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MATHEMATICAL FORMULATION, ANALYSIS, AND DESCRIPTION
OF THE FRICKE DIFFUSION KINETICS CODE

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ABSTRACT

Based on the classical theory of diffusion and reaction kinetics, the kinetics of radiation of chemical reactions in fluid systems is represented by a system of parabolic partial differential equations. A code for the solution of a mathematical model which allows up to two radicals and two solutes to be present simultaneously is devised; it gives the concentrations as functions of time and space, and the recombination integrals as functions of time. When the model is applied to water, the radicals may be thought of as H and OH, and the solutes as forming together a redox couple. The reactions are thought to be initiated either by a narrow beam of γ rays or α particles.

INTRODUCTION

Based on the classical theories of diffusion and reaction kinetics, the kinetics of radiation of chemical reactions in fluid systems can be represented by a system of simultaneous second-order partial differential equations.^{1,2,3} Over the last several years, the problem of solving these equations by numerical integration has been studied at the Argonne National Laboratory through cooperation between the divisions of Chemistry and Applied Mathematics. The simple case of a One Radical-One Solute model was first dealt with in footnotes 4, 5, and 6. In 1959 a study was begun on a Two Radicals-Two Solute model in which, when the model is applied to water, the radicals may be thought of as H and OH and the solutes as forming together a redox couple. As before, 1) the initial radical distribution functions were assumed to be Gaussians, characterised by spherical or

¹H. Fricke, *Ann. N. Y. Acad. Sci.*, 59, 567 (1955).

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⁴D. A. Flanders and H. Fricke, *J. Chem. Phys.*, 28, 1126 (1958).

⁵H. Fricke and D. L. Phillips, *J. Chem. Phys.*, 32, 1183 (1960).

⁶H. Fricke and D. L. Phillips, *J. Chem. Phys.*, 34, 905 (1961).

cylindrical symmetry; 2) secondary reactions were neglected. The model requires, then, the solution of four differential equations. The problem was programmed for the IBM 704. The object of this report is to give a detailed description of the technical procedure used in the programming process.

The radicals are called X_1 and X_2 , the solutes X_3 and X_4 . The reactions considered are

If we denote the concentrations of X_1 , X_2 , X_3 , and X_4 by n_1 , n_2 , n_3 , and n_4 respectively, the change in these concentrations per unit time is given by:

$$\frac{\partial n_i}{\partial t} = \frac{\partial^2 n_i}{\partial r^2} + \frac{\epsilon}{r} \frac{\partial n_i}{\partial r} - \begin{cases} 2 k_{11} n_1^2 + k_{12} n_1 n_2 + k_{13} n_1 n_3 & i=1 \\ 2 k_{22} n_2^2 + k_{12} n_1 n_2 + k_{24} n_2 n_4 & i=2 \\ k_{13} n_1 n_3 - k_{24} n_2 n_4 & i=3 \\ k_{24} n_2 n_4 - k_{13} n_1 n_3 & i=4 \end{cases}$$

where r is the distance from the center of symmetry, the k_{ij} are reaction rates, and

$$\epsilon = \begin{cases} 2 & \text{for spherical symmetry} \\ 1 & \text{for cylindrical symmetry} \end{cases}$$

The initial conditions are assumed to be

$$\begin{aligned} n_i(r,0) &= C_i e^{-r^2/b_i^2} \quad \text{where } C_i = N_0/(\sqrt{\pi} b_i)^{1+\epsilon} \quad i=1,2 \\ &= C_i \quad (\text{constant over all space}) \quad i=3,4 \end{aligned}$$

Here N_0 is the number of radicals H or OH (i.e., X_1 or X_2 , respectively) initially produced (a) in all space for $\epsilon = 2$, or (b) per unit length of axis for $\epsilon = 1$. The quantity b_i ($i=1,2$) characterizes the initial Gaussian distribution, and C_i is the concentration at the origin.

The boundary conditions are

$$\frac{\partial n_i(0,t)}{\partial r} = 0 \quad ; \quad n_i(\infty,t) = \begin{cases} 0 & i=1,2 \\ C_i & i=3,4 \end{cases} .$$

Assuming we have solved our system of equations, then the fractional numbers of radicals consumed in the reactions are given by the recombination integrals

$$F_{ij}(t) = \frac{1 + \delta_{ij}}{N_0} \int_0^t \int_{\text{space}} k_{ij} n_i n_j dV dt \quad ,$$

wherein $dV = 2\epsilon\pi r^{\epsilon} dr$

for $(ij) = (11), (12), (13), (22), (24)$.

The fractional numbers of uncombined radicals are

$$F_{i0}(t) = \frac{1}{N_0} \int_{\text{space}} n_i(t) dV \quad \text{for } i=1,2 \quad .$$

With the aid of these integrals we can derive a number of material-balance equations. These equations serve to check the numerical work and, as it turns out, are actually used to compute certain of the yields which are difficult to compute directly with sufficient accuracy.

The material balance is for

$$\text{H:} \quad F_{10} + F_{11} + F_{12} + F_{13} = 1 \quad [X_1]$$

$$\text{OH:} \quad F_{20} + F_{21} + F_{22} + F_{24} = 1 \quad [X_2]$$

$$\text{I:} \quad F_{24} - F_{13} = \frac{1}{N_0} \int_{\text{all space}} [n_3(t) - C_3] dV \quad [X_3]$$

$$\text{I}^-: \quad F_{24} - F_{13} = \frac{1}{N_0} \int_{\text{all space}} [C_4 - n_4(t)] dV \quad [X_4]$$

It should be noted that these equations hold at any time $t \geq 0$.

The quantities that can be determined experimentally for the case of γ rays are, for $t \rightarrow \infty$,

$$R_1 = \frac{F_{22}}{F_{11}} \approx 1.62 \quad ; \quad R_2 = \frac{F_{10} + F_{20}}{F_{11} + F_{22}} \approx 2.40$$

when no (in practice, just a trace of) solute is present. The problem is to explain and predict the reaction integrals when a solute is present. Some results of the calculation are presented in ANL-6560.

SECTION ONE: THE MATHEMATICAL SOLUTION OF THE PROBLEM

I. Transformations

At this stage, the model contains 14 parameters: $N_0, b_1, b_2, C_3, C_4, D_1, D_2, D_3, D_4, k_{11}, k_{12}, k_{22}, k_{13}, k_{24}$. The system of equations is normalized by using the following transformations:

$$\begin{aligned} \tau &= (D_1/b_1^2)t & \beta &= b_1/b_2 & \kappa_{ij} &= k_{ij}/k_{11} & ij &= 11, 12, 13, \\ & & & & & & & 22, 24 \\ \rho &= r/b_1 & \theta_i &= D_i/D_1 & E &= \frac{\epsilon}{2} \frac{b_1^2}{D_1} \cdot C_1 k_{11} \\ \mu_i &= n_i/C_i & \gamma_i &= C_i/C_1 & \gamma_2 &= \beta^{(1+\epsilon)} \end{aligned}$$

The transformed system of equations contains only 11 parameters and is

$$\frac{\partial u_i}{\partial \tau} = \theta_i \left(\frac{\partial^2}{\partial \rho^2} + \frac{\epsilon}{\rho} \frac{\partial}{\partial \rho} \right) u_i - \frac{2E}{\epsilon} V_i(u) \quad i = 1, 2, 3, 4$$

$$[H]: V_1(u) = [2 u_1 + \kappa_{12} \gamma_2 u_2 + \kappa_{13} \gamma_3 u_3] u_1$$

$$[OH]: V_2(u) = [\kappa_{12} u_1 + 2 \kappa_{22} \gamma_2 u_2 + \kappa_{24} \gamma_4 u_4] u_2$$

$$[I]: V_3(u) = \kappa_{13} u_1 u_3 - \kappa_{24} (\gamma_4 \gamma_2 / \gamma_3) u_2 u_4$$

$$[I^-]: V_4(u) = \kappa_{24} \gamma_2 u_2 u_4 - \kappa_{13} (\gamma_3 / \gamma_4) u_1 u_3$$

The initial conditions are

$$\begin{aligned} u_1(\rho, 0) &= e^{-\rho^2} & u_3(\rho, 0) &= 1 \\ u_2(\rho, 0) &= e^{-(\rho\beta)^2} & u_4(\rho, 0) &= 1 \end{aligned}$$

The boundary conditions are

$$\frac{\partial u_i(0, \tau)}{\partial \rho} = 0 \quad ; \quad u_i(\infty, \tau) = \begin{cases} 0 & i = 1, 2 \\ 1 & i = 3, 4 \end{cases} .$$

This system is to be solved numerically over all space and time. To this end we transform the plane ($\rho \geq 0, \tau \geq 0$) onto the unit square [$0 \leq R \leq 1; 0 \leq T \leq 1$] by the transformation

$$T = 1/(1 + 4\tau)^{1/\epsilon}$$

$$R = e^{-\rho^2 T^\epsilon} .$$

$$U_i(R, T) = u_i(\rho, \tau) .$$

We note that the point $\rho = 0$, $\tau = 0$ becomes $R = 1$, $T = 1$, and the point $\rho = \infty$, $\tau = \infty$ becomes $R = 0$, $T = 0$. Figure 2 (Appendix E) illustrates the general shape of the expected solutions after the transformations. The differential equations after transformation are

$$\frac{T}{\epsilon} \frac{\partial U_i}{\partial T} = \theta_i R^2 \ln R \frac{\partial^2 U_i}{\partial R^2} + R \left[(\theta_i - 1) \ln R + \theta_i \frac{\epsilon+1}{2} \right] \frac{\partial U_i}{\partial R} + \frac{E}{2\epsilon T \epsilon} V_i(U)$$

and are singular at $T = 0$.

The initial conditions become

$$\text{at } T = 1 (t=0): \quad U_1 = R \quad ; \quad U_2 = R^{(\beta^2)} \quad ; \quad U_3 = U_4 = 1 \quad ,$$

and are seen to have reduced to a very simple form. The boundary conditions become

$$\text{at } R = 1 (r=0): \quad \frac{\partial U}{\partial R} < \infty \quad ,$$

$$\text{at } R = 0 (r=\infty): \quad U_i = \begin{cases} 0 & i = 1, 2 \\ 1 & i = 3, 4 \end{cases} .$$

It is interesting to note that instead of the homogeneous condition $\partial u_i / \partial \rho = 0$ at $\rho = 0$, $R = 1$ there is now an undetermined boundary.

The former condition is satisfied because

$$\frac{\partial u_i}{\partial \rho} = \frac{\partial U_i}{\partial R} \frac{\partial R}{\partial \rho} + \frac{\partial U_i}{\partial T} \frac{\partial T}{\partial \rho} = 0 \quad ,$$

$$\text{for } \frac{\partial R}{\partial \rho} = -2\rho R \rightarrow 0 \quad ; \quad \frac{\partial T}{\partial \rho} = 0 \quad ; \quad \text{and } \frac{\partial U_i}{\partial R} < \infty \quad .$$

The recombination integrals are now

$$F_{ij}(T) = \frac{\epsilon}{2} (1 + \delta_{ij}) \pi^{(1-\epsilon)/2} \kappa_{ij} \gamma_i \gamma_j E \int_T^1 \frac{dT}{T^{3\epsilon}} \int_0^1 dR \frac{(-\ln R)^{(\epsilon-1)/2}}{R} U_i U_j$$

for $ij = (11), (12), (13), (22), (24)$; where $0 \leq T \leq 1$, and

$$F_{i0}(T) \begin{cases} = \epsilon \pi^{(1-\epsilon)/2} \gamma_i T^{-\epsilon(\epsilon+1)/2} \int_0^1 \frac{dR (-\ln R)^{(\epsilon-1)/2} U_i}{R} & \text{for } 0 < T \leq 1 \\ = 0 & \text{for } T = 0 \end{cases} ,$$

for $(i = 1, 2)$.

The equations for material balance remain as before:

$$F_{11} + F_{12} + F_{13} + F_{10} = 1 \quad \text{for any } T$$

$$F_{21} + F_{22} + F_{24} + F_{20} = 1 \quad \text{for any } T.$$

We see that the advantage of having a finite domain is somewhat offset by the singular integrals.

II. Numerical Solution of the System of Partial Differential Equations

For the numerical solution, an explicit finite-difference scheme is chosen. The interval $(0,1)$ of the R axis is subdivided into P equal intervals, where P is an integer and, as will be seen later, must be an uneven number. Hence, $R = p/P$, where $p = 0,1,2,\dots,P$, at the endpoints of these intervals. The subdivision of the T axis consists of intervals of varying length, ΔT , such that $T_s - T_{s+1} = \Delta T$ (not $T_{s+1} - T_s = \Delta T$), where T_s and T_{s+1} are consecutive time steps in the course of computation.*

The following approximations are made:

$U_i(p/P, T_s)$ approximated by $U_{i,p,s}$

$$\frac{\partial U_i}{\partial \tau} \quad \text{approximated by} \quad \frac{U_{i,p,s} - U_{i,p,s+1}}{\Delta T} \quad \text{for } 0 < p \leq P,$$

$$\frac{\partial U_i}{\partial R} \quad \text{approximated by} \begin{cases} (U_{i,p+1,s} - U_{i,p-1,s})P/2 & \text{for } 0 < p < P, \\ (U_{i,p,s} - U_{i,p-1,s})P & \text{for } p = P, \end{cases}$$

$$\frac{\partial^2 U_i}{\partial R^2} \quad \text{approximated by} \quad (U_{i,p-1,s} - 2U_{i,p,s} + U_{i,p+1,s})P^2 \quad \text{for } 0 < p < P.$$

The initial conditions are, then, for $T_0 = 1$ and $0 \leq p \leq P$,

$$U_{1,p,0} = p/P$$

$$U_{2,p,0} = (p/P)\beta^2$$

$$U_{3,p,0} = U_{4,p,0} = 1.$$

The boundary conditions are

$$U_{1,0,s} = U_{2,0,s} = 0 \quad ; \quad U_{3,0,s} = U_{4,0,s} = 1.$$

*Because the original initial conditions (for $\tau = 0$) are transformed into the R, T -system, the computation starts at $T = T_0 = 1$. It follows that $T_{s+1} < T_s$; hence $T_s - T_{s+1} = \Delta T > 0$.

Substituting these approximations into the differential equations and collecting terms, we obtain the following system of difference equations:

$$U_{i,p,s+1} = K(a_{ip} + b_{ip}) U_{i,p-1,s} + K(a_{ip} - b_{ip}) U_{i,p+1,s} \\ + (1 - K 2 a_{ip}) U_{i,p,s} - K E V_{ips} / (2 T \epsilon)$$

for $i = 1, 2, 3, 4$; $p = 1, 2, \dots, P$.

Here

$$a_{ip} = \epsilon p^2 \theta_i \ln(P/p) > 0, \quad \text{for } 0 < p < P,$$

$$a_{iP} = b_{iP} > 0,$$

$$b_{ip} = \frac{\epsilon p}{2} \left[(1 - \theta_i) \ln(P/p) + \theta_i \frac{\epsilon + 1}{2} \right] > 0, \quad \text{for } 0 < p \leq P,$$

$$K = \Delta T / T$$

where $T_s \geq T \geq T_{s+1}$ and, for convenience, T is set equal to T_s . The condition for numerical stability of this explicit scheme is obtained as follows: The first variation of the difference equation yields

$$\delta U_{i,p,s+1} = \left[1 - K \left(2 a_{ip} + \frac{E}{2 T \epsilon} \frac{\partial V_{ips}}{\partial U_i} \right) \right] \delta U_{ips} + K [a_{ip} + b_{ip}] \delta U_{i,p-1,s} \\ + K [a_{ip} - b_{ip}] \delta U_{i,p+1,s} - K \frac{E}{2 T \epsilon} \sum_{j \neq i} \frac{\partial V_{ips}}{\partial U_j} \delta U_{jps}.$$

Assume that all but δU_{ips} are zero. Local numerical stability is then achieved if

$$\left| 1 - K \left(2 a_{ip} + \frac{E}{2 T \epsilon} \frac{\partial V_{ips}}{\partial U_i} \right) \right| \leq 1.$$

In general, however, not all $\delta U_i = 0$. We require that

$$\left| \delta U_{i,p,s+1} \right| \leq \max_{\substack{j=1,2,3,4 \\ p'=p-1,p,p+1}} \left| \delta U_{jp's} \right|.$$

Hence, a sufficient condition for local stability is

$$\left| 1 - K \left(2 a_{ip} + \frac{E}{2T\epsilon} \frac{\partial V_{ips}}{\partial U_i} \right) \right| + K \left[a_{ip} + b_{ip} + \left| a_{ip} - b_{ip} \right| + \frac{E}{2T\epsilon} \sum_{j \neq i} \left| \frac{\partial V_{ips}}{\partial U_j} \right| \right] \leq 1.$$

We would like to have K as large as possible. Assume, then, that

$$K \left[2 a_{ip} + \frac{E}{2T\epsilon} \frac{\partial V_i}{\partial U_i} \right] > 1.$$

But, since

$$1 < K \left[2 a_{ip} + \frac{E}{2T\epsilon} \frac{\partial V_i}{\partial U_i} \right] \leq 2,$$

and $a_{ip} + b_{ip} + |a_{ip} - b_{ip}| = 2 \max[a_{ip}, b_{ip}]$, the condition can be written as

$$K \left[2 a_{ip} + \frac{E}{2T\epsilon} \frac{\partial V_{ips}}{\partial U_i} + 2 \max(a_{ip}, b_{ip}) + \frac{E}{2T\epsilon} \sum_{j \neq i} \left| \frac{\partial V_{ips}}{\partial U_j} \right| \right] - 1 \leq 1.$$

Hence, the condition for local stability is

$$K \leq \frac{2}{2 a_{ip} + 2 \max(a_{ip}, b_{ip}) + \frac{E}{2T\epsilon} \sum_{j=1}^4 \left| \frac{\partial V_{ips}}{\partial U_j} \right|}.$$

For practical purposes, K must be independent of p and i . By examining our previous formulas, we note that:

$$\max \theta_i = 1, \text{ since } D_1 = \max_i D_i;$$

$$\max [p^2 \ln(P/p)] = P^2/2e; \quad (e = 2.71828),$$

$$\max(a_{ip}, b_{ip}) = a_{ip}.$$

From this it follows that $\max a_{ip} = \epsilon P^2/2e$. The sufficient condition for numerical stability is therefore

$$0 \leq K \leq \frac{e}{\epsilon P^2 + \frac{Ee}{4T\epsilon} \max \sum_{j=1}^4 \left| \frac{\partial V_{ips}}{\partial U_j} \right|}.$$

It should be noted that the stability depends on the solutions U_i [through $V_i(U)$] and T . However, up to about $T = 0.1$, one may use

$$K = \frac{e^*}{\epsilon P^2} ,$$

where $e^* < e$ (we took $e^* = 2$ or 2.5 usually).

To choose K as the critical parameter, together with the use of the notation presented here, had important consequences.

i) Reduction of number of multiplications.

To solve the system of difference equations, we first compute

$$Y = 1 - \frac{e^*}{\epsilon P^2} \text{ and } K = 1 - Y \text{ (this eliminates rounding errors in } K)$$

$$D = \frac{1}{2} EK$$

$$\left. \begin{aligned} A_{ip} &= K(a_{ip} + b_{ip}) \\ B_{ip} &= K(a_{ip} - b_{ip}) \\ C_{ip} &= 1 - 2K a_{ip} \end{aligned} \right\} \begin{aligned} p &= 1, 2, \dots, P \\ i &= 1, 2, 3, 4 \end{aligned}$$

These coefficients are time independent.

After the initial values are set, the following equations are used repeatedly:

$$\begin{aligned} T_s &= T_{s-1} Y \quad (T_s = Y^s) \\ U_{i,p,s+1} &= A_{ip} U_{i,p+1,s} + B_{ip} U_{i,p+1,s} + C_{ip} U_{ips} - \frac{D}{T_s \epsilon} V_{ips} \end{aligned} .$$

Except for the single factor $1/T_s \epsilon$, this scheme is as fast as if we had a system with constant coefficients. In an earlier attempt to solve the one-radical model (i.e., just the first equation) by a similar method, the time steps Δt were kept constant, and the coefficients corresponding to the A_{ips} had to be computed anew for each time $T_s = 1 - s\Delta t$, and therefore used about 50% more computing time, if everything else is considered equal.

ii) Reduction of number of time steps

In order to advance from $T = 1$ to $T = \frac{1}{2}$, we need s steps, where s is determined from $Y^s = \frac{1}{2}$, or $s \ln Y = -\ln 2$, ($Y \equiv 1 - K$). The stability condition of the earlier method referred to just above, expressed in Δt , is $\Delta t \leq 1/(2P^2)$ [a somewhat less restrictive condition follows from our stability criterion

$$\Delta T = \frac{e^* T}{\epsilon P^2} = \frac{e^*}{2\epsilon P^2} \text{ at } T = \frac{1}{2} \quad .$$

It turned out that at $T = \frac{1}{2}$, the ΔT 's actually used were identical. Hence for $T = \frac{1}{2}$,

$$\Delta T = \frac{1}{2} K \quad .$$

The number of steps in the earlier method, s_1 , is then for an advancement from $T = 1$ to $T = \frac{1}{2}$:

$$s_1 = \frac{1}{2} / \left(\frac{1}{2} K \right) = \frac{1}{K} \quad .$$

In our method, the number of time steps, s , is

$$s = - \frac{\ln 2}{\ln(1-K)}$$

and the ratio

$$\begin{aligned} \frac{s_1}{s} &= \frac{1}{K} \frac{\ln(1-K)}{-\ln 2} = \frac{1}{\ln 2} \left(1 + \frac{K}{2} + \frac{K^2}{3} + \dots \right) \\ &\doteq 1.45 \left(1 + \frac{K}{2} + \dots \right) \quad . \end{aligned}$$

Because the former method used equal time steps, the stability condition was investigated for $T = \frac{1}{2}, \frac{1}{4}, \frac{1}{8}$, etc. Everything else considered equal, about 45% more steps were required to sweep $\frac{1}{2}$ of the square.

iii) Simplified and hence more accurate integration

This needs some further explanation, and will become evident after having read the following sections.

III. Evaluation of the Integrals $F_{ij}(T)$

1. Space Integration

At each time step T_s , the integrals $F_{ij}(T)$ are computed. We first perform the integration with respect to R . We choose an uneven number of points, usually $P = 33$. Between $p = 1$ and $p = P$, Simpson's rule is used. Because of the singularity at the origin, the integrals

$$\int_0^{\Delta R (=1/P)} \frac{dR [\ln(1/R)]^{(\epsilon-1)/2}}{R} U_i U_j \quad , \quad \begin{array}{l} i = 1, 2, 3, 4 \\ j = 0, 1, 2, 3, 4 \end{array}$$

where $U_0 \equiv 1$, need special treatment.

It has been assumed, and later verified by calculation, that for the interval $(0, 1/P)$ and $i = 1, 2$,

$$U_i(R) \approx U_{i,1,s} PR \quad (\text{i.e., linear functions}).$$

Define

$$\begin{aligned} \eta_{10} &= \int_0^{\Delta R (=1/P)} \frac{dR [\ln(1/R)]^{(\epsilon-1)/2}}{R} R = \int_0^{\Delta R} dR [\ln(1/R)]^{(\epsilon-1)/2} \quad , \\ \eta_{11} &= \int_0^{\Delta R} \frac{dR [\ln(1/R)]^{(\epsilon-1)/2}}{R} R^2 = \int_0^{\Delta R} dR [\ln(1/R)]^{(\epsilon-1)/2} R \quad . \end{aligned}$$

Then,

$$\int_0^{\Delta R} \frac{dR [\ln(1/R)]^{(\epsilon-1)/2}}{R} U_i U_j \approx \begin{cases} U_{i1s} U_{j1s} \eta_{11} & \text{for } (ij) = (11), (12), (22) \\ U_i U_j \eta_{10} & \text{for } (ij) = (10), (20), (13), (24) \end{cases} .$$

For $\epsilon = 1$, there is no problem

$$\eta_{10} = \Delta R = 1/P$$

$$\eta_{11} = 1/2P^2 \quad .$$

For $\epsilon = 2$,

$$\int_0^1 \sqrt{\ln(1/R)} dR = \frac{\sqrt{\pi}}{2} ,$$

$$\int_0^1 \sqrt{\ln(1/R)} R dR = \frac{\sqrt{\pi}}{4\sqrt{2}} ,$$

$$\eta_{10} = \frac{\sqrt{\pi}}{2} - \int_{\Delta R}^1 dR \frac{\sqrt{\ln(1/R)}}{R} R ,$$

$$\eta_{11} = \frac{\sqrt{\pi}}{4\sqrt{2}} - \int_{\Delta R}^1 dR \frac{\sqrt{\ln(1/R)}}{R} R^2 ,$$

where the integrals on the right are computed on the machine with the routine for $p = 1$ to $p = P$ already described above (Simpson's rule). Since the initial condition for U_1 is always $U_1 = R = p/P$, there is no problem. It turned out that η_{11} was not needed for maintaining the required accuracy. We replace η_{10} by $H_1 + \eta(\epsilon-1)$ and have, based upon the above principle, an integration formula valid for both $\epsilon = 1$ and $\epsilon = 2$:

$$S_{ij}(T_s) \approx \left[\int_0^1 dR \frac{\sqrt{\ln(1/R)}^{\epsilon-1}}{R} U_i U_j \right]_{T=T_s}$$

$$= [H_1 + \eta(\epsilon-1)] U_{i,1,s} U_{j,1,s} + \frac{1}{3} \sum_{p=1}^P H_p U_{ips} U_{jps} ,$$

$$H_p = \omega_p \begin{cases} 1/p & \text{for } \epsilon = 1 \\ \sqrt{\ln(P/p)}/p & \text{for } \epsilon = 2 \end{cases} ,$$

$$\omega_p = \begin{cases} 1 & \text{for } p = 1, P \\ 2 & \text{for } p = 3, 5, \dots, P-2 \\ 4 & \text{for } p = 2, 4, \dots, P-1 \end{cases}$$

$$\eta = \left[\sqrt{\pi}/2 - S_{10}(1) \right] \eta_{=0} \cdot P ; \quad U_0 \equiv 1 .$$

It is now obvious that P is always an uneven integer greater than four.

2. Time Integration

Since the integration of the differential equations with respect to time is of first order, we approximate $S_{ij}(T)$ by a linear functional:

$$S_{ij}(T) = S_{ij}(T_s) + \frac{S_{ij}(T_s) - S_{ij}(T_{s-1})}{T_s - T_{s-1}} (T - T_s) \quad .$$

Integrating S_{ij} between T_{s+1} and T_s , and expanding $(1-K)^{1-3\epsilon}$ and $(1-K)^{2-3\epsilon}$ with respect to K , yields

$$\int_{T_{s+1}}^{T_s} S_{ij}(T) T^{-3\epsilon} dT = \frac{K}{2 T_s^{3\epsilon-1}} [a S_{ij}(T_s) + b S_{ij}(T_{s+1})] \quad ,$$

where

$$a = 1 + \epsilon K + \frac{1}{4} \epsilon(3\epsilon + 1) K^2 \quad ,$$

$$b = 1 + 2\epsilon K + \frac{3}{4} \epsilon(3\epsilon + 1) K^2 \quad .$$

This is a fourth-order approximation in K , since higher terms cancel each other. If we set

$$A_{ij} = \frac{\epsilon(1 + \delta_{ij}) \kappa_{ij} \gamma_i \gamma_j \epsilon K}{4(\sqrt{\pi})^{\epsilon-1}} \quad ,$$

we have the recurrence formula for the recombination fractions:

$$F_{ij}(T_{s+1}) = F_{ij}(T_s) + A_{ij} \frac{a S_{ij}(T_s) + b S_{ij}(T_{s+1})}{T_s^{3\epsilon-1}}$$

$$(ij) = (11), (12), (13), (22), (24) \quad .$$

Again, A_{ij} , a , and b are time independent and can be computed in advance. This recurrence formula requires only a little more work than the trapezoidal rule but is much more accurate.

Finally, for $(ij) = (10)$ and (20) , we have

$$F_{i0}(T_s) = \left(\frac{2}{\sqrt{\pi}} \right)^{\epsilon-1} \gamma_i \frac{S_{i0}(T_s)}{T_s^{\frac{\epsilon(\epsilon+1)}{2}}} \quad (i = 1, 2) \quad .$$

To check the accuracy of our computations, we can now apply the material balance equations:

$$\left. \begin{aligned} F_{10} + F_{11} + F_{12} + F_{13} &= 1 \\ F_{20} + F_{12} + F_{22} + F_{24} &= 1 \end{aligned} \right\} \text{ for } 1 \geq T \geq 0 .$$

IV. Estimation of Remainder and Extrapolation

We can stop our computing process and estimate the remainders at any time T which is smaller than a certain time T_c , where T_c is the time when the assumptions (1), (2), and (3) of page 18 hold with sufficient accuracy.

Since U_1 and U_2 approach zero for small T , the quadratic terms U_1^2 , $U_1 U_2$, and U_2^2 lose their significance, and we have to deal with an almost linear problem. Then, our differential equations are, for $i = 1, 2$,

$$\frac{T}{\epsilon} \frac{\partial U_i}{\partial T} = \theta_i R^2 \ln R \frac{\partial^2 U_i}{\partial R^2} + R \left[(\theta_i - 1) \ln R + \theta_i \frac{\epsilon+1}{2} \right] \frac{\partial U_i}{\partial R} + \frac{B_i}{T^\epsilon} U_i ,$$

where

$$B_i \approx \frac{E}{2\epsilon} \kappa_{i,i+2} \gamma_{i+2} U_{i+2}$$

and U_{i+2} is nearly a constant function.

If B_i is constant, a solution for U_i is

$$u_i(R, T) = U_i(1, T_c) \left\{ 1 + \beta_i^2 \theta_i \left[\left(\frac{T_c}{T} \right)^\epsilon - 1 \right] \right\}^{-(\epsilon+1)/2} e^{-\left\{ \frac{B_i}{T_c^\epsilon} \left[\left(\frac{T_c}{T} \right)^\epsilon - 1 \right] - \frac{\beta_i^2 \ln R}{1 + \beta_i^2 \theta_i \left[\left(\frac{T_c}{T} \right)^\epsilon - 1 \right]} \left(\frac{T_c}{T} \right)^\epsilon \right\}}$$

which the reader may verify. At $T = T_c$, we have

$$u_i(R, T_c) = U_i(1, T_c) R^{\beta_i^2} .$$

Assuming we have found a β_i such that $u_i(R, T_c)$ approximates $U_i(R, T_c)$ well, we may insert u_i in the formulas for F_{ij} and proceed analytically. That such an approximation is possible, is seen from Figures 3 and 4 (Appendix E), which were derived from a representative case. The simplest method to determine β_i is by a collocation method for u_i and an R between $\frac{1}{2}$ and $\frac{3}{4}$, whereas a more sophisticated method requires that

$F_{i0}(U_i) = F_{i0}(u_i)$. However, the actual determination of β_i will not be required for the final extrapolation formula and is only necessary to check the validity of the theoretical assumption made above. Now, the remainders of F_{ij} for any time $T_s < T_c$ for $(ij) = (11), (12),$ and (22) are approximated as follows:

$$F_{ij}(0) - F_{ij}(T_s)$$

$$\begin{aligned} & \doteq \frac{\epsilon}{2} (1 + \delta_{ij}) \pi^{(1-\epsilon)/2} \kappa_{ij} \gamma_i \gamma_j E \int_0^{T_s} \frac{dT}{T^{3\epsilon}} \int_0^1 dR \frac{(-\ln R)^{(\epsilon-1)/2}}{R} u_i u_j \\ & = C_{ij} \int_0^{T_s} \frac{dT}{T^{3\epsilon}} \frac{\left(\left\{ 1 + \beta_i^2 \theta_i \left[\left(\frac{T_c}{T} \right)^\epsilon - 1 \right] \right\} \left\{ 1 + \beta_j^2 \theta_j \left[\left(\frac{T_c}{T} \right)^\epsilon - 1 \right] \right\} \right)^{-(\epsilon+1)/2} e^{-\frac{B_i+B_j}{T_c^\epsilon} [(T_c/T)^\epsilon - 1]}}{\left(\frac{\beta_i^2 \left(\frac{T_c}{T} \right)^\epsilon}{1 + \beta_i^2 \theta_i \left[\left(\frac{T_c}{T} \right)^\epsilon - 1 \right]} + \frac{\beta_j^2 \left(\frac{T_c}{T} \right)^\epsilon}{1 + \beta_j^2 \theta_j \left[\left(\frac{T_c}{T} \right)^\epsilon - 1 \right]} \right)^{(\epsilon+1)/2}} \\ & = \frac{C_{ij} e^{-\frac{B_i+B_j}{T_c^\epsilon}}}{\beta_i^2 \beta_j^2 (\theta_i + \theta_j)^{(\epsilon+1)/2} T_c^{3\epsilon-1}} \int_0^{T_s/T_c} \frac{e^{-\frac{B_i+B_j}{T_c^\epsilon} \tau^{-\epsilon}} d\tau}{\tau^{\epsilon+1} \left[\left(\frac{\beta_i^2 + \beta_j^2}{\beta_i^2 \beta_j^2 (\theta_i + \theta_j)} - 1 \right) + \tau^{-\epsilon} \right]^{(\epsilon+1)/2}} \\ & = \frac{C_{ij} e^{-\frac{B_i+B_j}{T_c^\epsilon}}}{\epsilon \beta_i^2 \beta_j^2 (\theta_i + \theta_j)^{(\epsilon+1)/2} T_c^{3\epsilon-1}} \begin{cases} \int_{(T_c/T_s)^\epsilon}^\infty \frac{dt}{\left[\left(\frac{\beta_i^2 + \beta_j^2}{\beta_i^2 \beta_j^2 (\theta_i + \theta_j)} - 1 \right) + t \right]^{(\epsilon+1)/2}} & \text{for } B_i + B_j = 0 \\ \left(\frac{B_i+B_j}{T_c^\epsilon} \right)^{(\epsilon-1)/2} Q \left(-\frac{\epsilon+1}{2}, \rho_{ij} \right) & \text{for } B_i + B_j \neq 0 \end{cases} \end{aligned}$$

where

$$C_{ij} = \frac{1}{2} (1 + \delta_{ij}) \kappa_{ij} \gamma_i \gamma_j E U_i(1, T_c) U_j(1, T_c) ,$$

$$\rho_{ij} = \frac{B_i+B_j}{T_c^\epsilon} \left[\left(\frac{\beta_i^2 + \beta_j^2}{\beta_i^2 \beta_j^2 (\theta_i + \theta_j)} - 1 \right) + \left(\frac{T_c}{T_s} \right)^\epsilon \right] > 0 ,$$

and

$$Q(z, \rho) = \int_{\rho}^{\infty} e^{-t} t^z dt = z! - (z, \rho)! \quad ,$$

where $z!$ and $(z, \rho)!$ are the factorial and incomplete factorial functions, respectively. This result is obtained by first integrating with respect to R from 0 to 1, then making the transformations $\tau = T/T_c$, and

$$t = \frac{B_i + B_j}{T_c^\epsilon} \left[\left(\frac{\beta_i^2 + \beta_j^2}{\beta_i^2 \beta_j^2 (\theta_i + \theta_j)} - 1 \right) + \tau^{-\epsilon} \right]$$

and concurrently some algebraic rearrangements. One should also note that $3\epsilon - \frac{1}{2}\epsilon(\epsilon+1) = \epsilon + 1$ for $\epsilon = 1, 2$.

Hence, under the assumptions that

- (1) $u_i(R, T_c) = U_i(1, T_c) R^{\beta_i^2}$,
- (2) the terms U_1^2 , $U_1 U_2$, and U_2^2 are negligible, and
- (3) U_{i+2} is constant,

we have analytic expressions for the remainder terms of F_{11} , F_{12} , and F_{22} at $T = T_s$. We see that for $\epsilon = 1$ and $B_i + B_j = 0$, none of the above integrals F_{ij} exist.

$$\text{For } \epsilon = 1, \quad Q\left(-\frac{\epsilon+1}{2}, \rho\right) = -\text{Ei}(-\rho) \quad .$$

$$\text{For } \epsilon = 2, \quad Q\left(-\frac{\epsilon+1}{2}, \rho\right) = 2 \left[e^{-\rho} \rho^{-1/2} - \pi^{1/2} \text{erfc}(\rho^{1/2}) \right] \quad .$$

Therefore, the Q -functions have been reduced to well-known and tabulated functions.

$$\underline{\text{For } \epsilon = 2 \text{ and } (B_i + B_j)/T_c^\epsilon \rightarrow 0 \quad ,}$$

$$\left(\frac{B_i + B_j}{T_c^\epsilon} \right)^{(\epsilon-1)/2} Q\left(-\frac{\epsilon+1}{2}, \rho\right) \rightarrow 2 \left[\frac{\beta_i^2 + \beta_j^2}{\beta_i^2 \beta_j^2 (\theta_i + \theta_j)} - 1 + \left(\frac{T_c}{T_s} \right)^\epsilon \right]^{-(\epsilon-1)/2}$$

We derive now a working formula for the extrapolation of $F_{ij}(T_s)$ to $F_{ij}(0)$. To simplify the notation, we define

$$Q_s = Q\left(-\frac{\epsilon+1}{2}, \rho_{ij}(T_s)\right) \quad ,$$

$$F_s = F_{ij}(T_s) \quad .$$

Under the assumptions made above, we define

$$\alpha_s = \frac{Q_s - Q_{s+L}}{Q_{s-L} - Q_s} = \frac{F_{s+L} - F_s}{F_s - F_{s-L}},$$

where the F_{s-L} , F_s , and F_{s+L} are obtained as output from the machine calculations. Hence

$$\begin{aligned} F_s - F_{s-L} &= (F_s - F_{s-L}) \\ F_{s+L} - F_s &= \alpha_s (F_s - F_{s-L}) \\ F_{s+2L} - F_{s+L} &= \alpha_{s+L} \alpha_s (F_s - F_{s-L}) \\ F_{s+3L} - F_{s+2L} &= \alpha_{s+2L} \alpha_{s+L} \alpha_s (F_s - F_{s-L}) \end{aligned}$$

etc. Adding both sides yields

$$F_\infty - F_{s-L} = (F_s - F_{s-L}) (1 + \alpha_s + \alpha_s \alpha_{s+L} + \alpha_s \alpha_{s+L} \alpha_{s+2L} + \dots).$$

If $\alpha_s = \alpha_{s+L} = \alpha_{s+2L} = \dots < 1$, the right-hand side represents a geometric series. If $1 > \alpha_s \geq \alpha_{s+L} \geq \alpha_{s+2L} \geq \dots$,

$$F_\infty - F_{s-L} \leq \frac{F_s - F_{s-L}}{1 - \alpha_s} = \frac{(F_s - F_{s-L})^2}{2F_s - (F_{s-L} + F_{s+L})}.$$

We must show that $\alpha_k < 1$ for $k = s, s+L, s+2L, \dots$. To simplify the proof, we define and/or state

$$\rho_s = \frac{B_i + B_j}{T_c^\epsilon} \left[\left(\frac{\beta_i^2 + \beta_j^2}{\beta_i^2 \beta_j^2 (\theta_i + \theta_j)} - 1 \right) + \left(\frac{T_c}{T_s} \right)^\epsilon \right]$$

$$\rho_{s+L} - \rho_s = \frac{B_i + B_j}{T_s^\epsilon} \left(\frac{1}{T_L^\epsilon} - 1 \right) = \Delta_s$$

$$\rho_s - \rho_{s-L} = \frac{B_i + B_j}{T_s^\epsilon} (1 - T_L^\epsilon) = T_L^\epsilon \Delta_s$$

$$Q(-z, \rho) = \int_\rho^\infty e^{-t} t^{-z} dt = +e^{-\rho} \rho^{-z} \left[1 - \frac{z}{\rho} + \frac{z(z+1)}{\rho^2} + \dots + (-1)^n \frac{z(z+1) \dots (z+n-1)}{\rho^n} \right] + R_n$$

$$R_n = (-1)^n z(z+1) \dots (z+n) \int_\rho^\infty e^{-t} t^{-(z+n+1)} dt.$$

It is always possible to make ρ_s as large as one pleases, and Δ_s/ρ_s as small as one pleases through proper choice of s , L , and K . (Remember $T_1 = 1 - K$; hence, $T_L = T_1^L$, $T_L^\epsilon = T_{\epsilon L}$, etc.) Now, it follows that

$$\alpha_s = \frac{Q_s - Q_{s+L}}{Q_{s-L} - Q_s} = \frac{\int_{\rho_s}^{\rho_{s+L}} e^{-t} t^{-(\epsilon+1)/2} dt}{\int_{\rho_{s-L}}^{\rho_s} e^{-t} t^{-(\epsilon+1)/2} dt} = \frac{\left| e^{-\rho} \rho^{-(\epsilon+1)/2} \left[1 - \frac{\epsilon+1}{2\rho} + \dots \right] \right|_{\rho_s}^{\rho_{s+L}}}{\left| e^{-\rho} \rho^{-(\epsilon+1)/2} \left[1 - \frac{\epsilon+1}{2\rho} + \dots \right] \right|_{\rho_{s-L}}^{\rho_s}}$$

After some elementary algebraic operations, it follows for large ρ_s that

$$\alpha_s \approx e^{-T_L^\epsilon \Delta_s} \left(1 - \frac{T_L^\epsilon \Delta_s}{\rho_s} \right) \left[1 + o\left(\frac{1}{\rho_{s-L}}\right) \right],$$

i.e., $\alpha \rightarrow 0$ for $s \rightarrow \infty$, which is a stronger result than needed. Although ρ_s always becomes very large eventually, with its limit being $+\infty$, it is of equal importance for practical applications to investigate the behavior when $\rho \ll 1$. Then, e.g.,

$$\int_{\rho_s}^{\rho_{s+L}} e^{-t} t^{-(\epsilon+1)/2} dt \approx \int_{\rho_s}^{\rho_{s+L}} t^{-(\epsilon+1)/2} (1 + t + \dots) dt.$$

We consider first the case for $\epsilon = 2$.

$$\alpha_s = \frac{Q_s - Q_{s+L}}{Q_{s-L} - Q_s} \approx \frac{\rho_s^{-1/2} - \rho_{s+L}^{-1/2}}{\rho_{s-L}^{-1/2} - \rho_s^{-1/2}} = \frac{1 - \frac{\left[\beta^* + \left(\frac{T_c}{T_s} \right)^2 \right]^{1/2}}{\beta^* + \frac{1}{T_{2L}} \left(\frac{T_c}{T_s} \right)^2}}{\left[\frac{\beta^* + \left(\frac{T_c}{T_s} \right)^2}{\beta^* + T_{2L} \left(\frac{T_c}{T_s} \right)^2} \right]^{1/2} - 1},$$

where we set $\beta^* = \left(\frac{\beta_i^2 + \beta_j^2}{\beta_i \beta_j (\theta_i + \theta_j)} - 1 \right)$ for convenience. This function has

a small variation with respect to changes in T_s for a wide range of T_c/T_s and β^* , which lies between 0 and 1.2 in practical applications. This is best demonstrated by numerical examples.

For $\beta^* = 0$ (a frequent case is $\beta^* \approx 0$): $\alpha_s = T_L$ (a constant!)

For $\beta^* = 1$ we must consider several extreme cases:

$T_L = 1$ (for small L , $T_L \approx 1$): $\alpha_s = 0$ (a constant!)

$T_L = 0.6325$ (a value smaller than used in any of the actual calculations). The results for different values of T_C/T_s are as follows:

$T_C/T_s =$	10	100	∞
$\alpha_s =$	0.643	0.633	0.6325 ($= T_L$)

Therefore, the α_s 's can be expected to remain almost unchanged over thousands of computing steps, starting at about $T = 0.1$. To check this theory, machine calculations have been performed for this unfavorable case up to 10,000 steps.

Hence, we can use the formula for the estimation of the remainder of F_{ij} (page 19) as an extrapolation formula, replacing the symbol $\leq$ by $\doteq$, i.e.,

$$F_\infty \doteq F_{s-L} + \frac{F_s - F_{s-L}}{1 - \alpha_s}, \quad \text{where } F_s = F_{ij}(T_s), \text{ etc.}$$

In practical applications, we simply continue computing until all α 's become sufficiently stationary (which is at about $T = 0.1$) and then use the formula above to adjust for the final values. We do make a very small error, since the $\alpha_s \rightarrow 0$. This error can be easily estimated. Assume, after S steps, α_s drops suddenly to zero. Then

$$F_{s+S} - F_{s+S-L} < \alpha_s^{S/L} (F_s - F_{s-L})$$

and the remainder

$$F_\infty - F_{s+S-L} < \alpha_s^{S/L} \frac{F_s - F_{s-L}}{1 - \alpha_s}.$$

Take $\alpha_s = 0.9$ (this is unfavorably high) and $S/L = 32$; then the error in the correction is less than 0.035.

In practice, this means that only the 5th significant figure would be affected. Table I illustrates the success of the extrapolation in an unfavorable case.

Table I

RESULTS OF EXTRAPOLATION OF $F_{22}(T_s)$ IN AN
UNFAVORABLE CASE IN SPHERICAL GEOMETRY ($\epsilon=2$)

Case 141 (Spherical Geometry)

S(No. of Steps)	T_s	α_s	Correction	F_{22} for $S = \infty$
1000	0.399	0.912	0.120	0.301
2000	0.159	0.907	0.044	0.297
3000	0.064	0.907	0.016	0.297
4000	0.025	0.904	0.006	0.296
5000	0.010	0.878	0.002	0.296
6000	0.004	0.728	0.000	0.295
7000	0.002	0	0	0.295

Input data for above problem:

$$\epsilon = 2; \quad \beta = 1; \quad E = 0.87$$

$$D_2/D_1 = 0.45454545; \quad D_3/D_1 = 0.15; \quad D_4/D_1 = 0.15$$

$$\kappa_{12} = 2; \quad \kappa_{13} = 2; \quad \kappa_{22} = 1; \quad \kappa_{24} = 2;$$

$$B_3 = 10^{-5}; \quad B_4 = 10^{-5}$$

For large ρ_{ij} ,

$$\alpha_s \approx e^{-T \epsilon L \Delta_s} \left(1 - \frac{T \epsilon L \Delta_s}{\rho_s} \right),$$

i.e., the α 's are much smaller, and the error in the above extrapolation formula can again be neglected; this formula is therefore general.

For $\epsilon = 1$, and small ρ_{ij}

$$\alpha_s \approx \frac{\log(\rho_{s+L}/\rho_s)}{\log(\rho_s/\rho_{s-L})}.$$

If $\beta^* \ll T_c/T_s$, which will occur eventually, then $\alpha_s \rightarrow 1$, and we must expect a poor convergence. This is also in accordance with the integral representation of $F_\infty - F_s$ for $B_i + B_j = 0$ (page 17), which yields a term $\log \infty$, and with the function $-Ei(-\rho)$ which tends to infinity for $\rho \rightarrow 0$.

It is therefore advisable to carry the computations until the α 's and $(F_s - F_{s-L})$ are small enough to have a negligible remainder term according to the inequality of page 19. Table II illustrates the validity of this point.

Table II

INCONSISTENT BEHAVIOR OF EXTRAPOLATED VALUES FOR F_{11} IN CYLINDRICAL GEOMETRY. THE THEORETICAL INVESTIGATION SHOWS THAT COMPUTATION FOR $\epsilon=1$ SHOULD BE CARRIED ON UNTIL THE CORRECTION TERMS ARE NEGLIGIBLE, IN CONTRAST TO CALCULATIONS WITH $\epsilon=2$, WHERE EXTRAPOLATION IS VERY EFFICIENT AND RELIABLE

Case 570 (Cylindrical Geometry)

No. of Steps	T_s	α	Correction	F_{11} for $S \rightarrow \infty$
1000	0.090	0.872	0.104	0.243
1500	0.012	0.898	0.072	0.264
2000	0.002	0.908	0.048	0.271
2500	0.0002	0.890	0.024	0.265
3000	0.00003	0.718	0.003	0.254
3500	0.000004	0.140	0.000	0.253

Input data for above problem:

$$\epsilon = 1; \quad \beta = 1; \quad E = 0.1875;$$

$$D_2/D_1 = 0.25; \quad D_3/D_1 = 0.15; \quad D_4/D_1 = 0.15$$

$$\kappa_{12} = 2; \quad \kappa_{13} = 2; \quad \kappa_{22} = 0.55; \quad \kappa_{24} = 2;$$

$$B_3 = 10^{-5}; \quad B_4 = 10$$

We assume now that F_{11} , F_{12} , and F_{22} can be obtained with any desired accuracy for $T = 0$ ($t = \infty$). Then, the F_{10} , F_{20} , F_{13} , and F_{24} can also be determined at that time, as described below for both cylindrical and spherical cases.

V. Final Determination of F_{10} and F_{20} , R_1 , and R_2

For the 2-radical-no solute model, F_{10} and F_{20} are computed from the material balance:

$$F_{10} = 1 - (F_{11} + F_{12})_{S \rightarrow \infty} \quad \text{since } F_{13} = 0 \quad ,$$

$$F_{20} = 1 - (F_{22} + F_{12})_{S \rightarrow \infty} \quad \text{since } F_{24} = 0 \quad .$$

For the 2-radical-2-solute model, F_{13} and F_{24} are computed from the material balance:

$$F_{13} = 1 - (F_{11} + F_{12})_{S=\infty} \quad \text{since } F_{10} = 0 \text{ at } T_S = 0 \quad ,$$

$$F_{24} = 1 - (F_{22} + F_{12})_{S=\infty} \quad \text{since } F_{20} = 0 \text{ at } T_S = 0 \quad .$$

With these values, we can determine R_1 (and R_2)

For all cases: $R_1 = (F_{22}/F_{11})_{S=\infty}$

and

for the 2-radical-no-solute case: $R_2 = \left(\frac{F_{10} + F_{20}}{F_{11} + F_{22}} \right)_{S=\infty} = \frac{2(1 - F_{12})}{F_{11} + F_{22}} - 1 \quad .$

SECTION TWO: DESCRIPTION OF IBM 704 CODE PROGRAM LIBRARY 670/CHM116

General Method of Solution:

The code performs integrations over time and space to study the recombination of the free radicals (H and OH) produced by exposure of solutions to α rays or γ rays, assuming cylindrical or spherical symmetry, respectively. The system may have up to two radicals and two solutes. The formula for the final amount F_{ij} of recombination products is

$$F_{ij} = \frac{1 + \delta_{ij}}{N_0} \int_0^\infty \int_0^\infty k_{ij} n_i n_j \, dV \, dt$$

for $ij = 11, 12, 22, 13$, and 24 , where the n_i ($i = 1, 2, 3, 4$) are solutions of partial differential equations as described in the preceding section.

The machine program first calculates the initial concentrations of the various reactants at $t = 0$ for $P+1$ points in space, and then traces the reaction over larger and larger time intervals, utilizing various constant factors in an integration subroutine.

Variables have been transformed so that instead of integrating over space and time from zero to infinity, the integrations are from one to zero, with even increments in the space direction and smaller and smaller "time" increments. See Appendix A2 for real time calculations and equivalents.

The computation proceeds until the reaction is complete or until the system has become linear, so final concentrations of radical:radical combination products may be hand-calculated by means of an extrapolation procedure.

In either case, the amounts of the original reactants remaining at $t = \infty$, for cases with two radicals only, are calculated by difference, as are the amounts of products formed as the result of secondary reactions and/or of radicals combining with solutes.

Machine: IBM 704F. Compiled by Fortran II for an $\geq 8K$ memory. Uses printer and/or one tape unit for output and one tape unit for restart information.

Running Time:

The average case takes about $1\frac{1}{2}$ hr of machine time for the integrations to be carried to completion, i.e., until such "time" as the amount of uncombined radicals is insignificant. The machine time involved in

computing from "time" T to "time" $T/10$ is $(8\epsilon P^3/e^*)10^{-4}$ min for four-component cases, and only half this long if only the two radicals are involved.

A more general expression for the machine time involved is

$$(9)(10^{-5})(P) (\text{no. of steps}) (\text{no. of components}) \log (1/T_{\text{final}}) ,$$

where the number of steps is $(2.22) (\epsilon) (P^2/e^*)$ and the number of components = 2, 3, and 4 for codes A, C, and B respectively.

See Appendix A3 for charts showing machine time for various values of P and e^* . The final "time" T_f , to which a case must be run for all of the radicals to recombine is determined by the following:

1) For cylindrical cases, T_f is about one-tenth of the value of the smallest B_i involved.

Note: For smaller values of E , correspondingly smaller values of B_i still exhibit changes in the final concentrations of reaction products. However, 10^{-15} is a practical limit on the value of B_i , because the present machine code involves T^2 , and thus underflow would result in loss of significance. Actually, 10^{-5} is as small as B_i can be experimentally!

2) For spherical cases, T_f is about equal to the square root of one-tenth the value of the smallest B_i .

e.g.: for $B_i = 1$	0.1	10^{-3}	10^{-5}
$T_f = 0.3$	0.1	0.01	0.001

Thus, spherical cases need only be run until the log of the "time" is half of that to which cylindrical cases must be run; however, because the time increment is half as large, it takes twice as long to get to the same "time." Thus, all things being equal, a spherical case takes just as long as a cylindrical case.

It was found that the running time for 3- or 4-component spherical cases can be reduced by two-thirds by setting TMIN to 0.1 instead of 0.001, for example, and extrapolating the results (see Special Features section, Item 2). The running time for 2-component spherical cases can be similarly reduced by one-third, and an extrapolation carried out to give sufficiently accurate final F_{ij} 's. This results from the fact that after certain quantities become sufficiently small, a linear relationship holds. See Appendix A4 for elaboration of the extrapolation principle. It should be noted that final U_i values will not be readily available.

Accuracy:

It was concluded that the final concentrations, F_{11} , F_{12} , and F_{22} , were accurate to about 3 figures, although material balances were off by two or three per cent. This was based on the fact that for cases run with wide and narrow meshes, most of the variation was in the F_{13} (or F_{10}) and F_{24} (or F_{20}) while the above quantities remained accurate. Thus, final values for F_{13} (or F_{10}) and F_{24} (or F_{20}) were calculated by difference, based on the material balance equalities (see Special Features section, item 2b). See Appendix A5 for comparison of cases run with varying mesh sizes. The accuracy from the program may be affected by the choice of the integration subroutines. At the present time the formula used is based on Simpson's rule, but a trapezoidal quadrature subroutine could be used if desired.

See Appendix A6 for results of various integration procedures.

The accuracy is also affected by the mesh density, which may be varied in the space and/or time directions, by altering P or e^* .

The machine time varies inversely as e^* , which may be set equal to 2.5 for most cases. However, it is frequently necessary to limit it to 2.0, in cases for which B_3 is larger than B_4 , since such cases tend to be more unstable. Actually, the final accuracy is noticeably better when smaller values of e^* are used initially. This is especially useful for cases with a large B_1 , and for cylindrical cases, because extrapolation seemingly retains more accuracy than running a case to completion with its resulting poorer material balance.

The machine time varies as the cube of P , due to the fact that P also affects the time increment that must be used to ensure stability. It seems necessary to use at least 25-33 points to obtain the desired accuracy, although more points continue to give improved results, especially for cases that must be run to completion. However, a point is rapidly reached at which very little is gained by increasing P at the cost of much machine time. It should also be noted that P may not be altered during the running of a case (as e^* can be). See Appendix A7 for effects of P and e^* upon the results.

Input Information:

For each case there will be 4-7 cards of input data. Integers must be placed all the way to the right of the 6-column fields. Other numbers may be written with the decimal point in any of the 12 columns of the field, or with the decimal point assumed to be between the 6th and 7th columns of the field.

If a specific value of B_3 is desired, specify $\gamma_3 = (2\epsilon/\kappa_{13}E)B_3$.

If a specific value of B_4 is desired, specify $\gamma_4 = (2\epsilon/\kappa_{24}E)B_4$.

Automatically γ_2 is set equal to $\beta(1+\epsilon)$.

PREPARATION OF INPUT DATA

Card	Columns	Standard Value	Label	Description
1	1-3	3	ICG	- 3 or 4 ICG = IVG
	4-6	4	IVG	- 3 or 4, B _{IVG} will be output as "B"
	7-12	33	P	The number of points at which the concentrations will be evaluated for integration. This must be odd. $4 < P < 200$.
	13-18	100	CPS	Results will be calculated and output every CPS steps, and tests made to determine if the case is done.
	19-24	1 or 2	ϵ	$\begin{cases} -1 & \text{for cylindrical case.} \\ 2 & \text{for spherical case} \end{cases}$
	25-30	1	KEYOUT	$\begin{cases} -1 & \text{for off-line output only.} \\ +1 & \text{for on-line summary as described under output} \end{cases}$
	31-36	1	NGS	Number of γ_{IVG} 's for the γ_{ICG} given. $1 \leq NGS \leq 20$
	37-48	2.0	e^*	This must be less than 2.7128 from stability considerations
	49-60	0.0001 or 0	ACC	This is a termination criterion for the case being done, i.e., if F_{10} and F_{20} are less than ACC, the case is finished. Or, for the 2-radical only case, if the differences between successively calculated values of F_{10} and F_{20} are $\leq$ ACC, the case is finished
	61-72	0 or 0.001	TMIN	The case will always be considered finished when the "TIME" has reached TMIN. $TMIN \geq 10^{-15}$.
2	1	1	none	$\begin{cases} = 1 & \text{to start each case on a new page} \\ = 0 & \text{to double space between cases} \end{cases}$
	2-72	none	CASEID	Description of the case, including date, case number, components, type of case, etc
3	1-12	1.0	β	b_1/b_2 (must = 1 for Special Code C)
	13-24	0.87	E (Radicals)	$-(1/2)E$ (molecules)
	25-36	γ_3	γ_{ICG}	$-C_{ICG}/C_1$ where C is concentration (must = 1 for Special Code C)
	37-48	0.4545	θ_2	D_2/D_1 where D is diffusion
	49-60	0.15	θ_3	D_3/D_1 $\begin{cases} \text{If both } \theta_3 \text{ and } \theta_4 = 0, \text{ specify short code} \\ \text{If } \theta_3 = 0, \text{ specify special code. Otherwise} \end{cases}$
	61-72	0.15	θ_4	$-D_4/D_1$ $\begin{cases} \text{use regular code} \end{cases}$
4	1-12	2.0	κ_{12}	$-k_{12}/k_{11}$ where k_{ij} is rate of reaction for U_i combining with U_j
	13-24	2.0	κ_{13}	$= k_{13}/k_{11}$
	25-36	1.0	κ_{22}	$-k_{22}/k_{11}$ $\begin{cases} \text{If both } \kappa_{13} \text{ and } \kappa_{24} = 0, \text{ specify short code.} \\ \text{If } \kappa_{13} = 0, \text{ specify special code.} \\ \text{Otherwise use regular code.} \end{cases}$
	37-48	2.0	κ_{24}	$-k_{24}/k_{11}$
	49-60	γ_4	γ_{IVG}	$-C_{IVG}/C_1$ (must = 1 for Special Code C).
	61-72	0	γ_{IVG}	- another C_{IVG}/C_1 if $NGS > 1$ only.
	5,6,7 not normally used		γ_{IVG}	= additional values only if $NGS > 2$. Insert up to 6 on a card allowing 12 columns each.

The last case should be followed by blank cards to get to final stop.

See Special Features, item 5, for planned restart option if it is desirable to change an input parameter during the course of running the case.

COST CODE _____

OF

AMD 9 19 60

704 INPUT DATA

FORM II

TAPE 0 RESTART INFORMATION FOR SHORT CODE

COST CODE _____

PROGRAM										PROBLEM 670/CHM 116										ORIGINATOR										DATE										PAGE										OF																																							
1										2										3										4										5										6										7										8																			
1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8	9	0	1	2	3	4	5	6	7	8	9	0
The following information may be punched from the Tape 1 output to prepare a Tape 0 for restarting, in case Tape 0 is not available.																																																																																									
STEP										TIME										F ₁₁										F ₁₂										F ₂₂																														not necessary CARD CASE																			
																																																																						R, S, 1																			
CPC										CCC										NU										S ₁₁ = S ₁₁										S ₁₂ = S ₂₂										S ₁₄ = S ₂₂																				not necessary CARD CASE																			
																																																																						R, S, 2																			
wherein, CCC = STEP (MOD 500)																																																																																									
U ₁										U ₂										U ₁										U ₂																														not necessary P ₁ , P ₂ CASE																													
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Output Information:

The following summary is obtained as standard output either on-line or off-line on Tape 1, depending upon KEYOUT.

Case identification, Program Title, and the following Input Data:

$\beta =$	E	γ_{ICG}	θ_2	θ_3	θ_4
κ_{12}	κ_{13}	κ_{22}	κ_{24}		
ϵ	P	e^*	CPS	ACC	K
γ_{IVG}				B_{IVG}	

Under the following heading, results are listed initially and every CPS steps:

STEP	TIME	F_{11}	F_{12}	(F_{13})	F_{22}	(F_{24})	M_1	M_2	GS_1	GS_2
------	------	----------	----------	------------	----------	------------	-------	-------	--------	--------

The TIME starts at one and decreases toward zero. The F_{ij} 's represent the total amounts of combination products formed, and so start at zero and increase. (F_{13} and F_{24} are listed for four-component cases only.) M_1 and M_2 are material balances and should remain within a few per cent of one for satisfactory computation. The amount of free radicals remaining are given by GS_1 and GS_2 . These start at one and decrease as they recombine to: a) constant values for 2-radical cases, and b) zero for four-component cases.

For the 2-radical cases only, the final concentrations of the radicals X_1 and X_2 at each point are listed on-line as follows:

P	U_1	U_2
---	-------	-------

Also, restart information is output every 500 steps at the beginning of Tape 0. Thus, recent results as described above, plus some relevant integrals and all of the U_{ip} 's, are always available, although this information is written over if a new case is run 500 steps.

In addition, the standard output and/or supplementary information may be obtained on Tape 1 by depressing Sense Switches, as follows:

Sense Switch	Output
1	Case Identification, Program Title, and Input Data.
2	γ_{IVG} , B_{IVG} , and the heading; STEP TIME...as above.
3	The F_{ij} 's etc. are output every CPS steps.
4	Relevant integrals, n, and all the U_{ip} 's are output every CPS steps.

The above sense switches may be changed at any time during the course of running a case. In general, cases were run with KEYOUT positive, to give the standard output on-line, and with Sense Switches 1, 2, 3, and 4 down, to give complete information off-line. Thus, the course of the reactions in selected cases could be analyzed later, by plotting the concentrations of the various components against time and space.

Special Features:

1. Three machine programs exist.

The first two codes deal with the following five reactions and the associated differential equations for the changes in the concentrations of X_1 , X_2 , X_3 , and X_4 .

$$\begin{array}{ll}
 X_1 + X_1 \xrightarrow{k_{11}} X_{11} & \frac{\partial n_1}{\partial t} = D_1 \nabla^2 n_1 - (2 k_{11} n_1 + k_{12} n_2 + k_{13} n_3) n_1 \\
 X_1 + X_2 \xrightarrow{k_{12}} X_{12} & \\
 X_2 + X_2 \xrightarrow{k_{22}} X_{22} & \frac{\partial n_2}{\partial t} = D_2 \nabla^2 n_2 - (k_{12} n_1 + 2 k_{22} n_2 + k_{24} n_4) n_2 \\
 \text{-----} & \\
 X_1 + X_3 \xrightarrow{k_{13}} X_4 + X_5 & \frac{\partial n_3}{\partial t} = D_3 \nabla^2 n_3 - (k_{13} n_1 n_3 - k_{24} n_2 n_4) \\
 X_2 + X_4 \xrightarrow{k_{24}} X_3 + X_6 & \frac{\partial n_4}{\partial t} = D_4 \nabla^2 n_4 - (k_{24} n_2 n_4 - k_{13} n_1 n_3)
 \end{array}$$

where D_i is the diffusion rate and

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + (\epsilon/r) \frac{\partial}{\partial r} \quad .$$

These codes are: a SHORT code A, made available to study reactions of the radicals X_1 and X_2 only, in the first three equations; the REGULAR code B, used to study any or all of the above; a SPECIAL code C, for studying the first three reactions above, and in addition,

a secondary reaction, where X_4^* is X_{22} .

The differential equations thus become for C:

$$\frac{\partial n_1}{\partial t} = D_1 \nabla^2 n_1 - (2k_{11}n_1 + k_{12}n_2)n_1$$

$$\frac{\partial n_2}{\partial t} = D_2 \nabla^2 n_2 - (k_{12}n_1 + 2k_{22}n_2 + k_{24}^*n_4^*)n_2$$

$$\frac{\partial n_4^*}{\partial t} = D_4^* \nabla^2 n_4^* - (k_{24}^*n_4^* - k_{22}n_2)n_2 \quad ,$$

where the D_i are the diffusion rates for X_1 , X_2 , and X_4^* .

2. Hand Calculations

a. Extrapolation procedure: See Appendix A4 for discussion. For the F_{ij} to be extrapolated, use the last value output, F_{+1} , and the two preceding values taken 100 steps apart, F_0 and F_{-1} . Proceed as follows, retaining 7 figures in each number:

$$\Delta F_0 = F_{+1} - F_0$$

$$\Delta F_{-1} = F_0 - F_{-1}$$

$$\alpha = \frac{\Delta F_0}{\Delta F_{-1}}$$

$$\Sigma \Delta F = \frac{\Delta F_0}{1 - \alpha}$$

$$\boxed{F_\infty = F_0 + \Sigma \Delta F} \quad .$$

In some cases, the last 5 values, F_{+2} , F_{+1} , F_0 , F_{-1} , and F_{-2} , were utilized and a double extrapolation employed where applicable. An extrapolated value, $F_{1 \text{ ext}}$, was calculated as described above, and, in addition, $F_{0 \text{ ext}}$ and $F_{-1 \text{ ext}}$. In most cases these were almost constant, but in others there was a small drift, so an extrapolation was performed on these three F 's as above, giving a better value of F_∞ .

b. In any case, Material Balance equations should be used to calculate F_{13} (or GS_1) and F_{24} (or GS_2) By Difference, for 4-component (or 2-radical only) cases, as follows:

$$F_{13} \text{ (or } GS_1) = 1 - (F_{11} + F_{12})$$

$$F_{24} \text{ (or } GS_2) = 1 - (F_{12} + F_{22}) \quad .$$

3. Stability Considerations. There are two criteria for stability.

a. Approximate Criterion: As long as the time increment is based on multiplying the previous time by $[1 - (e^*/\epsilon P^2)]$, where $e^* \approx e$, the integration procedure should be stable. It was found that some cases (e.g., if $\gamma_3 > \gamma_4$) tended to be more unstable than others, so an even smaller value of e^* had to be used. This instability becomes obvious eventually in the on-line output as meaningless overflowed numbers begin filling in the spaces between the columns. Actually, it first shows up as a few negative U's or in the U's getting out of order at one side of the spatial configuration. Such cases may sometimes be extrapolated satisfactorily from before this point, or rerun with a smaller value of e^* . Increasing P only serves to stall off the overflow a few steps. It should be noted that a couple of very small negative U's may be obtained for $p = 1$ or 2, and need cause no alarm!

b. Sufficient Criterion:

$$\kappa \leq \frac{e}{\epsilon P^2 + \frac{Ee}{4T\epsilon} \max \sum_{j=1}^4 \left| \frac{\partial V_{ips}}{\partial U_j} \right|}.$$

Although the above expression cannot be calculated in advance, the condition should hold throughout the computation.

4. Limitations on Input Parameters

In general, good results are obtained when the values of the parameters are not too different from the values used in the sample problem. It may be necessary to increase the mesh density to get sufficient accuracy for other cases.

Four-component cases with small γ_3 and large γ_4 gave poor results with 33 points, but were good when 49 points were used. Two-radical cases with very small values of θ_i and κ_{ij} cause the most trouble. Normally, cases should first be run with the usual P and e^* , and then if poor material balances are obtained, the mesh density may be increased and the cases rerun, keeping in mind the fact that using 50% more points takes more than three times as much machine time.

Cases for which $\beta < 1$ may be attempted, but it is doubtful if any will run properly. The discrepancy in the material balance becomes obvious in the initial printout. The spatial distribution becomes so skewed that not enough points may be taken to give values anywhere near one. For example, a case with $\beta = \frac{1}{2}$ gave 0.50 for 33 points, 0.53 for 45 points, and still only 0.65 for 199 points, because X_2 varies most at small p's.

5. RESTART Options. Case may be restarted from Tape 0 as described under 5a and 5b.

Tape 0 will not be available for restarting a case: 1) when a different case has written its restart information over it, or 2) if it is decided to continue a case that wasn't planned on, or 3) if there was an error in writing on the Tape 0. Restart information must then be punched on cards as indicated on Input Forms.

a. Unforeseen Circumstances. Sense Switch 5 may be set down to restart a case utilizing Tape 0 along with the code and data cards:

- 1) in case of a power dump or other machine failure, or
- 2) if a case had to be taken off the machine before it had finished, or
- 3) if it is desired to run a case further, when it is realized that it was taken off prematurely, changing the accuracy criterion or TMIN, or
- 4) it may be necessary to rerun starting some time back with a smaller e^* if the case had become unstable.

b. Planned Operation. A restart card containing -1 in columns 35-36 is inserted, followed by the revised data cards, in order to alter CPS, KEYOUT, or e^* during the course of running the case. Thus, a case may be run one way until a certain accuracy or TMIN is reached, and then run further a different way.

6. Sense Switch 6 may be used to record the most recent restart information on Tape 0 and to bring the program to a stop.

7. The output should be checked for the following indications of inaccurate results and/or instability.

- a. Material balances, M_1 and M_2 , should remain close to 1.00 (at least within 5%).
- b. The values printed out for F's and GS's should not oscillate, that is, each one should be always increasing or decreasing.
- c. No case need be continued after the GS's have both vanished.
- d. No case should be continued after the time has gotten down to 10^{-15} .

- e. No negative number should be obtained, with the possible exception of very small values for GS's or U's.
- f. No overflowed numbers should be obtained in the on-line summary. (When this occurs, there are no spaces between two or more columns.)
- g. The F's and GS's should never exceed 1.0.

GENERAL OPERATING INSTRUCTIONS

704 PROGRAM 670/CHM116 A,B,C,

READER: 72-72 board

PUNCH: not used

USED NOT USED

DRUM: ☐ ☒

PRINTER: Share Board #2

UF SWITCH: ☒ ☐

SENSE SWITCH SETTINGS: 1,2,3,4 DOWN for Tape 1 output

5 { UP for start
DOWN for restart
6 UP

TAPES: 0 blank for new case or RESTART tape for RESTART of a case

1 blank for output. Use large reel

TIME BEFORE OUTPUT: 1 minute

RUNNING TIME: varies from 10 minutes to 7 hours

OFF-LINE PRINTING: print Tape 1 on program control - one file

print Tape 0 (1 page and save if GS's did not both go to zero)

RUNNING PROCEDURE:

START: Place code, data, and blanks in card reader
CLEAR and LOAD CARDS

RESTART: Replace Tape 0 and set SS #5 DOWN. Either follow START procedure, or, if the code is already in the machine, put the data in the reader and manually ENTER INSTRUCTION 0020046

MONITOR: Watch printout and stop case if the numbers go out of range, or if either M_1 or $M_2 < .95$, or if either M_1 or $M_2 > 1.05$, or if any number is negative. Contact requestor before continuing cases.

INTERRUPT: Set SS #6 DOWN so machine stops before completing the case, or FEED cards and insert blank in reader so machine comes to its regular stop after completing the case.

STORAGE REGISTER ADDRESSES for getting off the machine:

1030 = Regular Stop: Tape 1 has EOF. May START to do next case.

STOPS (OCTAL): 2035 = Stop when SS #6 is DOWN. May reset SS #6 and START to continue case, or ENTER INSTRUCTION 0020076 and START to do next case.

Refer to the manual for FORTRAN error stops.

APPENDIX A

A1. DEFINITIONS OF PARAMETERS

For purposes of the following definitions, X_i denotes the i^{th} reactant.

Symbol	Physical Significance and Definition
A_{ij}	$[\epsilon(1 + \delta_{ij}) \kappa_{ij} \gamma_i \gamma_j (EK)] / [4 \sqrt{\pi^{\epsilon-1}}]$
A_{ip}	$K(a_{ip} + b_{ip})$
a	$1 + \epsilon K + (\epsilon/4)(3\epsilon + 1)K^2$
a_{ip}	$\epsilon p^2 \theta_i \ln(P/p)$: note: $a_{ip} = b_{ip}$
$B_i (i = 1, 2)$	$E \kappa_{i,i+2} \gamma_{i+2} U_{i+2} / 2\epsilon$: If constant, yields theoretically exact extrapolation
$B_i (i = 3, 4)$	$E \kappa_{i-2,i} \gamma_i / 2\epsilon$: a function of the concentration, useful for plotting results
B_{ip}	$K(a_{ip} - b_{ip})$
b	$1 + 2\epsilon K + 3(\epsilon/4)(3\epsilon + 1)K^2$
b_i	this characterizes the initial Gaussian distribution whereby $n_i(r, 0) = C_i e^{-r^2/b_i^2}$ for X_1 and X_2 . The larger b_i is, the more evenly X_i is distributed, whereas the smaller it is, the more X_i is concentrated at the origin.
b_{ip}	$(\epsilon p/2)[(1 - \theta_i) \ln(P/p) + \theta_i(\epsilon + 1)/2]$
C_i	initial concentration of X_i at the origin; equals $N_0 / (\sqrt{\pi} b_i)^{1+\epsilon}$ for free radicals, and is constant over all space for solutes
C_{ij}	$(1 + \delta_{ij}/2) \kappa_{ij} \gamma_i \gamma_j E U_i(1, T_c) U_j(1, T_c)$
C_{ip}	$1 - 2Ka_{ip}$

c	the number of time steps after which an extrapolation may be done to $T = 0$ (i.e., $t = \infty$)
D	$(1/2)EK$
D_i	rate of diffusion for X_i
E	$\epsilon b_1^2 C_1 k_{11} / 2D_1$: a measure of the initial concentration of X_1 . This E (radicals) is half of the E (molecules) used by Flanders and Fricke, and is a <u>dimensionless</u> parameter.
$E_i(-\rho)$	$-\int_{\rho}^{\infty} \frac{e^{-t}}{t} dt$
e^*	a value less than e , suitably chosen to ensure stability
$\text{erfc}(\sqrt{\rho})$	$1 - (2/\sqrt{\pi}) \int_0^{\sqrt{\rho}} e^{-t^2} dt$
$\left. \begin{matrix} F_{ij}(t) \\ F_s \end{matrix} \right\}$	the fractional number of radicals consumed or reaction products created in each reaction at time t (after s steps)
$F_{io}(t)$	the fractional number of uncombined radicals at time t ($= 1$ at time 0)
H_p	$\omega_p(1/p)$ for $\epsilon = 1$; or $\omega_p(\sqrt{\ln(P/p)}/p)$ for $\epsilon = 2$
K	$\Delta T/T$ for the next step: $(T_S - T_{S+1})/T_S$. Thus, $T_{S+1} = T_S(1-K)$
k_{ij}	rate of reaction for X_i combining with X_j
L	the constant number of time steps between values of F used in extrapolation
N_0	Number of radicals of X_1 or X_2 initially produced, in all space for $\epsilon = 2$, or per unit lengths of axis for $\epsilon = 1$
$n_i(r,t)$	concentration of X_i at time t , for a definite position or overall space
P	the number of intervals in the R space. Must be odd and >4

p	the P + 1 end points for the P equal intervals in R = 0 to 1 are designated by p = 0,1,2,...P. Thus, R = p/P	
Q _s	Q(-(ε+1)/2, ρ _{ij} (T _s))	
Q(z,ρ)	$\int_{\rho}^{\infty} e^{-t} t^z dt$	
R	e ^{-ρ²T²} ; transformed space. [1 → 0]. <u>Dimensionless</u>	
Δ R	1/P: the increment for space direction of the mesh	
R ₁	F ₂₂ (t)/F ₁₁ (t) at t = ∞	} These ratios are the experimentally obtainable quantities upon which the data for the problem are adjusted
R ₂	(F ₁₀ + F ₂₀)/(F ₁₁ + F ₂₂) at t = ∞	
r	the distance in space from the center of symmetry [0 → ∞]	
S	number of time steps	
s	indicates the number of time steps that have been taken. It appears as a subscript for T, F _{ij} , ρ _{ij} , and others	
s ₁	the number of time steps in an earlier method of solving the problem	
S _{ij} (T _s)	$\left[\int_0^1 \frac{dR}{R} \left(\ln(1/R) \right)^{\frac{\epsilon-1}{2}} U_i U_j \right]$ at T = T _s	an unnormalized spatial integration of the concentrations
Δ T	T _s - T _{s+1} > 0: T _s and T _{s+1} are consecutive times	
T	1/(1 + 4τ) ^{1/ε} : transformed time [1 → 0]. <u>Dimensionless.</u>	
T _f	final value of T at which time the reaction is essentially complete (i.e., stability has been reached)	
t	real time in seconds [0 → ∞]	

U_0	($U_{ops} = 1$) A dummy concentration to aid in the formulation of the problem
$U_i(R, T) = u_i(\rho, \tau)$	concentration as before, but a function of R and T. <u>Dimensionless</u>
U_{ips}	$U_i(p/P, T_s)$
$u_i(\rho, \tau)$	$n_i(r, t)/C_i$: transformed concentration varying with time and space. <u>Dimensionless</u> variables
dV	a volume element: $dV = 2\pi r^\epsilon dr$
$V_i(u)$	This represents the expressions in $\kappa_{ij}, u_i, u_j, \gamma_i$, and γ_j in the equations for the changes in the concentrations of X_i 's, i.e., $V_1(u) = [2u_1 + \kappa_{12}\gamma_2u_2 + \kappa_{13}\gamma_3u_3] u_1$ $V_2(u) = [\kappa_{12}u_1 + 2\kappa_{22}\gamma_2u_2 + \kappa_{24}\gamma_4u_4] u_2$ $V_3(u) = \kappa_{13}u_1u_3 - \kappa_{24}(\gamma_4\gamma_2/\gamma_3) u_2u_4$ $V_4(u) = \kappa_{24}\gamma_2u_2u_4 - \kappa_{13}(\gamma_3/\gamma_4) u_1u_3$
Y	$1 - e^*/(\epsilon P^2)$: this is the basis for $K(=1 - Y)$. Thus, $T_{s+1} = Y \cdot T_s$ and $T_s = Y^s$
α_s	$(Q_S - Q_{S+L})/(Q_S - L - Q_S) \doteq (F_{S+L} - F_S)/(F_S - F_S - L)$
β	b_1/b_2 : a basis for comparing the distributions of X_1 and X_2
β^*	$(\beta_i^2 + \beta_j^2)/[\beta_i^2\beta_j^2(\theta_i + \theta_j)] - 1$
β_i	characterizes the distributions of U over space at T_c : $u_i(R, T_c) = U_i(1, T_c) R^{\beta_i^2}$
γ_i	C_i/C_1 : the ratio of the initial concentrations at the origin. Note: $\gamma_2 = \beta^{(1+\epsilon)}$ <u>dimensionless</u> parameters
Δ_s	$\rho_{s+L} - \rho_s$
δ_{ij}	the Krönecker Delta function, equals 0 if $i \neq j$, and 1 if $i = j$.

ϵ	a parameter to permit use of the same equations for both geometries set equal to 2 for spherical symmetry (γ rays) set equal to 1 for cylindrical symmetry (α rays)
η	$[\sqrt{\pi}/2 - S_{10}(T_0 = 1)]P$
η_{10}	$\int_0^{\Delta R} \frac{dR}{R} \left(\ln(1/R) \right)^{(\epsilon-1)/2}$ R: utilized in evaluation of S_{ij} integrals
η_{11}	$\int_0^R \frac{dR}{R} \left(\ln(1/R) \right)^{(\epsilon-1)/2} R^2$
θ_i	D_i/D_1 : relative diffusion rate. <u>Dimensionless</u> parameters
κ_{ij}	k_{ij}/k_{11} : relative reaction rate. <u>Dimensionless</u> variable
ρ	r/b_1 : transformed spatial distance. $[0 \rightarrow \infty]$. Dimensionless variable
ρ_{ij}, ρ_s	$\frac{(B_i + B_j)}{T_c^\epsilon} \left[\left(\frac{\beta_i^2 + \beta_j^2}{\beta_i^2 \beta_j^2 (\theta_i + \theta_j)} - 1 \right) + \left(\frac{T_c}{T_s} \right)^\epsilon \right]$
τ	$(D_1/b_1^2) t$: transformed time $[0 \rightarrow \infty]$. Dimensionless variable
ω_p	coefficients for Simpson's Rule Integration: 1 for $p = 1, P$; 2 for P odd; 4 for P even

A2. REAL TIME CALCULATIONS AND TRANSFORMED EQUIVALENTS

Calculation of real time from transformed "time."

Definitions: t = real time in seconds goes from 0 to ∞

$$\tau = (D_1/b_1^2) t, \text{ a dimensionless quantity going from 0 to } \infty$$

$$T = 1/(1 + 4\tau)^{1/\epsilon}, \text{ a dimensionless "time" going from 1 to 0}$$

Rearrangements:

$$\text{Thus, } T^\epsilon = \frac{1}{1 + 4\tau}, \text{ so } (1 + 4\tau) = \frac{1}{T^\epsilon}, \text{ and } \tau = \frac{1}{4} \left(\frac{1}{T^\epsilon} - 1 \right).$$

$$\text{Also, } t = \tau(b_1^2/D_1) = \frac{b_1^2}{D_1} \frac{1}{4} \left(\frac{1}{T^\epsilon} - 1 \right).$$

Determination of b_1 from the transformed parameters that constitute the input:

By definition,

$$E = \frac{\epsilon b_1^2 C_1 k_{11}}{2 D_1},$$

where

$$C_1 = \frac{N_0}{(\sqrt{\pi} b_1)^{1+\epsilon}}.$$

Thus,

$$E = \frac{\epsilon b_1^2 k_{11} N_0}{2 D_1 (\sqrt{\pi} b_1)^{1+\epsilon}};$$

so

$$b_1^{(\epsilon-1)} = \frac{\epsilon k_{11} N_0}{2 D_1 E (\sqrt{\pi})^{\epsilon+1}}.$$

It follows that for $\epsilon = 2$ (spherical geometry),

$$b_1 = k_{11} N_0 / (E D \pi^{3/2}).$$

For the cases under consideration, $D_1 = 7 \cdot 10^{-5}$ and $k_{11} = 10^{-11}$.

Standard I cases were run with

$$E = 0.87, \quad \kappa_{12} = 2, \quad \kappa_{22} = 1, \quad \text{and } D_2/D_1 = 0.4545 \dots,$$

for which it was determined that $N_0 = 5.0411$.

Therefore,

$$b_1 = \frac{10^{-11} (5.0411)}{0.87(7)(10^{-5}) \sqrt{30.00628}} = (14.8654) 10^{-8}.$$

$$\text{Finally, } t = \frac{[(14.8654)(10^{-8})]^2}{(28) 10^{-5}} \left(\frac{1}{T^2} - 1 \right) = \boxed{(0.78921)(10^{-10}) \left(\frac{1}{T^2} - 1 \right)}$$

and

$$T^2 = \frac{(0.78921)(10^{-10})}{(0.78921)(10^{-10}) + t},$$

so

$$T = \frac{(0.88838)(10^{-5})}{\sqrt{(0.78921)(10^{-10}) + t}}$$

Comparisons of real time t and transformed "time" T for Standard I cases.

1) Cases were usually run with $P = 33$ and $e^* = 2.0$. After 100 time steps, $T = 0.967477$ and $t = (0.053952)(10^{-10})$ sec.

2) Values of t for given values of T .

T	t (in sec)	T	t (in sec)
1.0	0	0.001	$(0.7892) 10^{-4}$
0.1	$(0.7813) 10^{-8}$	0.0001	$(0.7892) 10^{-2}$
0.01	$(0.78913) 10^{-6}$		

3) Values of T for given values of t

t (in sec)	T	t (in sec)	T
0	1.0	10^{-4}	0.000888
10^{-12}	0.994	10^{-3}	0.0002809
10^{-11}	0.942	10^{-2}	0.0000888
10^{-10}	0.664	10^{-1}	0.00002809
10^{-9}	0.2705	1	0.00000888
10^{-8}	0.0885	10	0.00000281
10^{-7}	0.02808	100	0.000000888
10^{-6}	0.00888	1000	0.000000281
10^{-5}	0.002809		

A3. TABLES SHOWING MACHINE TIME AS A FUNCTION OF e^* AND P

Running time for a case with complete output to reach "time" $T = 0.1$ is about $[(2)(10^{-4})(P^3)(\epsilon)(\text{number of components})/e^*]$ minutes.

1. The following table gives the machine time in minutes for spherical cases ($\epsilon = 2$) with $e^* = 2.0$ and various values of P.

$\begin{array}{c} \text{Code} \backslash P \\ \hline \end{array}$	21	33	45	49	55	75
A. Short	4	16	38	50	70	175 min
B. Regular	8	30	75	100	140	6 hr
C. Special	6	23	57	75	105	$4\frac{1}{2}$ hr

2. The following table is for code A (2 radicals only) with $\epsilon = 2$.

$\begin{array}{c} \text{e}^* \backslash P \\ \hline \end{array}$	21	33	45	49	55	75
2.5	3	12	30	40	56	140 min
2.0	4	15	38	50	70	175 min
1.5	6	20	50	67	95	240 min
1.0	8	30	75	100	140	6 hr
0.5	16	60	150	200	280	9 hr

3. The following table is for code B (4 components) with $\epsilon = 2$.

$\begin{array}{c} \text{e}^* \backslash P \\ \hline \end{array}$	21	33	45	49	55	75
2.5	6	24	60	80	112	290 min
2.0	8	30	75	100	140	6 hr
1.5	11	40	100	135	190	8 hr
1.0	16	60	150	200	280	12 hr
0.5	32	120	300	400	560	24 hr

A4. EXTRAPOLATION

As various quantities become small during the machine computation, the system becomes approximately linear. The amounts by which F_{11} , F_{12} , and F_{22} are then increased at each step maintain a constant ratio to the previous increment.

Figure 1 illustrates for a representative case that a constant ratio is established before $T = 0.1$.

Thus:

$$F_s = F_{s-1} + \Delta F_{s-1}$$

and

$$F_{s+1} = F_s + \Delta F_s = F_s + \alpha \Delta F_{s-1} \quad ,$$

where

$$\alpha = \Delta F_s / \Delta F_{s-1} \quad \text{which has become constant.}$$

Since

$$F_\infty = F_s + \Delta F_s + \Delta F_{s+1} + \Delta F_{s+2} + \dots \quad ,$$

it follows that

$$F_\infty = F_s + \Delta F_s + \alpha \Delta F_s + \alpha(\alpha \Delta F_s) + \alpha(\alpha \Delta F_s) + \dots$$

and

$$F_\infty = F_s + \sum_{n=0}^{\infty} \alpha^n \Delta F_s = F_s + \Delta F_s \sum_{n=0}^{\infty} \alpha^n \quad .$$

Inserting the expression for the geometric series gives:

$$F_\infty = F_s + \Delta F_s \left(\frac{1}{1 - \alpha} \right) \quad .$$

Figure 1
Verification of Extrapolation
Formula (Case 257)

A5. COMPARISONS OF RESULTS USING DIFFERENT MESH SIZES

The following cases were run to certain "times" with different mesh sizes to compare the accuracy of the results. It is apparent that even in the extreme cases $\oplus$, there are only slight differences between the values of F_{11} , F_{12} , and F_{22} obtained, whereas F_{10} , F_{20} , F_{13} , and F_{24} are subject to considerable error, and should be calculated by difference.

SHORT CASES: 2 RADICALS ONLY

P	e*	"Time" T	F_{11}	F_{12}	F_{22}	F_{10}	F_{20}	M_1	M_2
33	2.0	0.0764	0.1301	0.1611	0.2173	0.6931	0.6563	0.9844	1.0346
55	2.25	0.0768	0.1305	0.1608	0.2157	0.7002	0.6427	0.9915	1.0192
	Difference		0.0004	0.0003	0.0016	0.0071	0.0136	0.0071	0.0154
$\oplus$ 33	2.0	0.0092	0.1383	0.1616	0.1954	0.6796	0.7626	0.9796	1.1197
55	2.0	0.0091	0.1389	0.1611	0.1929	0.6899	0.7146	0.9898	1.0682
	Difference		0.0006	0.0005	0.0025	0.0103	0.0480	0.0102	0.0515
33	2.0	0.05	0.1622	0.2332	0.2590	0.5845	0.4945	0.9800	0.9865
55	2.0	0.05	0.1627	0.2336	0.2590	0.5929	0.5057	0.9892	0.9984
	Difference		0.0005	0.0004	0.0000	0.0084	0.0112	0.0092	0.0119

REGULAR CASES: 4 COMPONENTS

P	e*	"Time" T	F_{11}	F_{12}	F_{22}	F_{13}	F_{24}	M_1	M_2
33	2.0	0.692	0.0062	0.0120	0.0873	0.9604	0.0829	0.9787	1.0183
55	2.0	0.695	0.0064	0.0121	0.0866	0.9738	0.0819	0.9923	1.0188
	Difference		0.0002	0.0001	0.0007	0.0134	0.0010	0.0136	0.0005
33	1.0	0.1668	0.0064	0.0121	0.2146	0.9700	0.3083	0.9885	1.0300
55	2.0	0.1677	0.0063	0.0122	0.2130	0.9732	0.3071	0.9917	1.0154
	Difference		0.0001	0.0001	0.0016	0.0032	0.0012	0.0032	0.0146
$\oplus$ 33	2.0	0.001	0.1633	0.0667	0.0498	0.6802	0.8935	0.9103	1.0106
49	2.5	0.001	0.1633	0.0668	0.0499	0.7425	0.8905	0.9725	1.0071
	Difference		0.0001	0.0001	0.0001	0.0623	0.0030	0.0622	0.0035

A6. COMPARISONS OF MATERIAL BALANCES OBTAINED USING DIFFERENT INTEGRATION METHODS

Comparable runs utilizing different integration schemes gave the following material balances at time 0.05:

Integration Case Parameters		Simpson's vs. Trapezoidal		ΔM
M_1	$\epsilon = 1$	0.9612	0.9604	0.0008
	$\epsilon = 2$			
	1 η	0.9338	0.9295	0.0043
	2 η 's	0.9265	0.9281	0.0016
M_2	$\epsilon = 1$	1.0093	1.0084	0.0009
	$\epsilon = 2$			
	1 η	1.0776	1.0721	0.0055
	2 η 's	1.0687	1.0677	0.0010

$\epsilon = 2$ only		1 η vs. 2 η 's		ΔM
M_1	Simpson's	0.9338	0.9265	0.0073
	Trapezoidal	0.9295	0.9281	0.0014
M_2	Simpson's	1.0776	1.0687	0.0089
	Trapezoidal	1.0721	1.0677	0.0044

All three η 's are defined in Appendix A1. Actually, the "2 η 's" are determined by

$$\eta_{ij} = \frac{[S_{ij}(1) - S_{ij}(1)] P^{(1+\delta_{ij})}}{\text{Theoretical for } \eta = 0} \quad \text{for } j = 0, 1,$$

where $S_{10}(1) = \sqrt{\pi}/2$ and $S_{11}(1) = \sqrt{\pi}/(4\sqrt{2})$. Then η_{10} is used for any further computations involving S_{10} , S_{20} , S_{13} , and S_{24} , while η_{11} is used for S_{11} , S_{12} , and S_{22} .

A7. INFLUENCE OF P AND e^* UPON THE ACCURACY

The values obtained for the material balances measure the accuracy of a run. The following results were obtained for a representative cylindrical case ($\epsilon = 1$) for runs with increasing overall mesh sizes. Spherical cases behaved similarly.

P	e^*	Running Time ¹		% Deviation of Material Balance from 1.0 ($\epsilon = 1$)						
		$\epsilon = 1$	$\epsilon = 2$	<u>T = 0.57</u>	<u>0.33</u>	<u>0.10</u>	<u>0.033</u>	<u>0.01</u>	<u>0.001</u>	<u>0.0001</u>
33	2.0	90	30	0.6	1.0	1.4	1.5	1.6	1.7	1.7
25	0.5 $\rightarrow$ 2.5** T = 0.30 ¹ ϵ	41	21	0.5	0.8	1.3	1.6	1.7		
25	0.5 $\rightarrow$ 2.5** T = 0.67 ¹ ϵ	34	14	0.5	0.9	1.4	1.7	1.8		
25	1.0	75	25	0.7	1.1	1.5	1.7	1.8	1.9	2.0
21	0.5 $\rightarrow$ 2.5** T = 0.57 ¹ ϵ	21	9	0.6	1.2	1.7	2.0	2.1	2.2	2.2
25	2.0	38	13	1.1	1.5	2.0	2.2	2.3		
21	2.5	18	6	1.8	2.3	2.9	3.1			
15	2.5	6	2	-	4.1	4.8	5.2			

** e^* was changed from 0.5 to 2.5 at the indicated time T.

¹ The running times are based on the fact that: (1) cylindrical cases must be run until the reaction is complete at about $T = 10^{-6}$, whereas (2) spherical cases may be extrapolated after $T = 0.1$.

NOTE: It takes as long for a spherical case to reach $T = 0.1$ as it does for a cylindrical case to reach $T = 0.01$!

The P and e^* combination in the outlined run above was used successfully for many cases since it provided a margin of safety for keeping the error within 3%, and the machine time required was moderate.

APPENDIX B

B1. Master Flow Chart

NOTE: THE OPERATIONS DESCRIBED IN 4 DASHED ENCLOSURES ARE INCLUDED IN THE CODE FOR 2 COMPONENTS ONLY.

B2. EQUATIONS USEDInput:

Physical Parameters:

$$(1) \quad \beta, E, \gamma_4, \theta_2, \theta_3, \theta_4, \kappa_{12}, \kappa_{13}, \kappa_{22}, \kappa_{24}, \epsilon, \gamma_3 \text{ (up to 20 values of } \gamma_3)$$

Computational Parameters:

$$(2) \quad P, e^*, CPS, ACC, T_{\min}, \text{RESTART.}$$

Note: $\gamma_1 = 1, \theta_1 = 1, \kappa_{11} = 1, \epsilon = 1, 2, P = 2N + 1$ (uneven integer) $e^* < 2.7183$

Coefficient Preparation:

$$(3) \quad \gamma_2 = (\beta)^{1+\epsilon}$$

$$(4) \quad K = \frac{e^*}{\epsilon P^2}$$

$$(5) \quad Y = 1 - K \quad K = 1 - Y$$

$$(6) \quad L_p = \ln(P/p) \quad (p = 1, 2, \dots, P)$$

$$(7) \quad \begin{cases} a_{ip} = \frac{\epsilon p K}{2} \left\{ 2\theta_{ip} L_p + \left[(1 - \theta_i) L_p + \theta_i \frac{\epsilon + 1}{2} \right] \right\} & (p = 1, 2, \dots, P-1) \\ a_{iP} = \epsilon p K \theta_i \frac{\epsilon + 1}{2} & (i = 1, 2, 3, 4) \end{cases}$$

$$(8) \quad \begin{cases} b_{ip} = \frac{\epsilon p K}{2} \left\{ 2\theta_{ip} L_p - \left[(1 - \theta_i) L_p + \theta_i \frac{\epsilon + 1}{2} \right] \right\} & (p = 1, 2, \dots, P-1) \\ b_{iP} = 0 & (i = 1, 2, 3, 4) \end{cases}$$

$$(9) \quad \begin{cases} c_{ip} = 1 - \epsilon p K 2 \theta_{ip} L_p & (p = 1, 2, \dots, P-1) \\ c_{iP} = 1 - a_{iP} & (i = 1, 2, 3, 4) \end{cases}$$

$$(10) \quad H_p = \begin{cases} 1/p & \text{for } \epsilon = 1 \\ \sqrt{L_p}/p & \text{for } \epsilon = 2 \end{cases} \quad (p = 1, 2, \dots, P)$$

$$(11) \quad G = \begin{cases} 1 & \text{for } \epsilon = 1 \\ 2/\sqrt{\pi} & \text{for } \epsilon = 2 \end{cases}$$

$$(12) \quad a = 1 + \epsilon K + \frac{\epsilon(3\epsilon + 1)}{4} K^2$$

$$(13) \quad b = 1 + 2\epsilon K + 3 \frac{\epsilon(3\epsilon + 1)}{4} K^2$$

Change of Parameters:

$$(14) \quad \left[\gamma_3 = \frac{2\epsilon B}{\kappa_{13}E} \right]_{\text{omit}} \quad B_3 = \frac{\kappa_{13}E}{2\epsilon} \gamma_3 \quad B_4 = \frac{\kappa_{24}E}{2\epsilon} \gamma_4$$

$$(15) \quad A_{ij} = GK_{ij}\gamma_i\gamma_j EK \frac{1 + \delta_{ij}}{4} \quad (ij = 11, 12, 13, 22, 24)$$

Set of Initial Conditions:

$$(16) \quad S = 0$$

$$(17) \quad T_s = 1$$

$$(18) \quad U_{1,p,o} = p/P$$

$$(19) \quad U_{2,p,o} = \begin{cases} U_{1,p,o} & \text{for } \beta = 1 \\ [U_{1,p,o}]^{(\beta^2)} & \text{for } \beta \neq 1 \end{cases}$$

$$(20) \quad U_{3,p,o} = 1$$

$$(21) \quad U_{4,p,o} = 1$$

Note: $s = Q - q$

$U_{ops} \equiv 1$

$(p = 0, 1, 2, \dots, P)$

$(p = 0, 1, 2, \dots, P)$

$\left. \begin{array}{l} (20) \\ (21) \end{array} \right\} (p = 0, 1, 2, \dots, P)$

$$F_{11} = 0$$

$$S_{11} = 0$$

$$F_{12} = 0$$

$$S_{12} = 0$$

$$(22)-(31) \quad F_{13} = 0$$

$$S_{13} = 0$$

$$F_{22} = 0$$

$$S_{22} = 0$$

$$F_{24} = 0$$

$$S_{24} = 0$$

$$(32) \quad \left\{ \begin{array}{l} \text{Set } \eta = 0, \text{ then Compute} \\ \eta = \left[\frac{\sqrt{\pi}}{2} - S_{10}(1) \right] P \end{array} \right.$$

Use Eqn. (38) for S_{10}

Subroutines:

$$(33) \quad T_s = Y T_{s-1}$$

$$(34) \quad \left\{ \begin{array}{l} U_{1,0,s+1} = 0 \\ U_{1,p,s+1} = a_{1p} U_{1,p-1,s} + b_{1p} U_{1,p+1,s} + c_{1p} U_{1ps} \\ \quad - \frac{KE}{2T_s^\epsilon} \left[2U_{1ps} + \kappa_{12}\gamma_2 U_{2ps} + \kappa_{13}\gamma_3 U_{3ps} \right] U_{1ps} \\ (p = 1, 2, 3, \dots, P) \end{array} \right.$$

$$(35) \quad \left\{ \begin{array}{l} U_{2,0,s+1} = 0 \\ U_{2,p,s+1} = a_{2p} U_{2,p-1,s} + b_{2p} U_{2,p+1,s} + c_{2p} U_{2,p,s} \\ \quad - \frac{KE}{2T_s^\epsilon} \left[\kappa_{12} U_{1ps} + 2\kappa_{22}\gamma_2 U_{2ps} + \kappa_{24}\gamma_4 U_{4,p,s} \right] U_{2ps} \\ (p = 1, 2, \dots, P) \end{array} \right.$$

$$(36) \quad \left\{ \begin{array}{l} U_{3,0,s+1} = 1 \\ U_{3,p,s+1} = a_{3,p} U_{3,p-1,s} + b_{3,p} U_{3,p+1,s} + c_{3p} U_{3,p,s} \\ \quad - \frac{KE}{2T_s^\epsilon} \left[\kappa_{13} U_{1ps} U_{3ps} - \frac{\kappa_{24}\gamma_2\gamma_4}{\gamma_3} U_{2ps} U_{4ps} \right] \\ (p = 1, 2, \dots, P) \end{array} \right.$$

$$(37) \quad \left\{ \begin{array}{l} U_{4,0,s+1} = 1 \\ U_{4,p,s+1} = a_{4,p} U_{4,p-1,s} + b_{4p} U_{4,p+1,s} + c_{4p} U_{4,p,s} \\ \quad - \frac{KE}{2T_s^\epsilon} \left[\kappa_{24}\gamma_2 U_{2ps} U_{4ps} - \frac{\kappa_{13}\gamma_3}{\gamma_4} U_{1,ps} U_{3,p,s} \right] \\ (p = 1, 2, \dots, P) \end{array} \right.$$

Note: "s + 1" is new value, "s" is old value

$$(38) \quad \left\{ \begin{array}{l} S_{ij}(T_s) = [H_1 + \eta(\epsilon - 1)] U_{i,1,s} U_{j,1,s} \\ \quad + \frac{1}{3} \left\{ H_1 U_{i,1,s} U_{j,1,s} + 2 \sum_{p=3,5,7,\dots,P-2} H_p U_{ips} U_{jps} \right. \\ \quad \left. + 4 \sum_{p=2,4,6,\dots,P-1} H_p U_{ips} U_{jps} + H_p U_{iPs} U_{jPs} \right\} \end{array} \right.$$

$$(39) \quad F_{ij}(T_s) = F_{ij}(T_{s-1}) + A_{ij} \frac{aS_{ij}(T_{s-1}) + b S_{ij}(T_s)}{T_{s-1}^{3\epsilon-1}}$$

$$(40) \quad F_{10}(T_s) = G \frac{S_{10}(T_s)}{T_s \frac{\epsilon(\epsilon+1)}{2}}$$

$$(41) \quad F_{20}(T_s) = G\gamma_2 \frac{S_{20}(T_s)}{T_s \frac{\epsilon(\epsilon+1)}{2}}$$

$$(42) \quad M_1(T_s) = F_{11}(T_s) + F_{12}(T_s) + F_{13}(T_s) + F_{10}(T_s)$$

$$(43) \quad M_2(T_s) = F_{12}(T_s) + F_{22}(T_s) + F_{24}(T_s) + F_{20}(T_s)$$

B3. OUTPUT FORM

Tape 1 and/or On Line:

Titles:

Main
Title

Diffusion Kinetics III

670/CHM116

$$B1/B2 = \beta \quad E = B1GE \quad C4/C1 = \gamma_4 \quad D1/D1 = \theta_2 \dots, \theta_3 \dots, \theta_4 \dots$$
$$\kappa_{12} = \quad \kappa_{13} = \quad \kappa_{24} =$$

Epsilon = ϵ

P = e* = CPS = ACC = K =

(44)

For
Each "B"

$$C_3/C_1 = \gamma_3 \dots$$
$$B_3 = \dots$$

STEP	TIME	F11	F12	F13	F22	F24	M1	M2	F ₁₀	F ₂₀
------	------	-----	-----	-----	-----	-----	----	----	-----------------	-----------------

(45)

Numerical Output:

Always
Required

S	T _S	F ₁₁	F ₁₂	F ₁₃	F ₂₂	F ₂₄	M ₁	M ₂	F ₁₀	F ₂₀
---	----------------	-----------------	-----------------	-----------------	-----------------	-----------------	----------------	----------------	-----------------	-----------------

Integers full accuracy	7 Decimals
------------------------	------------

(46)

Optional

U1 $U_{1ps} = x_{xxxxxx}(x), \dots, \dots, \dots, \dots, \dots, \dots, \dots, \dots$
 as many lines as needed for $p = 0, 1, 2, \dots, P$.

$$U_2 \quad U_{2ps} = \dots$$
$$U_3 \quad U_{3ps} = \dots$$
$$U_4 \quad U_{4ps} = \dots$$

} Full accuracy for all numbers in this table

SIJ $S_{11}(T_S)$, $S_{12}(T_S)$, $S_{13}(T_S)$, $S_{22}(T_S)$, $S_{24}(T_S)$, LOC. γ_3 , CCC, η

(47)

Note: γ_3 and γ_4 may be interchanged depending upon input

B4. STORAGE ALLOCATION

$\beta, E; \gamma_1 \gamma_2 \gamma_3 \gamma_4; \theta_1 \theta_2 \theta_3 \theta_4; \kappa_{11}, \kappa_{12}, \kappa_{13}, \kappa_{22}, \kappa_{24}; \epsilon; 1/\sqrt{\pi}, 1;$

$P, e, CPS, ACC.; T_{min}; K, Y; a, b, G, \tau_l, T_s; STEP; LOC. \gamma_3$

$F_{11}, F_{12}, F_{13}, F_{22}, F_{24}; M_1, M_2; S_{11}, S_{12}, S_{13}, S_{22}, S_{24}; F_{10}, F_{20}; A_{11} A_{12} A_{13} A_{22} A_{24}.$

a_{ip}	}	20 P Locations	$P < 200$
b_{ip}			
c_{ip}			
$U_{i,p,s}$			
$U_{i,p,s-1}$			

U_{ops} P Locations

H_p P Locations

L_p P Temporary Locations (May be $\equiv LOC. H_p$)

B5. DEFINITIONS OF FORTRAN VARIABLES

See Input Directions and Appendix A1 for physical significance of parameters. Reference is also made to the equations in Appendix B2.

Integer Variables

IJ	Takes on values up to 7 for the following subscript combinations of i and j: 1,1 1,2 1,3 2,2 2,4 1,0 2,0
I or J	takes on values up to 4 for reactants X_1 , X_2 , X_3 , X_4 ; and I equals 5 in the case of the dummy variable, $U_{Op}(T_s)$
ICG	the index i of the constant γ for the case, i.e., $i = 3$ or $4 \neq$ IVG
IVG	the index of the variable γ for the case, i.e., $i = 4$ or $3 \neq$ ICG
KBETA	this control is 1 if $\beta = 1$ and 2 if $\beta \neq 1$
KEEP1	$= \epsilon(\epsilon + 1)$
KEP1	$= \epsilon + 1$
KEYCCC	the number of time steps since the last dump for restart
KEYCPC	the number of time steps since the last printout
KEYCPS	the number of time steps between printouts
KEYE	$= \epsilon$
KEYOUT	this control determines whether output may be online or only offline
KEYP	$= P$
KEY	$= \epsilon - 1$
KEYS	number of time steps taken since $TIME = 0$
KPM1	$= P - 1$
KPP1	$= P + 1$
KPM2	$= P - 2$
KZ	$= 0$

LP	= p
L	= p - 1
N	this is used interchangeably with I as a subscript for U
N34	the index of the G34 currently being used as γ_{IVG}
NGS	the number of values of γ_{IVG} for the case.

Decimal Variables

ACC	The accuracy criterion
AEK	= a (Eqn. 12)
BEK	= b (Eqn. 13)
BETA	= β
BETASQ	= β^2
BIGB	= B_{IVG} (Eqn. 14)
BIGE	= E
CAPPA	= K (Eqn. 4)
CDTP	= $\log_e P$
E	= e^*
ELPKD2	= $\epsilon_p K/2$
EM1	= M1
EM2	= M2
EN	= η_{10} (Eqn. 32)
EP1	= $\epsilon + 1$
EPKD2	= $\epsilon PK/2$
ETTE	= $KE/(2 T_S^e)$
FE	= ϵ

FEM1	= $\epsilon - 1$
FLP	= p
FP	= P
G	= 1 for $\epsilon = 1$; $2/\sqrt{\pi}$ for $\epsilon = 2$
GS1	= $F_{10}(T_s)$ (Eqn. 40)
GS ₂	= $F_{20}(T_s)$ (Eqn. 41)
GS10	the previous GS1 } for comparison with GS's
GS20	
SIJ	saves the previous $S_{ij}(T_s)$ for calculation of F_{ij}
SQRTPI	= $\sqrt{\pi}$
SUM2	summation of the products involving odd ordinates in Eqn. 38
SUM3	summation of the products involving even ordinates in Eqn. 38
TEE	= $T_s \frac{\epsilon(\epsilon+1)}{2}$
TE	= $\theta_i(\epsilon+1)$
TEK	= $[(3\epsilon+1)/4]K$
TIME	= T_s (Eqn. 33)
TMIN	cutoff time
TTEM1	= $T_s^{\epsilon-1}$
TTPL	= $2 \theta_i p \ln (P/p)$
TT	= $(1-\theta_i) \ln (P/p) + \theta_i (\epsilon+1)/2$
Y	= $1 - K$

Dimensioned Variables:

A(I,LP)	= a_{ip} (Eqn. 7)
BIGA(IJ)	= A_{ij} (Eqn. 15)
B(I,LP)	= b_{ip} (Eqn. 8)
CAY(IJ)	= κ_{ij}
CDT(LP)	= $\ln(P/p)$

$$C(I,LP) = c_{ip} \text{ (Eqn. 9)}$$

$$D(I,J) = \delta_{ij}/4$$

$$F(I,J) = F_{ij} \text{ (Eqn. 39)}$$

$$G34(N34) \text{ the } \gamma_{IVG}'\text{'s for the case}$$

$$GAMMA(I) = \gamma_i$$

$$H(LP) = 1/p \text{ for } \epsilon = 1; \sqrt{\ell n(P/p)} / p \text{ for } \epsilon = 2$$

$$PL(LP) = p \ell n (P/p)$$

$$S(IJ) = S_{ij}(T_s) \text{ (Eqn. 38)}$$

$$STS(IJ) = "$$

$$T(I) = \theta_i$$

$$U1(I,LP) = U_{ip} (T_{s+1})$$

$$U(I,LP) = U_{ip} (T_s)$$

APPENDIX C

Listings of Fortran Codes

```

C      670 / CHEMISTRY 116      HUGO FRICKE / ANL / CC      SHORT CODE A
      DIMENSION T(4),G34(20),CDT(20),H(20),PL(20),GAMMA(4),F(5),S(7), DIM-1
      2A(4,20),B(4,20),C(4,20),D(5),CAY(5),BIGA(5),U(5,20),U1(4,20), DIM-2
      3STS(7)                                DIM-3
      EQUIVALENCE(STS(1),S(1)),(CDT(1),U1(1 )),(PL(1),U(1  ))
900 SENSE LIGHT 0
910 SGRTP1=1.77245385
920 CAY(1)=1.0
930 GAMMA(1)=1.0
940 T(1)=1.0
945 KZ=0
950 D(1)=0.25
960 D(2)=0.0
970 D(3)=0.0
980 D(4)=0.25
990 D(5)=0.0
995 IF(SENSE SWITCH 5)999,1000
999 SENSE LIGHT 1
1000 READ 100,ICG,IVG,KEYP,KFYCPS,KEYE,KEYOUT,NGS,E,          1000-1
      2ACC,TMIN          1000-2
100 FORMAT (2I3,5I6,3F12.6)
1010 IF(NGS)999,1020,1050
1020 END FILE 1
1030 PAUSE 1030
1040 GO TO 1000
1050 READ 105,BETA,BIGE,GAMMA(ICG),T(2),T(3),T(4),          1050-1
      2(CAY(IJ),IJ=2,5),(G34(N34),N34=1,NGS)          1050-2
105 FORMAT (72H1
      2              /(6E12.6))
1070 FP=FLCATF(KEYP)          C-1
1071 FE=FLCATF(KEYE)
1072 KEP1=KEYE+1
1073 GAMMA(2)=( BETA)**KEP1
1074 CAPP=E/(FE*(FP**2))          4
1060 IF(KEYOUT)1110,1065,1075
1065 PAUSE 1065
1067 GO TO 1000
1075 PRINT 105
1080 PRINT 108,BETA,BIGE,ICG,GAMMA(ICG),T(2),T(3),T(4),          1080-1
      2(CAY(IJ),IJ=2,5),IVG,(G34(N34),N34=1,NGS)          1080-2
108 FORMAT (54H0 DIFFUSION KINETICS 111          670 / CHM 116/108-1
      28H0 B1/B2=F12.6,9H , BIGE =F12.6,4H , C11,4H/C1=F12.6,9H , C1/D1=F108-2
      312.6,2F15.6/8H K12 =F12.6,9H , K13 =F12.6,9H , K22 =F12.6,9H , 108-3
      4 K24 =F12.6/3H C11,4H/C1=F12.6,5F15.6/(7F15.6))          108-4
1090 PRINT 109,KEYE,KEYP,E,KEYCPS,ACC,CAPPA
109 FORMAT (9H EPSILON=I2,5H , P=I3,6H , E=F12.6,8H , CPS=I4,7H , AC109-1
      2C=F12.6,5H , K=F12.6)          109-2
1100 IF(SENSE SWITCH 1)1110,1165
1110 WRITE OUTPUT TAPE 1,105
1120 WRITE OUTPUT TAPE 1,108,BETA,BIGE,ICG,GAMMA(ICG),          1120-1
      2T(2),T(3),T(4),(CAY(IJ),IJ=2,5),IVG,(G34(N34),N34=1,NGS)          1120-2
1130 WRITE OUTPUT TAPE 1,109,KEYE,KEYP,E,KEYCPS,ACC,CAPPA
1165 KEY=KEYE-1          C-2
1167 FEM1=FE-1.0
1170 Y=1.0-CAPPA          5
      CAPPA=1.0-Y

```

1175	EPKD2=FE*FP*CAPPA/2.0	
1180	KPM1=KEYP-1	
1185	G=1.0	11-1
1186	IF(KEY)1187,1200,1189	
1187	PAUSE 1107	
1188	GO TO 1000	
1189	G=2.0/SQRTPI	11-2
1200	CDTP=LOGF(FP)	
1210	DO 1270 LP=1,KEYP	
1220	FLP=FLOATF(LP)	
1230	CDT(LP)=CDTP-LOGF(FLP)	6
1240	H(LP)=1.0/FLP	10-1
1250	IF(KEY)1270,1270,1260	
1260	H(LP)=H(LP)*SQRTF(CDT(LP))	10-2
1270	PL(LP)=FLP*CDT(LP)	
1280	EP1=FLOATF(KEP1)	
1290	KEEP1=KEYE*KEP1	
1300	DO 1400 I=1,2	
1310	TE=T(I)*EP1	
1320	DO 1370 LP=1,KPM1	
1330	TTPL=2.0*T(I)*PL(LP)	
1335	ELPKD2=FE*FLOATF(LP)*CAPPA/2.0	
1340	TT=(1.0-T(I))*CDT(LP)+TE/2.0	
1350	A(I,LP)=ELPKD2*(TTPL+TT)	7-1
1360	B(I,LP)=ELPKD2*(TTPL-TT)	8-1
1370	C(I,LP)=1.0-2.0*ELPKD2*TTPL	9-1
1380	A(I,KEYP)=EPKD2*TE	7-2
1390	B(I,KEYP)=0.0	8-2
1400	C(I,KEYP)=1.0-A(I,KEYP)	9-2
1410	TEK=((3.0*FE+1.0)/4.0)*CAPPA	
1420	AEK=1.0+CAPPA*FE*(1.0+TEK)	12
1430	BEK=1.0+CAPPA*FE*(2.0+3.0*TEK)	13
1440	N34=1	D
1540	KEYCPC=KEYCPS	F
1542	GS10=2.0	
1544	GS20=2.0	
1545	KEYCCC=1	
1550	KEYS=0	16
1560	TIME=1.0	17
1565	KBETA=1	
1570	IF(BETA-1.0)1575,1590,1575	
1575	KBETA=2	
1580	BETASQ=BETA**2	
1590	KPP1=KEYP+1	
1600	DO 1650 LP=1,KPP1	
1610	U(1,LP)=FLOATF(LP-1)/FP	
1620	U(2,LP)=U(1,LP)	
1630	GO TO (1650,1640),KBETA	
1640	U(2,LP)=U(2,LP)**BETASQ	
1650	U(5,LP)=1.0	
1670	DO 1690 IJ=1,5	
1680	F(IJ)=0.0	
1690	S(IJ)=0.0	
1700	EN=0.0	32-1
1710	CALL SIJTS(H,U,FN,FEM1,STS(6),1,5,KEYP)	
1720	EN=(0.886726925-STS(6))*FP	32-2

```

1730 IF(SENSE LIGHT 1)1740,1765
1740 REWIND 10
1750 READ INPUT TAPE 10,175,KEYS,TIME,F(1),F(2),F(4)
175 FORMAT (1H015,E15.8,9F11.7)
1760 READ INPUT TAPE 10,176,N34,KEYCCC,EN,
2S(1),S(2),S(4),((U(N,LP),N=1,2),LP=1,KPP1)
176 FORMAT (1H 216,1P4E14.7/(4E14.7))
1765 GAMMA(IVG)=G34(N34)
1770 DO 1775 J=1,2
1775 BIGA(J)=G*CAY(J)*GAMMA(1)*GAMMA(J)*BIGE*
2CAPPA*(0.25+D(J))
1780 IJ=4
1785 J=2
1790 BIGA(IJ)=G*CAY(IJ)*GAMMA(2)*GAMMA(J)*
2BIGE*CAPPA*(0.25+D(IJ))
1800 BIGB=CAY(2*IVG-3)*BIGE*GAMMA(IVG)/(2.0*FE)
1805 IF(KEYOUT)1830,1810,1810
1810 PRINT 181,IVG,N34,GAMMA(IVG),BIGB
181 FORMAT (3H C11,4H/C1(I2,2H)=E12.6,50H
2 B=E12.6/120H0 STFP TIME F11
3 F12 F22 M1 M2 F10 F20
4 )
1820 IF(SENSE SWITCH 2)1830,1850
1830 WRITE OUTPUT TAPE 1,181,IVG,N34,GAMMA(IVG),BIGB
1850 IF(KEYCPS-KEYCPC)1860,1860,2100
1860 CALL SIJTS (H,U,EN,FEM1,STS(6),1,5,KFYP)
1870 CALL SIJTS (H,U,EN,FEM1,STS(7),2,5,KEYP)
1880 TEE=TIME**((KEEP1/2)
1890 GS1=G*STS(6)/TEE
1900 GS2=G*GAMMA(2)*STS(7)/TEE
1910 EM1=F(1)+F(2) +GS1
1920 EM2=F(2) +F(4)+GS2
1930 IF(KEYOUT)1960,1940,1940
1940 PRINT 175 ,KEYS,TIME,F(1),F(2),F(4),FM1,EM2,GS1,GS2
1950 IF(SENSE SWITCH 3)1960,1970
1960 WRITE OUTPUT TAPE 1,175,KEYS,TIME,F(1),F(2),F(4),
2EM1,EM2,GS1,GS2
1970 IF(SENSE SWITCH 6)1972,1975
1972 SENSE LIGHT 4
197 GO TO 1980
1975 IF(KEYCCC=500)2010,1977,1977
1977 KEYCCC=0
1980 REWIND 10
1990 WRITE OUTPUT TAPE 10,175,KEYS,TIME,F(1),F(2),F(4)
2000 WRITE OUTPUT TAPE 10,176,N34,KEYCCC,EN,
2S(1),S(2),S(4),((U(N,LP),N=1,2),LP=1,KPP1)
2010 IF(SENSE SWITCH 4)2020,2030
2020 WRITE OUTPUT TAPE 1,202,IVG,N34,GAMMA(IVG),
2KEYCCC,EN,(S(IJ),IJ=1,7),KZ,(((U(N,LP),N=1,2),LP=1,KPP1)
202 FORMAT (6H GAMMA11,1H(I2,2H)=F12.7,7H , CCC=I3,6H ,ETA=F12.6,&H ,
2SIJ=(3E18.7,2H )/29H LP U1 U2
3 4E20.7/(I4,2E17.7))
2030 IF(SENSE LIGHT 4)2035,2040
2035 PAUSE 2035
2040 KEYCPC=0
2050 IF(GS1-ACC)2060,2060,2070

```

H
RESTART

1760-1
1760-2

15-1-1
15-1-2

15-2-1
15-2-2
14

45
181-1
181-2
181-3
181-4

J
K-1
K-2

40
41
42
43
M

1960-1
1960-2
N SET UP
RESTART

2000-1
2000-2

2020-1
2020-2
202-1
202-2
202.3

P
Q

```

2060 IF(GS2-ACC)2080,2070,2070
2070 IF(TIME-TMIN)2080,2080,2072
2072 IF (GS1-GS10+ACC) 2100,2074,2074
2074 IF (GS2-GS20+ACC)2100,2080,2080
2080 N34=N34+1
2082 IF(KEYOUT)2086,2086,2084
2084 PRINT 202,IVG,N34,GAMMA(IVG),
2KEYCCC,EN,(S(IJ),IJ=1,7),KZ,(((U(N,LP),N=1,2),LP),LP=1,KPP1)
2086 WRITE OUTPUT TAPE 1,202,IVG,N34,GAMMA(IVG),
2KEYCCC,EN,(S(IJ),IJ=1,7),KZ,(((U(N,LP),N=1,2),LP),LP=1,KPP1)
2090 IF(N34-NGS)1540,1540,1000
2100 KEYS=KEYS+1
2102 GS10=GS1
2104 GS20=GS2
2105 KEYCCC=KEYCCC+1
2110 KEYCPC=KEYCPC+1
2120 ETTE=RIGE/(2.0*TIME**KEYE)*CAPPA
2125 TTEM1=TIME**({*KEYE-1})
2130 TIME=Y*TIME
2140 DO 2160 LP=2,KPP1
2145 L=LP-1
2150 U(1,LP)=A(1,L)*U(1,L)+B(1,L)*U(1,LP+1)+C(1,L)*U(1,LP)
2-ETTE*(2.0*U(1,LP)+CAY(2)*GAMMA(2)*U(2,LP))*U(1,LP)
2160 U(2,LP)=A(2,L)*U(2,L)+B(2,L)*U(2,LP+1)+C(2,L)*U(2,LP)
2-ETTE*(CAY(2)*U(1,LP)+2.0*CAY(4)*GAMMA(2)*U(2,LP))*U(2,LP)
2190 DO 2210 N=1,2
2200 DO 2210 LP=2,KPP1
2210 U(N,LP)=U1(N,LP)
2250 DO 2280 J=1,2
2260 SIJ=STS(J)
2270 CALL SIJTS (H,U,EN,FEM1,STS(J),1,J,KEYP)
2280 F(J)=F(J)+BIGA(J)*(AEK*SIJ+BЕК*STS(J))/TTEM1
2290 IJ=4
2300 J=2
2310 SIJ=STS(IJ)
2320 CALL SIJTS (H,U,EN,FEM1,STS(IJ),2,J,KEYP)
2330 F(IJ)=F(IJ)+BIGA(IJ)*(AEK*SIJ+BЕК*STS(IJ))/TTEM1
2350 GO TO 1850
END (0,1,0,0,0)
SUBROUTINE SIJTS(H,U,EN,FEM1,ANS,I,J,KEYP)
DIMENSION H(201),U(5,202)
10000 SUM2=0.0
10050 KPM2=KEYP-2
10100 DO 10200 LP=3,KPM2,2
10200 SUM2=SUM2+H(LP)*U(I,LP+1)*U(J,LP+1)
10300 SUM3=0.0
10350 KPM1=KEYP-1
10400 DO 10500 LP=2,KPM1,2
10500 SUM3=SUM3+H(LP)*U(I,LP+1)*U(J,LP+1)
10550 KPP1=KEYP+1
10600 ANS=(H(1)+EN*FEM1)*U(I,2)*U(J,2)
2+(H(1)*U(I,2)*U(J,2)+2.0*SUM2+4.0*SUM3
3+H(KEYP)*U(I,KPP1)*U(J,KPP1))/3.0
10700 RETURN
END (0,1,0,0,0)

```

R

X-2
T

U

V

2150-2

2160-2

W

39-1

39-2

```

C      670 / CHEMISTRY 116      HUGO FRICKE / ANL / CC      REGULAR CODE R
      DIMENSION T(4),G34(20),CDT(20),H(20),PL(20),GAMMA(4),F(5),S(7), DIM-1
      2A(4,20),E(4,20),C(4,20),U(5),CAY(5),RIGA(5),U(5,202),U(4,202), DIM-2
      3STS(7)                                DIM-3
      EQUIVALENCE(STS(1),S(1)),(CDT(1),U(1 )),(PL(1),U(1 ))
900 SENSE LIGHT 0
910 SQRTPI=1.77245385
920 CAY(1)=1.0
930 GAMMA(1)=1.0
940 T(1)=1.0
945 KZ=0
950 D(1)=0.25
960 D(2)=0.0
970 D(3)=0.0
980 D(4)=0.25
990 D(5)=0.0
995 IF(SENSE SWITCH 5)999,1000
999 SENSE LIGHT 1
1000 READ 100,ICG,IVG,KEYP,KEYCPS,KEYE,KEYOUT,NGS,E,      1000-1
      2ACC,TMIN      1000-2
      100 FORMAT (2I3,5I6,3F12.6)
1010 IF(NGS)999,1020,1050
1020 END FILE 1
1030 PAUSE 1030
1040 GO TO 1000
1050 READ 105,BETA,BIGE,GAMMA(ICG),T(2),T(3),T(4),      1050-1
      2(CAY(IJ),IJ=2,5),(G34(N34),N34=1,NGS)      1050-2
      105 FORMAT (72H1
      2              /(6E12.6))
1070 FP=FLOATF(KEYP)      C-1
1071 FE=FLOATF(KEYF)
1072 KEPI=KEYE+1
1073 GAMMA(2)=( BETA)**KEPI
1074 CAPPA=E/(FE*(FP**2))      4
1080 IF(KEYOUT)1110,1065,1075
1065 PAUSE 1065
1067 GO TO 1000
1075 PRINT 105
1080 PRINT 108,BETA,BIGE,ICG,GAMMA(ICG),T(2),T(3),T(4),      1080-1
      2(CAY(IJ),IJ=2,5),IVG,(G34(N34),N34=1,NGS)      1080-2
      108 FORMAT (54H0 DIFFUSION KINETICS 111      670 / CHM 116/108-1
      28H0 B1/B2=F12.6,9H , BIGE =F12.6,4H , C11,4H/C1=F12.6,9H , D1/D1=F108-2
      312.6,2F15.6/8H K12 =F12.6,9H , K13 =F12.6,9H , K22 =F12.6,9H , 108-3
      4 K24 =F12.6/3H C11,4H/C1=F12.6,5F15.6/(7F15.6))      108-4
1090 PRINT 109,KEYE,KEYP,E,KEYCPS,ACC,CAPPA
109 FORMAT (9H EPSILON=12,5H , P=13,6H , E=F12.6,8H , CPS=14,7H , AC109-1
      2C=F12.6,5H , K=E15.8)      109-2
1100 IF(SENSE SWITCH 1)1110,1165
1110 WRITE OUTPUT TAPE 1,105
1120 WRITE OUTPUT TAPE 1,108,BETA,BIGE,ICG,GAMMA(ICG),      1120-1
      2T(2),T(3),T(4),(CAY(IJ),IJ=2,5),IVG,(G34(N34),N34=1,NGS)      1120-2
1130 WRITE OUTPUT TAPE 1,109,KEYE,KEYP,E,KEYCPS,ACC,CAPPA
1165 KEY=KEYE-1      C-2
1167 FEMI=FE-1.0
1170 Y=1.0-CAPPA      5
      CAPPA=1.0-Y

```



```

1175 EPKD2=FE*FP*CAPPA/2.0
1180 KPM1=KEYP-1
1185 G=1.0
1186 IF(KEY)1187,1200,1189
1187 PAUSE 1107
1188 GO TO 1000
1189 G=2.0/SQRTPI
1200 CDTP=LOGF(FP)
1210 DO 1270 LP=1,KEYP
1220 FLP=FLOATF(LP)
1230 CDT(LP)=CDTP-LOGF(FLP)
1240 H(LP)=1.0/FLP
1250 IF(KEY)1270,1270,1260
1260 H(LP)=H(LP)*SQRTF(CDT(LP))
1270 PL(LP)=FLP*CDT(LP)
1280 EP1=FLOATF(KEP1)
1290 KEEP1=KEYP*KEP1
1300 DO 1400 I=1,4
1310 TE=T(I)*EP1
1320 DO 1370 LP=1,KPM1
1330 TTPL=2.0*T(I)*PL(LP)
1335 ELPKD2=FE*FLOATF(LP)*CAPPA/2.0
1340 TT=(1.0-I(I))*CDT(LP)+TE/2.0
1350 A(I,LP)=ELPKD2*(TTPL+TT)
1360 B(I,LP)=ELPKD2*(TTPL-TT)
1370 C(I,LP)=1.0-2.0*ELPKD2*TTPL
1380 A(I,KEYP)=ELPKD2*TE
1390 B(I,KEYP)=0.0
1400 C(I,KEYP)=1.0-A(I,KEYP)
1410 TEK=((3.0*FE+1.0)/4.0)*CAPPA
1420 AEK=1.0+CAPPA*FE*(1.0+TEK)
1430 BEK=1.0+CAPPA*FE*(2.0+3.0*TEK)
1440 N34=1
1540 KEYCPC=KEYCPS
1545 KEYCCC=1
1550 KEYS=0
1560 TIME=1.0
1565 KBETA=1
1570 IF(BETA-1.0)1575,1590,1575
1575 KBETA=2
1580 BETASQ=BETA**2
1590 KPP1=KEYP+1
1600 DO 1650 LP=1,KPP1
1610 U(1,LP)=FLOATF(LP-1)/FP
1620 U(2,LP)=U(1,LP)
1630 GO TO (1650,1640),KBL1A
1640 U(2,LP)=U(2,LP)*BETASQ
1650 U(5,LP)=1.0
1655 U(3,LP)=1.0
1660 U(4,LP)=1.0
1670 DO 1690 IJ=1,5
1680 F(IJ)=0.0
1690 S(IJ)=0.0
1700 EN=0.0
1710 CALL SIJTS(H,I,EN,FEV1,STS(6),1,5,KEYP)
1720 EN=(0.86226925-STS(6))*FP

```

11-1

11-2

6

10-1

10-2

7-1

8-1

9-1

7-2

8-2

9-2

12

13

D

F

16

17

32-1

32-2

```

1730 IF(SENSE LIGHT 1)1740,1765
1740 REWIND 10
1750 READ INPUT TAPE 10,175,KEYS,TIME,(F(IJ),IJ=1,5)
175 FORMAT (1H015,E15.8,9F11.7)
1760 READ INPUT TAPE 10,176,N34,KEYCCC,EN,
2(S(IJ),IJ=1,5),((U(N,LP),N=1,4),LP=1,KPP1)
176 FORMAT (1H 2I6,1P2E14.7/(4E14.7))
1765 GAMMA(IVG)=G34(N34)
1770 DO 1775 J=1,3
1775 BIGA(J)=G*CAY(J)*GAMMA(1)*GAMMA(J)*BIGE*
2CAPPA*(0.25+D(J))
1780 IJ=4
1785 DO 1795 J=2,4,2
1790 BIGA(IJ)=G*CAY(IJ)*GAMMA(2)*GAMMA(J)*
2BIGE*CAPPA*(0.25+D(IJ))
1795 IJ=5
1800 BIGB=CAY(2*IVG-3)*BIGE*GAMMA(IVG)/(2.0*FE)
1805 IF(KEYOUT)1830,1810,1810
1810 PRINT 181,IVG,N34,GAMMA(IVG),BIGB
181 FORMAT (3H C11,4H/C11(I2,2H)=E12.6,50H
2 B=E12.6/120H0 SIFP TIME F11
3 F12 F13 F22 F24 M1 M2 181-1
4 F10 F20 ) 181-2
181-3
181-4
1820 IF(SENSE SWITCH 2)1830,1850
1830 WRITE OUTPUT TAPE 1,181,IVG,N34,GAMMA(IVG),BIGB
1850 IF(KEYCPS-KEYCPC)1860,1860,2100
1860 CALL SIJTS (H,U,EN,FEM1,STS(6),1,5,KEYP)
1870 CALL SIJTS (H,U,EN,FEM1,STS(7),2,5,KEYP)
1880 TEE=TIME*(KEEP1/2)
1890 GS1=G*STS(6)/TEE
1900 GS2=G*GAMMA(2)*STS(7)/TEF
1910 EM1=F(1)+F(2)+F(3)+GS1
1920 EM2=F(2)+F(4)+F(5)+GS2
1930 IF(KEYOUT)1960,1940,1940
1940 PRINT 175 ,KEYS,TIME,(F(IJ),IJ=1,5),EM1,EM2,GS1,GS2
1950 IF(SENSE SWITCH 3)1960,1970
1960 WRITE OUTPUT TAPE 1,175,KEYS,TIME,(F(IJ),IJ=1,5),
2EM1,EM2,GS1,GS2
1970 IF(SENSE SWITCH 6)1972,1975
1972 SENSE LIGHT 4
197 GC TO 1980
1975 IF(KEYCCC-500)2010,1977,1977
1977 KEYCCC=0
1980 REWIND 10
1990 WRITE OUTPUT TAPE 10,175,KEYS,TIME,(F(IJ),IJ=1,5)
2000 WRITE OUTPUT TAPE 10,176,N34,KEYCCC,EN,
2(S(IJ),IJ=1,5),((U(N,LP),N=1,4),LP=1,KPP1)
2010 IF(SENSE SWITCH 4)2020,2030
2020 WRITE OUTPUT TAPE 1,202,IVG,N34,GAMMA(IVG),
2KEYCCC,EN,(S(IJ),IJ=1,7),KZ,(((U(N,LP),N=1,4),LP),LP=1,KPP1)
202 FORMAT (6H GAMMA11,1H(I2,2H)=F12.7,7H , CCC=I3,6H ,ETA=F12.6,8H ,
2SIJ=(4E14.7,1H)/59H LP U1 U2 L3 202-1
3 U4 3E17.7/(I4,4E17.7)) 202-2
2030 IF(SENSE LIGHT 4)2035,2040
2035 PAUSE 2035
2040 KEYCPC=0

```

H
RFSTART

1760-1
1760-2

15-1-1
15-1-2

15-2-1
15-2-2

14

45
181-1
181-2
181-3
181-4

J
K-1
K-2

40
41
42
43
N

1960-1
1960-2
N SET UP
RFSTART

C
2000-1
2000-2

2020-1
2020-2
202-1
202-2
202-3

P

```

2050 IF(GS1-ACC)2060,2060,2070
2060 IF(GS2-ACC)2080,2070,2070
2070 IF(TIME-TMIN)2080,2080,2100
2080 N34=N34+1
2090 IF(N34-NGS)1540,1540,1000
2100 KEYS=KEYS+1
2105 KEYCCC=KEYCCC+1
2110 KEYCPC=KEYCPC+1
2120 ETTE=BIGE/(2.0*TIME**KEYE)*CAPPA
2125 TTEM1=TIME** (3*KEYE-1)
2130 TIME=Y*TIME
2140 DO 2180 LP=2,KPP1
2145 L=LP-1
2150 U1(1,LP)=A(1,L)*U(1,L)+B(1,L)*U(1,LP+1)+C(1,L)*U(1,LP)
      2-ETTE*(2.0*U(1,LP)+CAY(2)*GAMMA(2)*U(2,LP))U(1,LP)
      3+CAY(3)*GAMMA(3)*U(3,LP))U(1,LP)
2160 U1(2,LP)=A(2,L)*U(2,L)+B(2,L)*U(2,LP+1)+C(2,L)*U(2,LP)
      2-ETTE*(CAY(2)*U(1,LP)+2.0*CAY(4)*GAMMA(2)*U(2,LP))U(2,LP)
      3+CAY(5)*GAMMA(4)*U(4,LP))U(2,LP)
2170 U1(3,LP)=A(3,L)*U(3,L)+B(3,L)*U(3,LP+1)+C(3,L)*U(3,LP)
      2-ETTE*(CAY(3)*U(1,LP)*U(3,LP)-CAY(5)*GAMMA(2)
      3*GAMMA(4)/GAMMA(3)*U(2,LP)*U(4,LP))
2180 U1(4,LP)=A(4,L)*U(4,L)+B(4,L)*U(4,LP+1)+C(4,L)*U(4,LP)
      2-ETTE*(CAY(5)*GAMMA(2)*U(2,LP)*U(4,LP)
      3-CAY(3)*GAMMA(3)/GAMMA(4)*U(1,LP)*U(3,LP))
2190 DO 2210 N=1,4
2200 DO 2210 LP=2,KPP1
2210 U(N,LP)=U1(N,LP)
2250 DO 2280 J=1,3
2260 SIJ=STS(J)
2270 CALL SIJTS (H,U,EN,FEM1,STS(J),1,J,KEYP)
2280 F(J)=F(J)+BIGA(J)*(AEK*SIJ+BЕК*STS(J))/TTEM1
2290 IJ=4
2300 DO 2340 J=2,4,2
2310 SIJ=STS(IJ)
2320 CALL SIJTS (H,U,EN,FEM1,STS(IJ),2,J,KEYP)
2330 F(IJ)=F(IJ)+BIGA(IJ)*(AEK*SIJ+BЕК*STS(IJ))/TTEM1
2340 IJ=5
2350 GO TO 1850
      END (0,1,0,0,1)
      SUBROUTINE SIJTS(H,U,EN,FEM1,ANS,I,J,KEYP)
      DIMENSION H(201),U(5,202)
10000 SUM2=0.0
10050 KPM2=KEYP-2
10100 DO 10200 LP=3,KPM2,2
10200 SUM2=SUM2+H(LP)*U(I,LP+1)*U(J,LP+1)
10300 SUM3=0.0
10350 KPM1=KEYP-1
10400 DO 10500 LP=2,KPM1,2
10500 SUM3=SUM3+H(LP)*U(I,LP+1)*U(J,LP+1)
10550 KPP1=KEYP+1
10600 ANS=(H(1)+EN*FEM1)*U(I,2)*U(J,2)
      2+(H(1)*U(I,2)*U(J,2)+2.0*SUM2+4.0*SUM3
      3+H(KEYP)*U(I,KPP1)*U(J,KPP1))/3.0
10700 RETURN
      END(0,1,0,0,0)

```

Q
RX-2
T

U

V

2150-2
2150-3

2160-2

W

39-1

39-2

```

C      670 / CHEMISTRY 116      HUGO FRICKE / ANL / CC      SPECIAL CODE C
C      SHOULD BE DIFFERENT, BUT OKAY IF G2=G3=G4=1
      DIMENSION T(4),G34(20),CDT(201),H(201),PL(201),GAMMA(4),F(5),S(7), DIM-1
      2A(4,201),B(4,201),C(4,201),D(5),CAY(5),BIGA(5),U(5,202),U1(4,202), DIM-2
      3STS(7) DIM-3
      EQUIVALENCE(STS(1),S(1)),(CDT(1),U1(1 )),(PL(1),U(1  ))
900 SENSE LIGHT 0
910 SQRTPI=1.77245385
920 CAY(1)=1.0
930 GAMMA(1)=1.0
940 T(1)=1.0
945 KZ=0
950 D(1)=0.25
960 D(2)=0.0
970 D(3)=0.0
980 D(4)=0.25
990 D(5)=0.0
995 IF(SENSE SWITCH 5)999,1000
999 SENSE LIGHT 1
1000 READ 100,ICG,IVG,KEYP,KEYCPS,KEYE,KEYOUT,NGS,E, 1000-1
      2ACC,TMIN 1000-2
      100 FORMAT (2I3,5I6,3F12.6)
1010 IF(NGS) 999,1020,1050
1020 END FILE 1
1030 PAUSE 1030
1040 GO TO 1000
1050 READ 105,BETA,BIGE,GAMMA(ICG),T(2),T(3),T(4), 1050-1
      2(CAY(IJ),IJ=2,5),(G34(N34),N34=1,NGS) 1050-2
      105 FORMAT (72H1
      2 /16E12.6))
1070 FP=FLOATF(KEYP) C-1
1071 FE=FLOATF(KEYE)
1072 KEP1=KEYE+1
1073 GAMMA(2)=( BETA)**KEP1
1074 CAPPA=E/(FE*(FP**2)) 4
1060 IF(KEYOUT)1110,1065,1075
1065 PAUSE 1065
1067 GO TO 1000
1075 PRINT 105
1080 PRINT 108,BETA,BIGE,ICG,GAMMA(ICG),T(2),T(3),T(4), 1080-1
      2(CAY(IJ),IJ=2,5),IVG,(G34(N34),N34=1,NGS) 1080-2
      108 FORMAT (54H0 DIFFUSION KINETICS 111 670 / CHM 116/108-1
      28H0 B1/B2=F12.6,9H , BIGE =F12.6,4H , C11,4H/C1=F12.6,9H , D1/D1=F108-2
      312.6,2F15.6/8H K12 =F12.6,9H , K13 =F12.6,9H , K22 =F12.6,9H ,108-3
      4 K24 =F12.6/3H C11,4H/C1=F12.6,5F15.6/(7F15.6)) 108-4
1090 PRINT 109,KEYE,KEYP,E,KEYCPS,ACC,CAPPA
109 FORMAT (9H EPSILON=12,5H , P=13,6H , E=F12.6,8H , CPS=14,7H , AC109-1
      2C=F12.6,5H , K=E15.8) 109-2
1100 IF(SENSE SWITCH 1)1110,1165
1110 WRITE OUTPUT TAPE 1,105
1120 WRITE OUTPUT TAPE 1,108,BETA,BIGE,ICG,GAMMA(ICG), 1120-1
      2T(2),T(3),T(4),(CAY(IJ),IJ=2,5),IVG,(G34(N34),N34=1,NGS) 1120-2
1130 WRITE OUTPUT TAPE 1,109,KEYE,KEYP,E,KEYCPS,ACC,CAPPA
1165 KEY=KEYE-1 C-2
1167 FEM1=FE-1.0
1170 Y=1.0-CAPPA 5

```

```

      CAPP=1.0-Y
1175 EPKD2=FE*FP*CAPP/2.0
1180 KPM1=KEYP-1
1185 G=1.0
1186 IF(KEY)1187,1200,1189
1187 PAUSE 1107
1188 GO TO 1000
1189 G=2.0/SQRTPI
1200 CDT=LOGF(FP)
1210 DO 1270 LP=1,KEYP
1220 FLP=FLOATF(LP)
1230 CDT(LP)=CDT-LOGF(FLP)
1240 H(LP)=1.0/FLP
1250 IF(KEY)1270,1270,1260
1260 H(LP)=H(LP)*SQRTF(CDT(LP))
1270 PL(LP)=FLP*CDT(LP)
1280 EPI=FLOATF(KEP1)
1290 KEPI=KEYE*KEP1
1300 DO 1400 I=1,4
1310 TE=T(I)*EPI
1320 DO 1370 LP=1,KPM1
1330 TTPL=2.0*T(I)*PL(LP)
1335 ELPKD2=FE*FLOATF(LP)*CAPP/2.0
1340 TT=(1.0-T(I))*CDT(LP)+TE/2.0
1350 A(I,LP)=ELPKD2*(TTPL+TT)
1360 B(I,LP)=ELPKD2*(TTPL-TT)
1370 C(I,LP)=1.0-2.0*ELPKD2*TTPL
1380 A(I,KEYP)=EPKD2*TE
1390 B(I,KEYP)=0.0
1400 C(I,KEYP)=1.0-A(I,KEYP)
1410 TEK=((3.0*FE+1.0)/4.0)*CAPP
1420 AEK=1.0+CAPP*FE*(1.0+TEK)
1430 BEK=1.0+CAPP*FE*(2.0+3.0*TEK)
1440 N34=1
1540 KEYCPC=KEYCPS
1545 KEYCCC=1
1550 KEYS=0
1560 TIME=1.0
1565 KBETA=1
1570 IF(BETA-1.0)1575,1590,1575
1575 KBETA=2
1580 BETASQ=BETA**2
1590 KPP1=KEYP+1
1600 DO 1650 LP=1,KPP1
1610 U(1,LP)=FLOATF(LP-1)/FP
1620 U(2,LP)=U(1,LP)
1630 GO TO (1650,1640),KBETA
1640 U(2,LP)=U(2,LP)**BETASQ
1650 U(5,LP)=1.0
1655 U(3,LP)=0.0
1660 U(4,LP)=0.0
1670 DO 1690 IJ=1,5
1680 F(IJ)=0.0
1690 S(IJ)=0.0
1700 EN=0.0
1710 CALL SIJTS(H,U,EN,FEM1,STS(6),1,5,KEYP)

```

11-1

11-2

6
10-1

10-2

7-1

8-1

9-1

7-2

8-2

9-2

12

13

D

F

16

17

32-1

```

1720 EN=(0.886226925-ST5(6))*FP
1730 IF(SENSE LIGHT 1)1740,1765
1740 REWIND 10
1750 READ INPUT TAPE 10,175,KEYS,TIME,(F(IJ),IJ=1,5)
175 FORMAT (1H015,E15.8,9F11.7)
1760 READ INPUT TAPE 10,176,N34,KEYCCC,EN,
2(S(IJ),IJ=1,5),((U(N,LP),N=1,4),LP=1,KPP1)
176 FORMAT (1H 216,1P2E14.7/(4E14.7))
1765 GAMMA(IVG)=G34(N34)
1770 DO 1775 J=1,3
1775 BIGA(J)=G*CAY(J)*GAMMA(1)*GAMMA(J)*BIGE*
2CAPPA*(0.25+D(J))
1780 IJ=4
1785 DO 1795 J=2,4,2
1790 BIGA(IJ)=G*CAY(IJ)*GAMMA(2)*GAMMA(J)*
2BIGE*CAPPA*(0.25+D(IJ))
1795 IJ=5
1800 BIGB=CAY(2*IVG-3)*BIGE*GAMMA(IVG)/(2.0*FE)
1805 IF(KEYOUT)1830,1810,1810
1810 PRINT 181,IVG,N34,GAMMA(IVG),BIGB
181 FORMAT (3H C11,4H/C1(I2,2H)=E12.6,50H
2 B=E12.6/120H0 STEP TIME F11
3 F12 F13 F22 F24 M1 M2
4 F10 F20 )
1820 IF(SENSE SWITCH 2)1830,1850
1830 WRITE OUTPUT TAPE 1,181,IVG,N34,GAMMA(IVG),BIGB
1850 IF(KEYCPS-KEYCPC)1860,1860,2100
1860 CALL SIJTS (H,U,EN,FEM1,STS(6),1,5,KEYP)
1870 CALL SIJTS (H,U,EN,FEM1,STS(7),2,5,KEYP)
1880 TEE=TIME**((KEEP1/2))
1890 GS1=G*STS(6)/TEE
1900 GS2=G*GAMMA(2)*STS(7)/TEE
1910 EM1=F(1)+F(2)+F(3)+GS1
1920 EM2=F(2)+F(4)+F(5)+GS2
1930 IF(KEYOUT)1960,1940,1940
1940 PRINT 175 ,KEYS,TIME,(F(IJ),IJ=1,5),EM1,EM2,GS1,GS2
1950 IF(SENSE SWITCH 3)1960,1970
1960 WRITE OUTPUT TAPE 1,175,KEYS,TIME,(F(IJ),IJ=1,5),
2EM1,EM2,GS1,GS2
1970 IF(SENSE SWITCH 6)1972,1975
1972 SENSE LIGHT 4
197 GO TO 1980
1975 IF(KEYCCC-500)2010,1977,1977
1977 KEYCCC=0
1980 REWIND 10
1990 WRITE OUTPUT TAPE 10,175,KEYS,TIME,(F(IJ),IJ=1,5)
2000 WRITE OUTPUT TAPE 10,176,N34,KEYCCC,EN,
2(S(IJ),IJ=1,5),((U(N,LP),N=1,4),LP=1,KPP1)
2010 IF(SENSE SWITCH 4)2020,2030
2020 WRITE OUTPUT TAPE 1,202,IVG,N34,GAMMA(IVG),
2KEYCCC,EN,(S(IJ),IJ=1,7),KZ,(((U(N,LP),N=1,4),LP),LP=1,KPP1)
202 FORMAT (6H GAMMA11,1H(I2,2H)=F12.7,7H , CCC=13,6H ,ETA=F12.6,8H ,
2SIJ=(4E14.7,1H) /59H LP U1 U2 U3
3 U4 3E17.7/(14,4E17.7))
2030 IF(SENSE LIGHT 4)2035,2040
2035 PAUSE 2035

```

32-2
H
RESTART

1760-1
1760-2

15-1-1
15-1-2

15-2-1
15-2-2

14

45
181-1
181-2
181-3
181-4

J
K-1
K-2

40
41
42
43
N

1960-1
1960-2
N SET UP
RESTART

0
2000-1
2000-2

2020-1
2020-2
202-1
202-2
202.3

```

2040 KEYCPC=0
2050 IF(GS1-ACC)2060,2060,2070
2060 IF(GS2-ACC)2080,2070,2070
2070 IF(TIME-TMIN)2080,2080,2100
2080 N34=N34+1
2090 IF(N34-NGS)1540,1540,1000
2100 KEYS=KEYS+1
2105 KEYCCC=KEYCCC+1
2110 KEYCPC=KEYCPC+1
2120 ETTE=BIGE/(2.0*TIME**KEYE)*CAPPA
2125 TTEM1=TIME**(3*KEYE-1)
2130 TIME=Y*TIME
2140 DO 2180 LP=2,KPP1
2145 L=LP-1
2150 U1(1,LP)=A(1,L)*U(1,L)+B(1,L)*U(1,LP+1)+C(1,L)*U(1,LP)
      2-ETTE*(2.0*U(1,LP)+CAY(2)*GAMMA(2)*U(2,LP))*U(1,LP)
2160 U1(2,LP)=A(2,L)*U(2,L)+B(2,L)*U(2,LP+1)+C(2,L)*U(2,LP)
      2-ETTE*(CAY(2)*U(1,LP)+2.0*CAY(4)*GAMMA(2)*U(2,LP))*U(2,LP)
      3+CAY(5)*GAMMA(4)*U(4,LP))*U(2,LP)
C      SHOULD BE DIFFERENT, BUT OKAY IF G2=G3=G4=1
2180 U1(4,LP)=A(4,L)*U(4,L)+B(4,L)*U(4,LP+1)+C(4,L)*U(4,LP)
      2-ETTE*(CAY(5)*GAMMA(2)*U(2,LP)*U(4,LP)
      3-CAY(4)*GAMMA(3)/GAMMA(4)*U(2,LP)*U(2,LP))
2190 DO 2210 N=1,4
2200 DO 2210 LP=2,KPP1
2210 U(N,LP)=U1(N,LP)
2250 DO 2280 J=1,2
2260 SIJ=STS(J)
2270 CALL SIJTS (H,U,EN,FEM1,STS(J),1,J,KEYP)
2280 F(J)=F(J)+BIGA(J)*(AEK*SIJ+BK*STS(J))/TTEM1
2290 IJ=4
2300 DO 2340 J=2,4,2
2310 SIJ=STS(IJ)
2320 CALL SIJTS (H,U,EN,FEM1,STS(IJ),2,J,KEYP)
2330 F(IJ)=F(IJ)+BIGA(IJ)*(AEK*SIJ+BK*STS(IJ))/TTEM1
2340 IJ=5
2350 GO TO 1850
      END (0,1,0,0,1)
      SUBROUTINE SIJTS(H,U,EN,FEM1,ANS,I,J,KEYP)
      DIMENSION H(201),U(5,202)
10000 SUM2=0.0
10050 KPM2=KEYP-2
10100 DO 10200 LP=3,KPM2,2
10200 SUM2=SUM2+H(LP)*U(I,LP+1)*U(J,LP+1)
10300 SUM3=0.0
10350 KPM1=KEYP-1
10400 DO 10500 LP=2,KPM1,2
10500 SUM3=SUM3+H(LP)*U(I,LP+1)*U(J,LP+1)
10550 KPP1=KEYP+1
10600 ANS=(H(1)+EN*FEM1)*U(I,2)*U(J,2)
      2+(H(1)*U(I,2)*U(J,2)+2.0*SUM2+4.0*SUM3
      3+H(KEYP)*U(I,KPP1)*U(J,KPP1))/3.0
10700 RETURN
      END(0,1,0,0,0)

```

P
Q
R

X-2
T

U

V

2150-2

2160-2

W

39-1

39-2

APPENDIX D

Sample Problem Input and Output

SAMPLE PROBLEM: STANDARD NO.1 SPHERICAL CASE WITH 4 COMPONENTS REG

DIFFUSION KINETICS III 670 / CHN 116

C1/C2= 1.000000 , B1C2 = 0.000000 , C3/C1= 0.000000 , D1/C1= 0.454545 0.150000 0.150000
 K12 = 2.000000 , K13 = 2.000000 , K22 = 1.000000 , K24 = 2.000000
 C4/C1= 2.000000
 EPSILON= 2 , P= 33 , E= 2.000000 , CPS= 100 , ACC= 0.000100 , K= 0.91827364E-03
 C4/C1(1)=0.229885E-04 B=0.100000E-04

STEP	TIME	F11	F12	F13	F22	F24	M1	M2	F10	F20
0	0.09999999E+01	0.	0.	0.	0.	0.	1.00000000	1.00000000	1.00000000	1.00000000
100	0.91222417E+00	0.0248787	0.0257258	0.0000020	0.0266422	0.0000020	0.9992049	1.0062088	0.9485985	0.9538388
200	0.85215289E+00	0.0447625	0.0475485	0.0000042	0.0507753	0.0000042	0.9985447	1.0112799	0.9062295	0.9129518
300	0.75910999E+00	0.0609915	0.0662381	0.0000068	0.0726904	0.0000068	0.9977460	1.0152596	0.8705096	0.8763243
400	0.69247838E+00	0.0744971	0.0824124	0.0000098	0.0926761	0.0000098	0.9968480	1.0183831	0.8399288	0.8432849
500	0.63167544E+00	0.0859039	0.0965177	0.0000133	0.1109402	0.0000132	0.9958928	1.0208264	0.8134580	0.8133553
600	0.57624769E+00	0.0956512	0.1088911	0.0000174	0.1276439	0.0000172	0.9949170	1.0227261	0.7903573	0.7861730

SAMPLE PROBLEM STANDARD NO.1- SPHERICAL CASE WITH 2 COMPONENTS

DIFFUSION KINETICS 111

670 / CHM 116

1/B2= 1.000000, BICE= 0.870000, C3/C1= 0.000023, DI/O1= 0.454545 0.150000 0.150000
 K12 = 2.000000, K13 = 2.000000, K22 = 1.000000, K24 = 2.000000
 C4/C1= 0.000023
 EPSILON= 2, P= 33, E= 2.000000, CPS= 100, ACC= 0.000100, K= 0.000918
 C4/C11 11=0.229885E-04 B=0.100000E-04

STEP	TIME	F11	F12	F22	M1	M2	F10	F20
0	0.09999999E-01	0.	0.	0.	1.00000000	1.00000000	1.00000000	1.00000000
GAMMA4(1)= 0.0000230, CCC= 1, ETA= 0.252128, SIJ=(0. 0. 0. 0. 0.8862269E 00 0.8862269E 00								
LP	U1	U2	0.					
0	0.	0.						
1	0.3030303E-01	0.3030303E-01						
2	0.6060606E-01	0.6060606E-01						
3	0.9090909E-01	0.9090909E-01						
4	0.1212121E-00	0.1212121E-00						
5	0.1515151E-00	0.1515151E-00						
6	0.1818182E-00	0.1818182E-00						
7	0.2121212E-00	0.2121212E-00						
8	0.2424242E-00	0.2424242E-00						
9	0.2727273E-00	0.2727273E-00						
10	0.3030303E-00	0.3030303E-00						
11	0.3333333E-00	0.3333333E-00						
12	0.3636364E-00	0.3636364E-00						
13	0.3939394E-00	0.3939394E-00						
14	0.4242424E-00	0.4242424E-00						
15	0.4545455E-00	0.4545455E-00						
16	0.4848485E-00	0.4848485E-00						
17	0.5151515E-00	0.5151515E-00						
18	0.5454545E-00	0.5454545E-00						
19	0.5757576E-00	0.5757576E-00						
20	0.6060606E-00	0.6060606E-00						
21	0.6363636E-00	0.6363636E-00						
22	0.6666667E-00	0.6666667E-00						
23	0.6969697E-00	0.6969697E-00						
24	0.7272727E-00	0.7272727E-00						
25	0.7575758E-00	0.7575758E-00						
26	0.7878788E-00	0.7878788E-00						
27	0.8181818E-00	0.8181818E-00						
28	0.8484848E-00	0.8484848E-00						
29	0.8787879E-00	0.8787879E-00						
30	0.9090909E-00	0.9090909E-00						
31	0.9393939E-00	0.9393939E-00						
32	0.9696970E-00	0.9696970E-00						
33	0.1000000E-01	0.1000000E-01						
34								

100 0.91222417E 00 0.0248788 0.0257259 0.0266423 0.9992036 1.0062075 0.9485989 0.9538392
 GAMMA4(1)= 0.0000230, CCC=101, ETA= 0.252128, SIJ=(-0.1550732E-00 0.1657146E-00 0.
 LP U1 U2 0.1776948E-00 0. 0.6381640E 00 0.6416894E 00
 --0 --0 --0
 1 0.2283546E-01 0.1879236E-01
 2 0.4542176E-01 0.3927645E-01
 3 0.6778814E-01 0.6176553E-01
 4 0.8994995E-01 0.8435367E-01

3 PLL PROBLE 17 0.10.1 SPH 10/L C4 IIF 2 CO POE 15

DIFFUSION KINETICS 111 07 / CH1 116

S1/S2= 1.000000 , SICE = 0.7 , S/C1= 0.023 , I1/I2= 0.44545 0.150000 0.150000
 K12 = 2.0000 , F13 = 0.0 , K22 = 1.000000 , I2/I1 = 2.000000
 C4/C1= 0.00023
 EPSILO1 = 2 , P= 33 , E= 2.000000 , CF = 100 , ACC= 0.000000 , K= 0.000000
 C4/C1(1)=0.220035E-04 0.100000E-04

STEP	TIME	F11	F12	F22	M1	M2	F10	F20
0	0.09999999E 01	0.	0.	0.	1.00000000	1.00000000	1.00000000	1.00000000
100	0.91222417E 00	0.0248788	0.0257259	0.0266423	0.9997036	1.0062075	0.485080	0.9538392
200	0.83215289E 00	0.0447627	0.0475480	0.0507756	0.9985471	1.0112773	0.9062306	0.9129529
300	0.7591999E 00	0.0609719	0.0662385	0.0726909	0.9977420	1.0177556	0.3705118	0.8763263
400	0.68247830E 00	0.0744976	0.0824130	0.0926708	0.9968431	1.0183702	0.09925	0.0432063
500	0.60316044E 00	0.0809046	0.0965185	0.1107413	0.9958868	1.020020	0.0134637	0.0133006
600	0.57674709E 00	0.0950521	0.1088923	0.1276452	0.9949009	1.0227137	0.7393655	0.7861814

APPENDIX E

Representative Examples

The figures on the following pages are the result of some representative cases computed with the codes described in this report. Figures 2 to 12 trace the concentrations of the various reactants and reaction products during the course of the reactions. The input parameters for these calculations are given in Table III.

Table III

PARAMETERS OF REPRESENTATIVE CALCULATIONS

Case	ϵ	β	E	D_2/D_1	D_3/D_1	D_4/D_1	κ_{12}	κ_{13}	κ_{22}	κ_{24}	B_3	B_4
141	2	1	.87	.4545..	.15	.15	2	2	1	2	10^{-5}	10^{-5}
143	2	1	.87	.4545..	.15	.15	2	2	1	2	10^{-5}	.1
145	2	1	.87	.4545..	.15	.15	2	2	1	2	10^{-5}	10
253	2	1	.87	.4545..	.15	.15	2	0	1	0	0	0
257	2	1	.87	.25	.15	.15	2	0	.55	0	0	0
303	2	1	.87	.25	.15	.15	2	2	.55	2	10^{-5}	.1

Figures 13-16 show the final concentrations resulting from varying selected parameters in standard sets. The usual values for the five standard sets of input parameters are given in Table IV.

Table IV

STANDARD PARAMETERS

Standard	β	E (for $\epsilon = 2$)	D_2/D_1	D_3/D_1	D_4/D_1	κ_{12}	κ_{22}	$\kappa_{13} = \kappa_{24}$
I	1	.87	.4545..	.15	.15	2	1	0 or 2
II	1	.87	.25	.15	.15	2	.55	0 or 2
III	1	.91	.25	.15	.15	4	.60	0 or 2
IV	1	.87	.25	.15	.15	1	.55	0 or 2
V	1	.87	.125	.15	.15	2	.30	0 or 2

Figure 2
General Shapes of Solutions $U_i(R,T)$

Figure 3
Preservation of Near-Gaussian Space Distribution

Figure 4
Preservation of Near-Gaussian Space Distribution

Figure 5 and 6
Space Distribution at Different Transformed Times

Figure 7 and 8
Real Time Dependence of Normalized
Concentrations at Origin

Figure 9 and 10

Time Dependence of Recombination Fractions for Some Representative Cases

Figure 11 and 12

Figure 13

Influence of Diffusion Coefficients on $F_{22}^{(B)}/F_{22}^{(O)}$

Figure 14

Influence of Reaction Rates on $F_{22}^{(B)}/F_{22}^{(O)}$

Figure 15

Influence of Initial Free Radical Concentrations
on $F_{11}^{(B)}/F_{11}^{(O)}$

Figure 16

Influence of Initial Free Radical Concentrations
on $F_{22}^{(B)}/F_{22}^{(O)}$