-$	3×10^{10}
5. $\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$	2.4×10^{10}
6. $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$	4×10^9
7. $\text{H}_3\text{O}^+ + e_{\text{Aq}}^- \rightarrow \text{H}$	2.3×10^{10}
8. $\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$	3×10^{10}
B. Reactions of Radicals with Product Molecules	
9. $\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH}$	1×10^8
10. $e_{\text{Aq}}^- + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}^-$	1.2×10^{10}
11. $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	5×10^7
12. $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	6×10^7
13. $\text{HO}_2 + \text{H} \rightarrow \text{H}_2\text{O}_2$	1×10^{10}
14. $e_{\text{Aq}}^- + \text{O}_2 \rightarrow \text{O}_2^-$	1.9×10^{10}

Table 3: Reactions in Irradiated Neutral Water
(cont.)

Reactions	Reaction rate constant $\ell/(\text{mol s})$
B. Reactions of Radicals with Product Molecules (cont.)	
15. $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	1×10^{10}
16. $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	2×10^6
17. $\text{H} + \text{O}_2 \rightarrow \text{HO}_2$	1×10^{10}
18. $\text{O}_2^- + \text{H}_3\text{O}^+ \rightarrow \text{HO}_2 + \text{H}_2\text{O}$	3×10^{10}
C. Dissociation Reactions	
19. $\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}$	$5.5 \times 10^{-6*}$
20. $\text{HO}_2 \rightarrow \text{H}_3\text{O}^+ + \text{O}_2^-$	$1 \times 10^6*$

*Rate constant, sec^{-1}

Table 4: Differential Equations for Transient Species and Radiation Products in Irradiated Neutral Water

$\frac{d(H)}{dt}$	$= - 2k_1(H)^2 - k_2(e^-_{Aq})(H) - k_5(H)(OH) + k_7(H_3O^+)(e^-_{Aq}) - k_9(H)(H_2O_2) + k_{12}(OH)(H_2)$ $- k_{13}(HO_2)(H) - k_{17}(H)(O_2)$	+ 0.55 I
$\frac{d}{dt}(e^-_{Aq})$	$= - k_2(e^-_{Aq})(H) - 2k_3(e^-_{Aq})^2 - k_4(e^-_{Aq})(OH) - k_7(H_3O^+)(e^-_{Aq}) - k_{10}(e^-_{Aq})(H_2O_2) - k_{14}(e^-_{Aq})(O_2)$	+ 2.65 I
$\frac{d}{dt}(OH)$	$= - k_4(e^-_{Aq})(OH) - k_5(H)(OH) - 2k_6(OH)^2 + k_9(H)(H_2O_2) + k_{10}(e^-_{Aq})(H_2O_2) - k_{11}(OH)(H_2O_2)$ $- k_{12}(OH)(H_2) - k_{15}(HO_2)(OH)$	+ 2.70 I
24 $\frac{d}{dt}(H_3O^+)$	$= - k_7(H_3O^+)(e^-_{Aq}) - k_8(H_3O^+)(OH^-) - k_{18}(H_3O^+)(O_2^-) + k_{19}(H_2O) + k_{20}(HO_2)$	+ 2.65 I
$\frac{d}{dt}(H_2O)$	$= k_5(H)(OH) + k_8(H_3O^+)(OH^-) + k_9(H)(H_2O_2) + k_{11}(OH)(H_2O_2) + k_{12}(OH)(H_2) + k_{15}(HO_2)(OH)$ $+ k_{18}(H_3O^+)(O_2^-) - k_{19}(H_2O)$	- 4.10 I
$\frac{d}{dt}(H_2)$	$= k_1(H)^2 + k_2(e^-_{Aq})(H) + k_3(e^-_{Aq})^2 - k_{12}(OH)(H_2)$	+ 0.45 I
$\frac{d}{dt}(H_2O_2)$	$= k_6(OH)^2 - k_9(H)(H_2O_2) - k_{10}(e^-_{Aq})(H_2O_2) - k_{11}(OH)(H_2O_2) + k_{13}(HO_2)(H) + k_{16}(HO_2)^2$	+ 0.70 I

Table 4: Differential Equations for Transient Species and
Radiation Products in Irradiated Neutral Water
(cont.)

$$\frac{d}{dt} (\text{OH}^-) = k_2(e^-_{\text{Aq}})(\text{H}) + 2k_3(e^-_{\text{Aq}})^2 + k_4(e^-_{\text{Aq}})(\text{OH}) - k_8(\text{H}_3\text{O}^+)(\text{OH}^-) + k_{10}(e^-_{\text{Aq}})(\text{H}_2\text{O}_2) + k_{19}(\text{H}_2\text{O})$$

$$\frac{d}{dt} (\text{HO}_2) = k_{11}(\text{OH})(\text{H}_2\text{O}_2) - k_{13}(\text{HO}_2)(\text{H}) - k_{15}(\text{HO}_2)(\text{OH}) - 2k_{16}(\text{HO}_2)^2 + k_{17}(\text{H})(\text{O}_2) + k_{18}(\text{H}_3\text{O}^+)(\text{O}_2^-) - k_{20}(\text{HO}_2)$$

$$\frac{d}{dt} (\text{O}_2) = -k_{14}(e^-_{\text{Aq}})(\text{O}_2) + k_{15}(\text{HO}_2)(\text{OH}) + k_{16}(\text{HO}_2)^2 - k_{17}(\text{H})(\text{O}_2)$$

$$\frac{d}{dt} (\text{O}_2^-) = k_{14}(e^-_{\text{Aq}})(\text{O}_2) - k_{18}(\text{H}_3\text{O}^+)(\text{O}_2^-) + k_{20}(\text{HO}_2)$$

Table 5

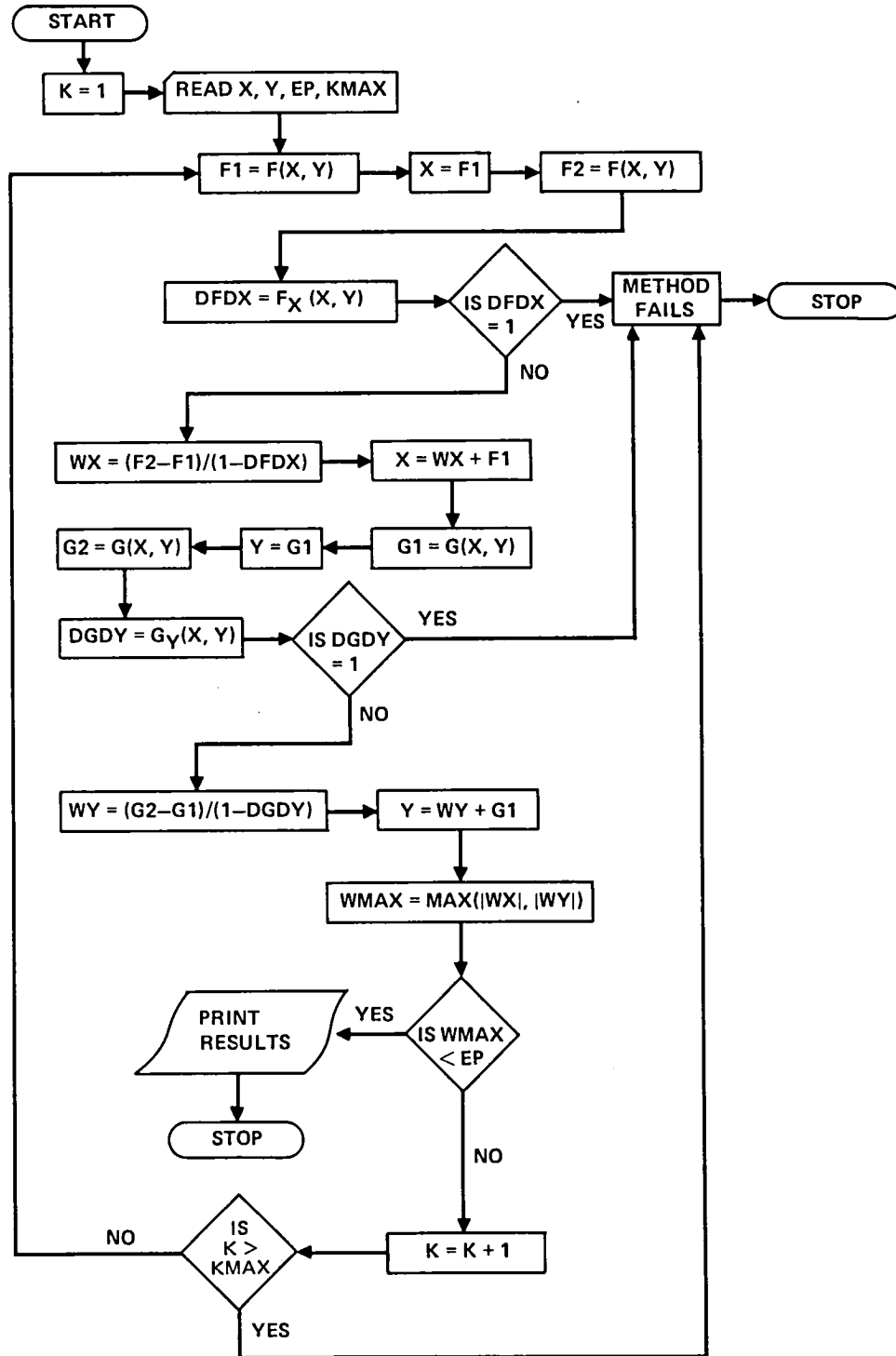
$\Delta t = 0.005$, $k =$ No. of iterations for convergence at a given time step.

t	Exact Solution		Dey		k
	x	y	x	y	
0	1.0	1.0	1.0	1.0	0
0.25	0.368021198	0.778953673	0.368799110	0.779286476	5
0.50	0.135369435	0.606629568	0.136012224	0.607287244	4
0.75	0.049796505	0.472436166	0.050160955	0.473250544	3
1.00	0.0183185671	0.367930928	0.018499225	0.368797576	3
1.25	0.73174825E-03	0.286467519	6.82246374E-03	0.287398821	3
1.50	2.47909732E-03	0.223160237	2.516106E-03	0.223965900	3
1.75	9.12006087E-04	0.173797232	9.27933E-04	0.174533507	2
2.0	3.35507793E-04	0.13535337	3.42219E-04	0.136011530	2
2.25	1.23426334E-04	0.105413292	1.26209E-04	0.105991891	2
2.5	4.54059955E-05	0.0820959478	4.6546E-05	0.082598004	2

Appendix: A

A flow chart to solve: $X = F(X, Y)$, $Y = G(X, Y)$ using perturbed functionals.

Notations: F_x = Partial Derivative of F with respect to X
 G_y = Partial Derivative of G with respect to Y
 KMAX = Maximun No. of iterations
 EP = Epsilon
 WX = Perturbation applied to X
 WY = Perturbation applied to Y



Courtesy of Charlie Dey

Figure Captions

1. Figure 1. Concentrations of Species (Ex: 3) vs. time for $I = 6.667 \times 10^{-6}$ in the logarithmic scale.
2. Figure 2. Concentrations of Species (Ex: 3) vs. time for $I = 6.667 \times 10^{-7}$ in the logarithmic scale.
3. Figure 3. Concentrations of Species (Ex: 3) vs. time for $I = 6.667 \times 10^{-8}$ in the logarithmic scale.
4. Figure 4. Concentrations of Species (Ex: 4) vs. time for $I = 6.667 \times 10^{-7}$ in the logarithmic scale, up to $t = 3 \times 10^{-2}$ sec.
5. Figure 5. Concentrations of Species (Ex: 4) vs. time for $I = 6.667 \times 10^{-7}$ in the logarithmic scale up to $t = 3$ secs.
6. Figure 6. Concentrations of Species (Ex: 4) vs. time for $I = 6.667 \times 10^{-7}$ in the logarithmic scale up to $t = 30$ secs.
(Here steady state is reached for all the species.)
7. Figure 7. Concentrations of Species (Ex: 4) vs. time for $I = 6.667 \times 10^{-7}$ in the logarithmic scale up to $t = 30$ secs.
(Initial value of $H_2O_2 = 10^{-4}$ moles/liter.)

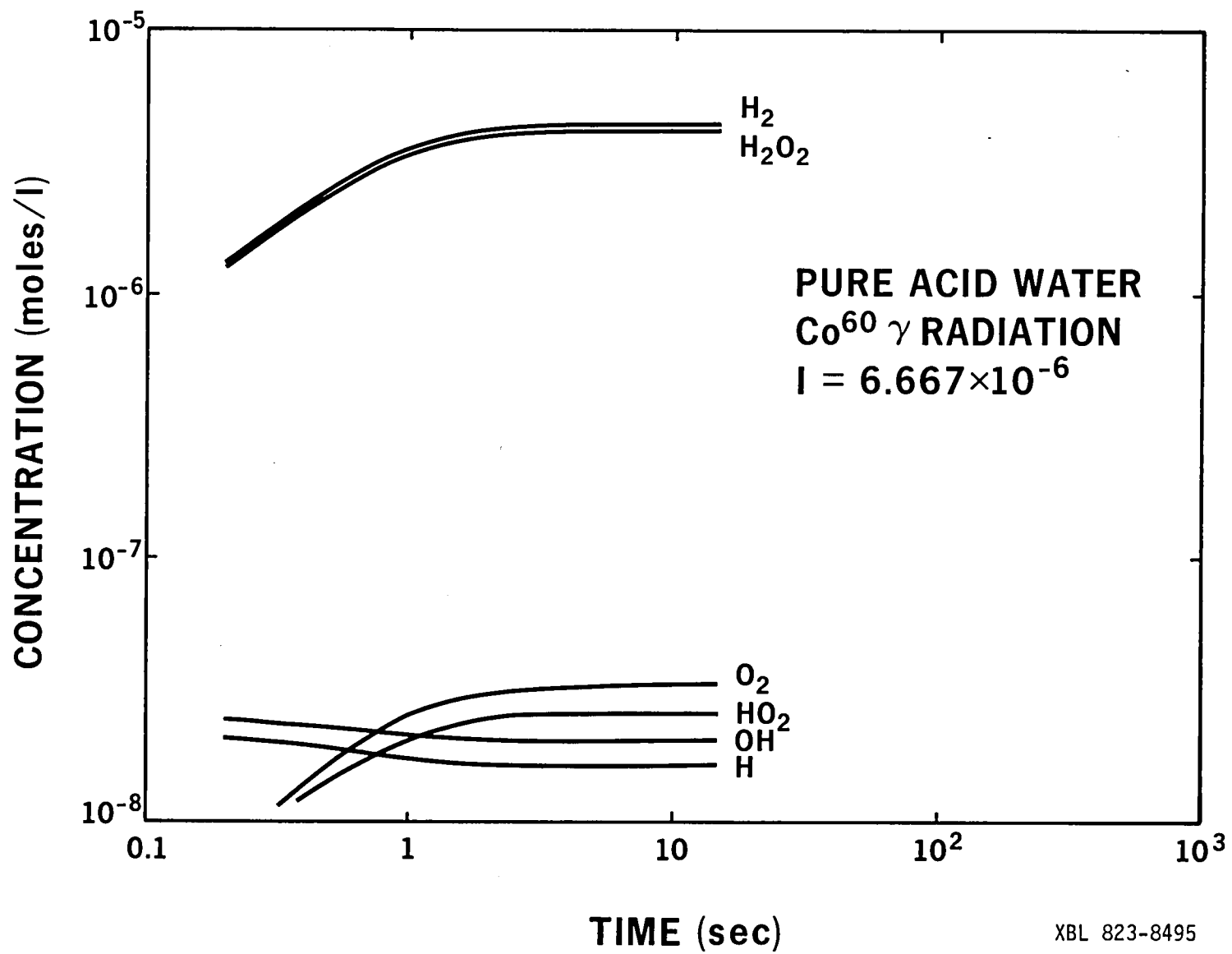


Fig. 1

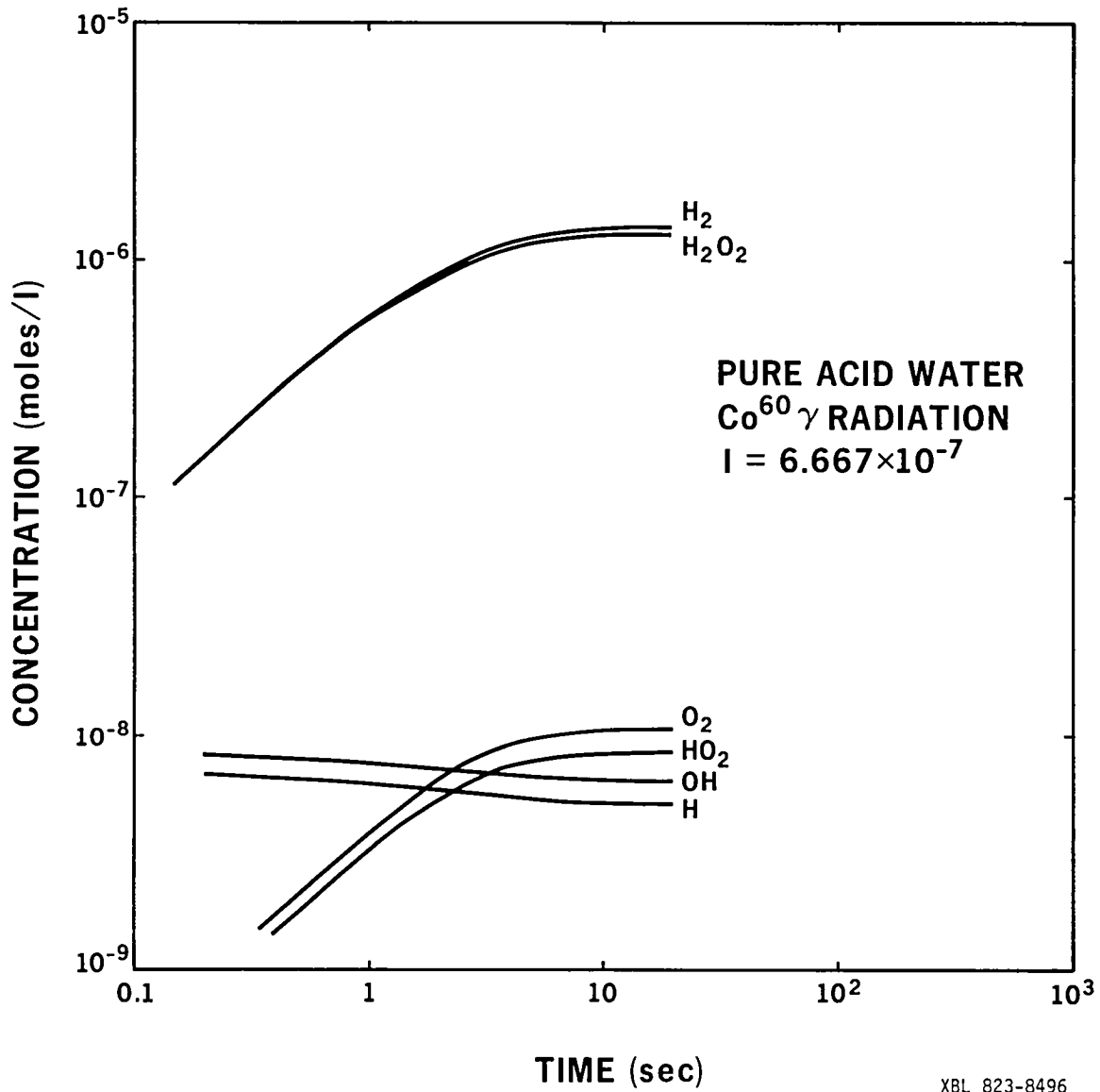


Fig. 2

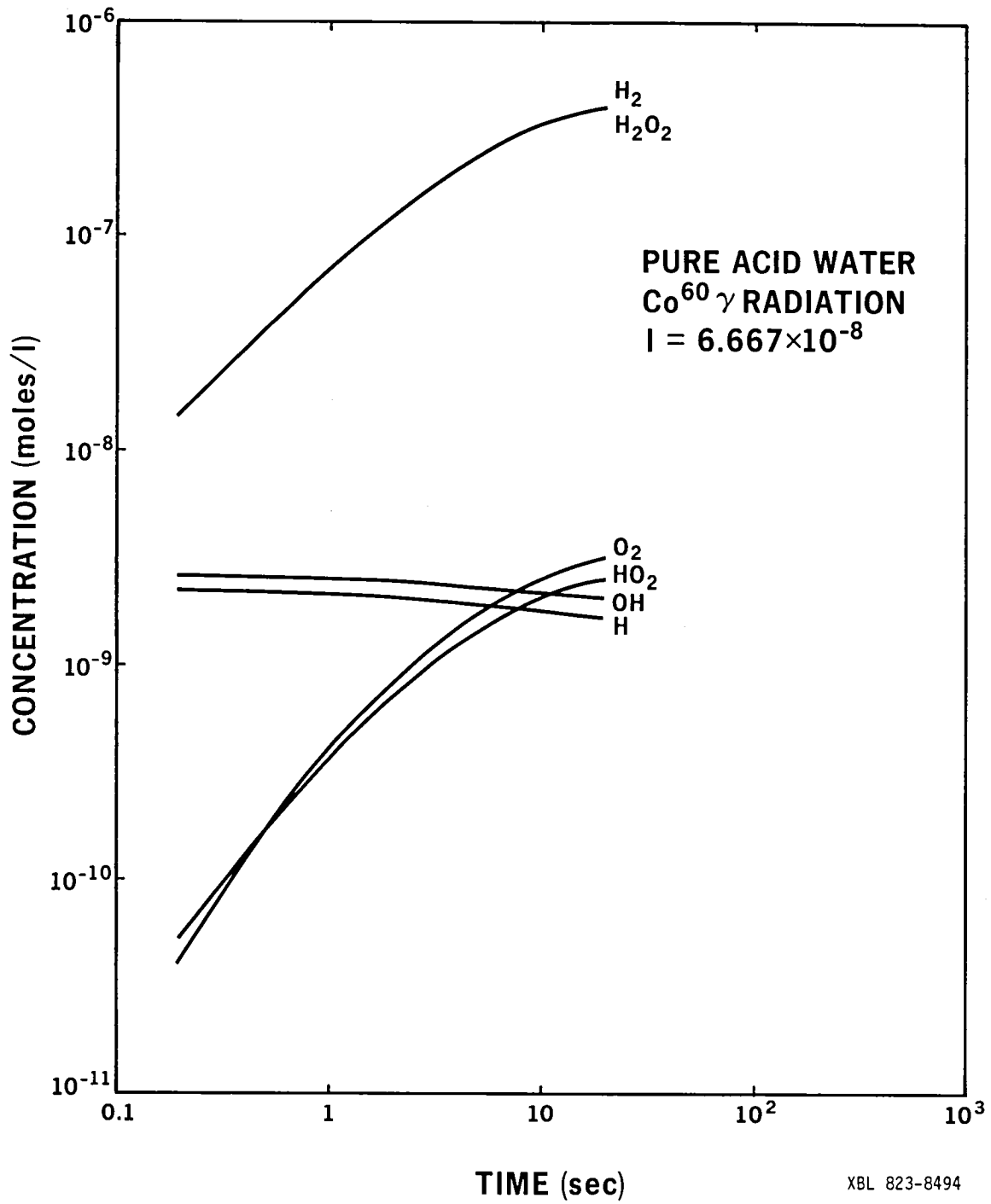
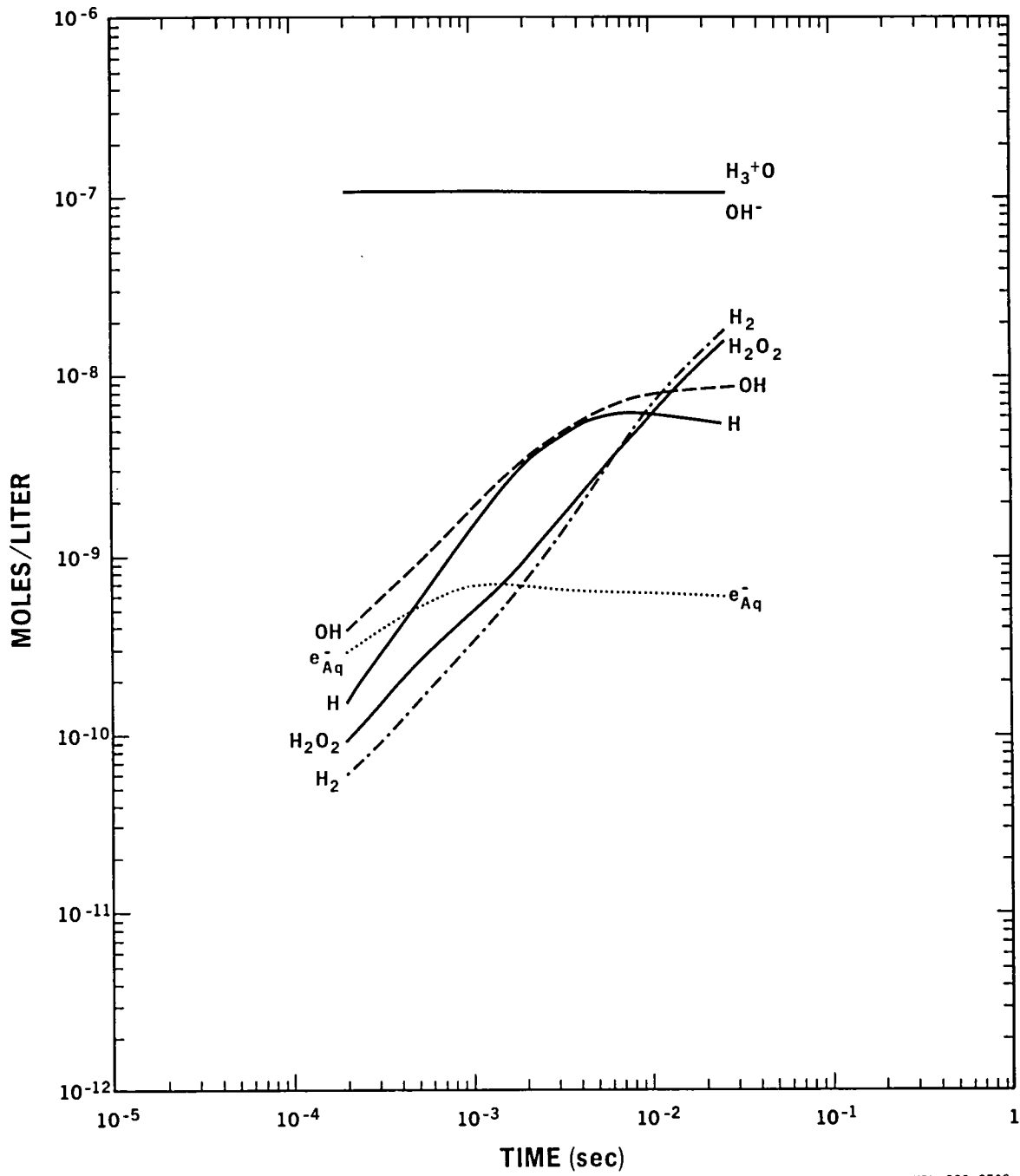


Fig. 3



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Fig. 4

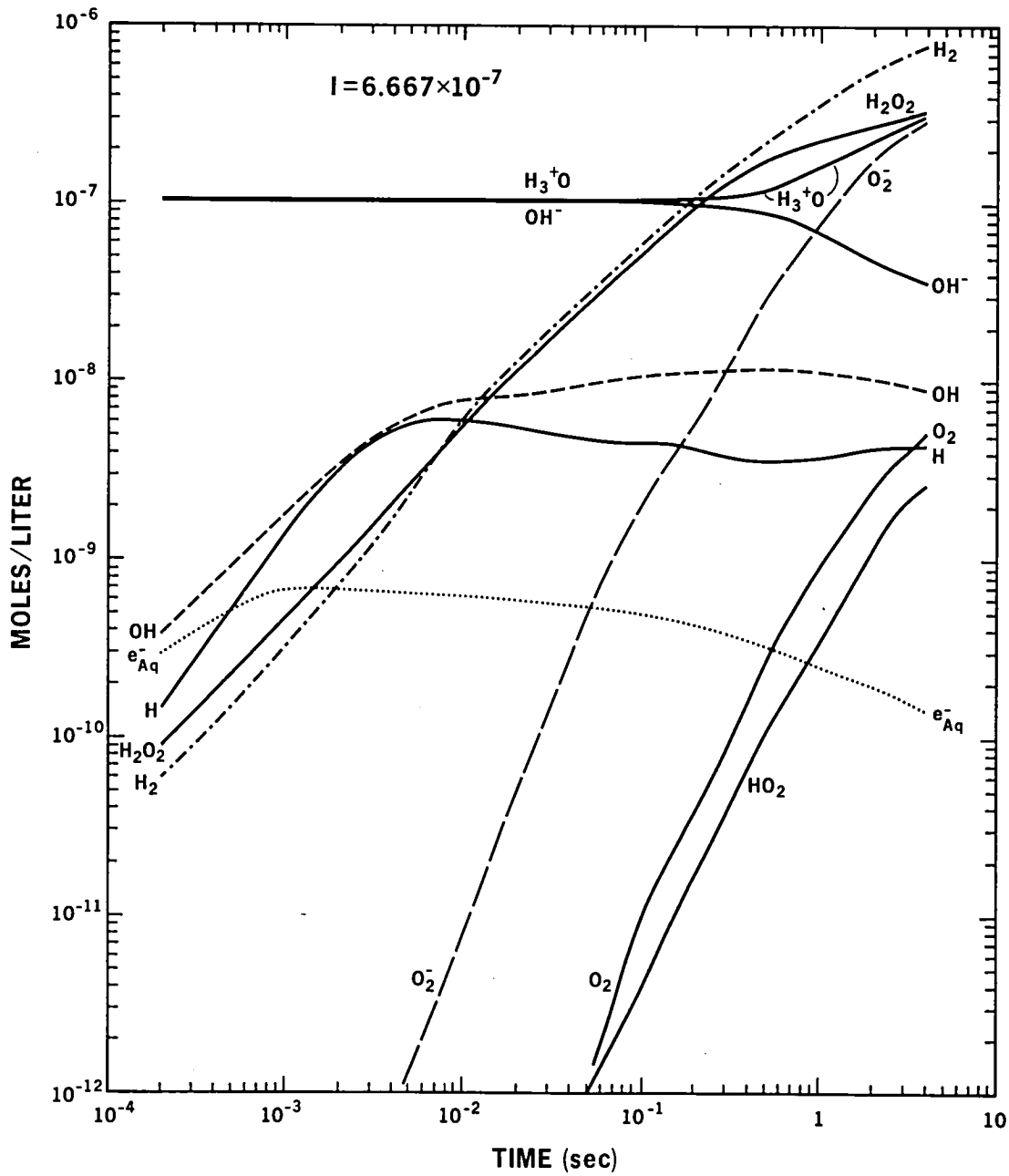


Fig. 5

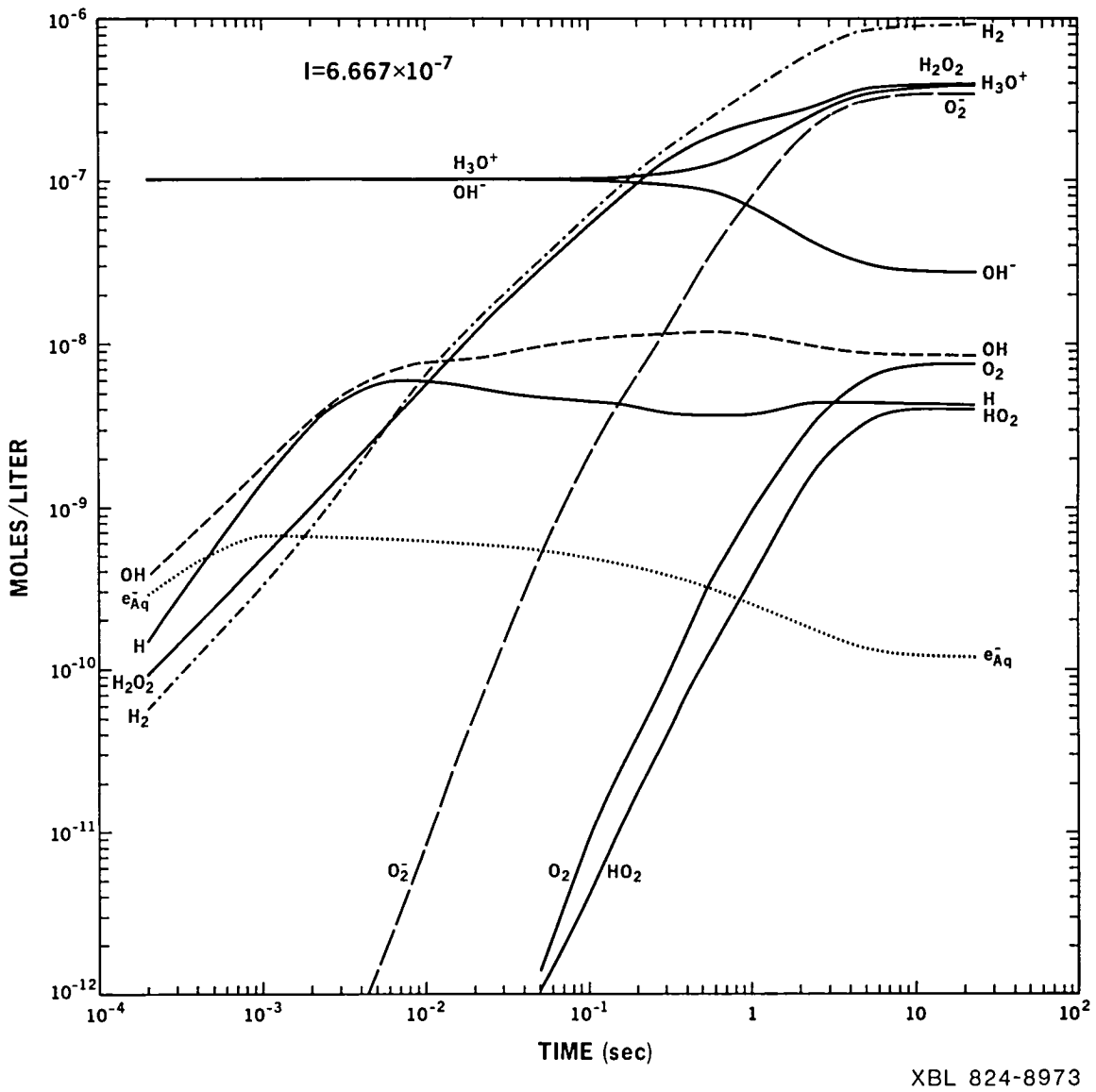
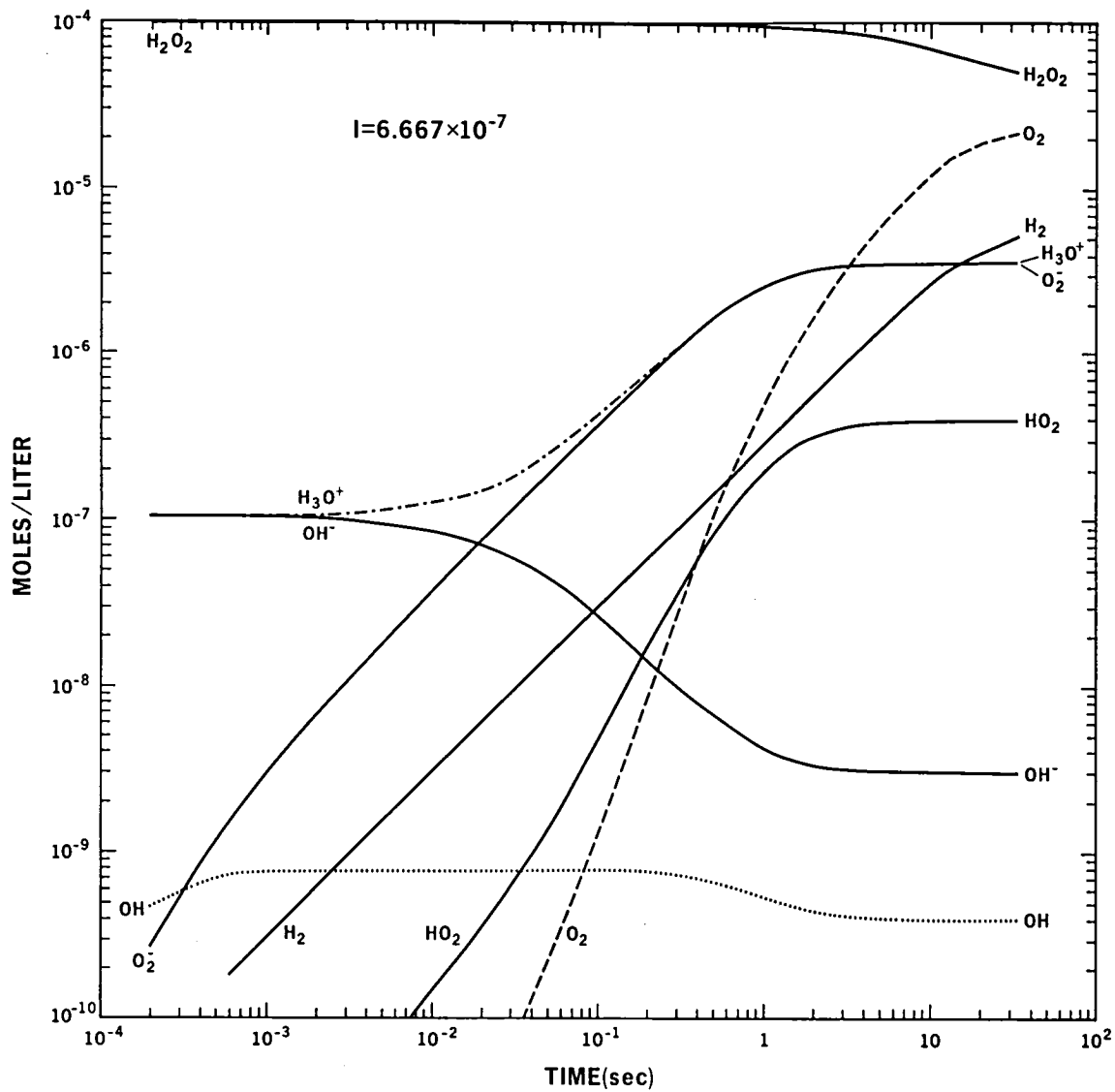


Fig. 6



XBL 824-9063

Fig. 7

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