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THE UNIVERSITY OF ALBERTA

SYSTEM IDENTIFICATION AS A BOUNDARY  
VALUE PROBLEM

BY



JOHN K. DONNELLY

A DISSERTATION

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## ABSTRACT

A study has been made of the problem of estimating parameters or coefficients in systems of ordinary differential equations from experimental data. The study was limited to a special class of problems. However, the basic concepts which were developed can, in principle, be extended to more general problems without much difficulty.

It was assumed that for a given physical system, several experiments have been performed with different, but known initial conditions. It was further assumed that some or all of the state variables had been measured at one or more values of the independent variable. Of course, it is also necessary to assume that the given physical system can be adequately modeled by a system of ordinary differential equations which is known to within a few parameters.

This identification problem was formulated as a multipoint boundary value problem which was inevitably nonlinear. Attempts to use quasilinearization directly did not always converge. To alleviate this difficulty, the concept of boundary value or data perturbation was introduced. This concept is based on the assumption that quasilinearization will converge provided the initial guess is sufficiently close. If this is so, then pseudo-boundary conditions can be set up near the trajectories produced by the initial guess.

These pseudo-boundary conditions are chosen so that the actual solution may be approached in a finite number of steps, each step being solved by quasilinearization. This procedure was found satisfactory for a number of examples.

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## TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. THEORY	6
A. Formulation	6
B. Quasilinearization and the Solution of Nonlinear Boundary Value Problems	9
C. Boundary Value or Data Perturbation	13
III. PRACTICAL APPLICATION	24
A. Data Perturbation and a Stepping Procedure	24
B. Quasilinearization	26
IV. APPLICATION IN CHEMICAL REACTION KINETICS	29
A. A Nonlinear Example	29
B. Sensitivity to the Choice of Experiments and to Experimental Error	44
C. A Non-Isothermal Reaction	55
D. A Catalytic Reaction	62
E. A Complex Nonlinear Reaction	72

V.	IDENTIFICATION OF SIMPLE CONTROL MODELS FOR COMPLEX SYSTEMS	94
	A. Flow of a Tracer Through a Packed Bed	95
VI.	DISCUSSION AND CONCLUSIONS	103
	A. Numerical Problems	103
	B. Experimental Design	104
	C. Computer Time Requirements	105
	D. Future Work	106
	NOMENCLATURE	108
	BIBLIOGRAPHY	112
APPENDIX A	- Documentation of the Basic Program and the Nonlinear Example	A-1
APPENDIX B	- The 1-Butene Problem	B-1
APPENDIX C	- Non-Isothermal Pyrolysis of Propane	C-1
APPENDIX D	- Catalytic Hydrogen Chloride Oxidation	D-1
APPENDIX E	- Chemcell Problem	E-1
APPENDIX F	- Tracer Problem	F-1



## LIST OF TABLES

Table No.	Title	Page
1	Data for the Nonlinear Example	32
2	Convergence of the Nonlinear Example Without Data Perturbation	34
3	Convergence of the Nonlinear Example With Data Perturbation	39
4	Convergence of the Last Step for the Nonlinear Example	43
5	Initial Conditions for 1-Butene Problem	48
6	Solution Using all Available Data for 1-Butene Problem	50
7	Solution Using Data from the Eigen- vector Directions	51
8	Solutions Using Data Set One	52
9	Solutions Using Data Set Two	53
10	Solutions for 1-Butene Problem Using Perturbed Initial Condition ( $\sigma = 0.001$ )	54
11	Solution for 1-Butene Problem Using Perturbed Initial Condition ( $\sigma = 0.1$ )	54
12	Convergence Rate for the First Propane Problem	60
13	Convergence Rate for the Second Propane Problem	61
14	Hydrogen Chloride Problem Results for 325°C Data	71

15	Chemcell Problem: Various Solutions for 100°C Data	80
16	Chemcell Problem: Various Solutions for 80°C Data	87
17	Data for Tracer Problem	97
18	Solutions of Tracer Problem	100
19	Deviation of the Model from the Actual Values for Tracer Problem	101

## LIST OF FIGURES

Figure No.	Title	Page
1	Illustration of Boundary Value or Data Perturbation	15
2	Convergence of Nonlinear Example Using Quasilinearization (Data Set One)	35
3	Convergence of Nonlinear Example Using Quasilinearization (Data Set Two)	36
4	Convergence of Nonlinear Example Using Quasilinearization (Data Set Three)	37
5	Convergence of Nonlinear Example Using Data Perturbation (Data Set One)	40
6	Convergence of Nonlinear Example Using Data Perturbation (Data Set Two)	41
7	Convergence of Nonlinear Example Using Data Perturbation (Data Set Three)	42
8	Phase Plan Diagram for 1-Butene Problem	49
9	Solution of Chemcell Problem (Data Set One at 100°C)	81
10	Solution of Chemcell Problem (Data Set Two at 100°C)	82
11	Solution of Chemcell Problem (Data Set Three at 100°C)	83
12	Solution of Chemcell Problem (Data Set Four at 100°C)	84

13	Solution of Chemcell Problem (Data Set Five at 100°C)	85
14	Solution of Chemcell Problem (Data Set Six at 100°C)	86
15	Solution of Chemcell Problem (Data Set One at 80°C)	88
16	Solution of Chemcell Problem (Data Set Two at 80°C)	89
17	Solution of Chemcell Problem (Data Set Three at 80°C)	90
18	Solution of Chemcell Problem (Data Set Four at 80°C)	91
19	Solution of Chemcell Problem (Data Set Five at 80°C)	92

## I. INTRODUCTION

In recent years, with the exponential advances in technology, it has been increasingly evident that more sophisticated mathematical models must be employed if industrial processes are to be designed and operated more efficiently.

Management, in the not too distant past, took pride in the amount of "over production" that was obtained from a particular plant. However, now with their thinking on a more sophisticated level, they realize that the "over production" is a direct result of inadequate design procedures which resulted in a considerable amount of investment capital being wasted on large safety factors.

Recent tendencies toward automation are completely dependent on having adequate mathematical models. A large part of optimization theory assumes that the models exist; hence the development of techniques for obtaining these models is of utmost importance.

Finding mathematical models which are adequate for these various uses is not a trivial problem. A purely theoretical approach is sufficient in only the simplest of cases. In more complex cases, either the system is not well enough understood or its model is so complicated that it can not be solved in a reasonable amount of time, if at all. The

definition of "a reasonable amount of time", of course depends on the particular problem. With these complex systems, a correlative procedure is needed.

For most control systems, the simplest acceptable correlative model is a system of ordinary differential equations. Theoretical considerations usually can be used to derive the system of ordinary differential equations in which only a few parameters need to be determined.

Similarly, many design models are also in the form of a system of ordinary differential equations, known except for a few constant parameters. Plug flow and batch reactors are the examples of this type of system; these are used extensively in this work.

In general, data taken from the actual system or a laboratory scaled model of the system are used to identify the unknown parameters in the mathematical model.

Unfortunately, once the data are taken, there are no completely satisfactory general techniques for finding these parameters. The techniques that do exist often depend on some specific characteristic of the problem (such as linearity).

A good summary of the existing techniques with an extensive list of pertinent references has been supplied by Cuenod and Gage (5).

Many of the existing techniques require that the experiments be performed and the data collected in a predetermined

manner. More specifically, the procedure for identifying certain control systems is based on observed deviations of the system from a target value or set point caused by disturbances introduced into the system. The nature of these disturbances is dependent on the particular method being employed. An example is the sinusoidal disturbance required for the frequency response method.

With many systems, it is not convenient to introduce arbitrary disturbances which are a function of the independent variable. This is especially true with the identification of certain design models.

There are a few methods for handling the identification problem which are not as dependent on the types of disturbances employed, provided that they adequately excite all the different modes of the system. To discuss some of these methods, a system will be considered described below

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}, \mathbf{a}, t) \quad (\text{I-1})$$

with  $\mathbf{y}$  being the state vector,  $t$  the independent variable, and  $\mathbf{a}$  the unknown parameter vector.

One approach that is quite favored because of its simplicity is to measure  $\mathbf{y}$  and  $\frac{d\mathbf{y}}{dt}$  as functions of the independent variable and minimize the objective function

$$z = \int_0^{t_f} \left\| \frac{d\hat{\mathbf{y}}}{dt} - \mathbf{g}(\hat{\mathbf{y}}, \mathbf{a}, t) \right\|^2 dt \quad (\text{I-2})$$

with  $\|\underline{x}\|$  being the length of the vector  $\underline{x}$ ,  $\frac{d\hat{y}}{dt}$  being the measured value of the derivative and  $\hat{y}$  being the measured value of the state vector. If the measurements are not taken continuously, but at discrete values of the independent variable, the corresponding objective function is

$$z = \sum_i \left\| \frac{d\hat{y}_i}{dt} - g(\hat{y}_i, \underline{a}, t_i) \right\|^2 \quad (\text{I-3})$$

The principal objection to this method is that it is quite sensitive to noise in the data which make it difficult to determine accurate values of  $\frac{d\hat{y}}{dt}$ . For some systems, the direct measurement of  $\frac{d\hat{y}}{dt}$  is not difficult and this method can be employed profitably.

An alternative approach is to reformulate the problem by letting the vector  $\underline{a}$  be a function of the independent variable which is a solution to the differential equation

$$\frac{d\underline{a}}{dt} = 0 \quad (\text{I-4})$$

Doing this, the identification problem may be formulated as an optimization problem with the objective function

$$z = \int_0^{tf} \|\hat{y} - y\|^2 dt \quad (\text{I-5})$$

if  $\hat{y}$  may be measured as a continuous function of time. If the measurements  $\hat{y}$  are made at discrete values of the independent



variable, then the objective function is

$$Z = \sum_i ||y_i - \underline{y}_i||^2 \quad (I-6)$$

With the first objective function (I-5) the identification problem has been formulated as an optimal control problem. When the second objective function must be used, the identification problem has been formulated as a multi-point boundary value problem. It is this formulation and the solution of the resultant boundary value problem that is the subject of the remainder of this work.

## II. THEORY

### A. Formulation of the Problem

Suppose that the behavior of a physical system can be adequately approximated by the following vector differential equation:

$$\frac{d\underline{x}}{dt} = \underline{f}(\underline{x}, \underline{a}, t) \quad (\text{II-1})$$

where  $\underline{x}$  = vector of state variables (order p)

$\underline{a}$  = vector of constant system parameters (order q)

t = independent variable

Suppose further that n different experiments have been conducted on the actual physical system with the initial conditions  $\underline{x}_j(0)$ ,  $j = 1, 2, \dots, n$ . At certain discrete values of t, some or all of the elements of  $\underline{x}$  have been observed and recorded as data.

The set of vector differential equations describing all these experiments is:

$$\frac{d\underline{x}_j}{dt} = \underline{f}_j(\underline{x}_j, \underline{a}, t), \quad j = 1, 2, \dots, n \quad (\text{II-2})$$

with the initial conditions  $\underline{x}_j(0)$  and the functions  $\underline{f}_j(\underline{x}_j, \underline{a}, t)$  being specified for each experiment. The data pertinent to the  $j^{\text{th}}$  experiment will be referred to as the  $j^{\text{th}}$  data set throughout the remainder of this work.

If  $t_{jk}$  is taken to be the  $k^{\text{th}}$  discrete value of  $t$  for the  $j^{\text{th}}$  experiment, then  $\hat{x}_{ijk}$  may be defined as the observed value of the  $i^{\text{th}}$  state variable at  $t_{jk}$ .

Since  $x_{ijk}$  represents the value predicted by equation (II-2) for the value  $t_{jk}$  of the independent variable, an error  $\epsilon_{ijk}$  may be defined as:

$$\epsilon_{ijk} = \hat{x}_{ijk} - x_{ijk} \quad (\text{II-3})$$

Let  $\underline{\epsilon}$  be defined as the error vector containing all the elements  $\epsilon_{ijk}$ , ordered in some arbitrary way.

The problem may now be posed mathematically as one of finding  $\underline{a}$  such that some objective function  $Z$  of  $\underline{\epsilon}$  is minimized. The two most popular objective functions are  
1) the "least squares" criterion:

$$Z = \underline{\epsilon}^T \underline{W} \underline{\epsilon} \quad (\text{II-4})$$

where  $W$  is a positive definite diagonal matrix with the diagonal elements representing weighting factors, and 2) the "Chebyshev" criterion:

$$Z = \max_{ijk} |w_{ijk} \epsilon_{ijk}| \quad (\text{II-5})$$

To solve this problem directly as it stands, an optimum seeking method would be required such as Rosenbrock's hill climbing procedure (25) or the Marquardt (22) procedure as proposed by Ball and Groenweghe (1). Another way to solve this problem, as shown by Bellman and Kalaba (2), is to

formulate it as a boundary value problem by taking the parameter vector  $\underline{a}$  to be the solution of the vector differential equation:

$$\frac{d\underline{a}}{dt} = \underline{0} \quad (\text{II-6})$$

Now the complete system of differential equations may be written as:

$$\frac{d\underline{x}_j}{dt} = \underline{f}_j(\underline{x}_j, \underline{a}, t) \quad j = 1, 2 \dots n \quad (\text{II-7})$$

$$\frac{d\underline{a}}{dt} = 0$$

The initial conditions  $\underline{x}_j(0)$  are specified for  $j = 1, 2 \dots n$  but  $\underline{a}(0)$  is unknown.

This is inherently a boundary value problem, as the initial condition for  $\underline{a}(0)$  is not known. Equation (II-7) may be rewritten in a more condensed form by letting:

$$\underline{y} = \begin{bmatrix} \underline{x}_1 \\ \cdot \\ \cdot \\ \underline{x}_n \\ \underline{a} \end{bmatrix}$$

and  $\underline{g}(\underline{y}, t) = \begin{bmatrix} \underline{f}_1(\underline{x}_1, \underline{a}, t) \\ \underline{f}_n(\underline{x}_n, \underline{a}, t) \\ \underline{0} \end{bmatrix} \quad (\text{II-8})$

Then, in the new notation, the problem becomes:

$$\frac{dy}{dt} = \underline{g}(\underline{y}, t) \quad (\text{II-9})$$

$\underline{y}$  and  $\underline{g}$  are vectors of order  $r \times 1$  where  $r = np + q$ .

The problem of determining the optimum parameters which characterize the given physical system has now been formulated as a boundary value problem. This boundary value problem is almost certainly nonlinear.

#### B. Quasilinearization and the Solution of Nonlinear Boundary Value Problems

There are no good general techniques for handling nonlinear boundary value problems. However, there exists powerful techniques for linear boundary value problems which make their solution almost routine. Bellman and Kalaba (2) have taken advantage of this, by using Kantorovich's (13) extension of the Newton-Raphson (6) method to function space, which results in a succession of linear boundary value problems which hopefully converge to the original nonlinear boundary value problem.

The sequence of linear problems is defined by the following recurrence relationship:

$$\begin{aligned} \frac{d\mathbf{y}^{(m+1)}}{dt} &= \mathbf{g}^{(m)} + \underline{\mathbf{J}}^m \left[ \mathbf{y}^{(m+1)} - \mathbf{y}^{(m)} \right] \\ &= \underline{\mathbf{J}}^{(m)} \mathbf{y}^{(m+1)} + \left[ \mathbf{g}^{(m)} - \underline{\mathbf{J}}^{(m)} \mathbf{y}^{(m)} \right] \end{aligned}$$

$m = 0, 1, 2, \dots$  (II-10)

where  $\underline{\mathbf{J}}^{(m)}(t)$  is the Jacobian matrix of partial derivatives.

$$\underline{\mathbf{J}}^{(m)} = \begin{bmatrix} \frac{\partial g_1}{\partial y_1} & \dots & \dots & \frac{\partial g_1}{\partial y_r} \\ \dots & \dots & \dots & \dots \\ \frac{\partial g_r}{\partial y_1} & \dots & \dots & \frac{\partial g_r}{\partial y_r} \end{bmatrix} \quad \text{(II-11)}$$

Given an initial guess solution  $\mathbf{y}^{(0)}$ , and solving the succession of linear problems represented by equation (II-10) with the same boundary conditions as given for the original problem, the recurrence relations will converge to the solution of the nonlinear problem such that:

$$\lim_{m \rightarrow \infty} \mathbf{y}^{(m)} = \mathbf{y} \quad \text{(II-12)}$$

To assure convergence of this scheme for any arbitrary initial guess  $\mathbf{y}^{(0)}$ , certain limitations on equation (II-9) must be imposed. First, each of the functions which make up the function vector  $\mathbf{g}(\mathbf{y}, t)$  must be strictly convex. By definition, this means that for each function, the Hessian

matrix is positive definite. The Hessian matrix is defined as:

$$\left[ \frac{\partial^2 g_k}{\partial x_i \partial x_j} \right] = \begin{bmatrix} \frac{\partial^2 g_k}{\partial x_1^2} & \cdot & \cdot & \cdot & \cdot & \frac{\partial^2 g_k}{\partial x_1 \partial x_r} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \frac{\partial^2 g_k}{\partial x_1 \partial x_r} & \cdot & \cdot & \cdot & \cdot & \frac{\partial^2 g_k}{\partial x_r^2} \end{bmatrix}$$

$$k = 1, 2 \dots r \quad \text{(II-13)}$$

This property makes it possible to write:

$$\frac{dy}{dt} = \underline{g}(\underline{y}, t) = \text{Max}_{\underline{z}} [\underline{g}(\underline{z}, t) + J(\underline{z}, t)(\underline{y} - \underline{z})] \quad \text{(II-14)}$$

Now if the function  $\underline{w}$  is introduced as the solution to the associated linear equation:

$$\frac{dw}{dt} = \underline{g}(\underline{z}, t) + J(\underline{z}, t)(\underline{w} - \underline{z}) \quad \text{(II-14)}$$

then, provided that a certain positivity property holds, it has been shown by Kalaba (12) that the solution of (II-14) is given by:

$$\underline{y} = \underset{\underline{z}}{\text{Max}} \underline{w} (t, \underline{z})^* \quad (\text{II-15})$$

Once this has been established, Kalaba (12) has further proved that the sequence of linear problems represented by equation (II-10) will converge monotonically and quadratically to the solution of the original nonlinear problem. The required positivity property is that if

$$\frac{d\underline{u}}{dt} - \underline{J} (\underline{z}, t) \underline{u} = \underline{\delta} \geq \underline{0}$$

with  $\underline{u} (0) = \underline{0}$  (II-16)

then  $\underline{u} \geq \underline{0}$ ,  $t \geq 0$

A sufficient condition for this property to hold is that the off-diagonal elements of  $\underline{J}$  should be non-negative as shown by Kalaba (12).

The convexity and positivity properties discussed above are not present in a large number of practical problems. However, this algorithm will often converge in spite of this, provided that the initial guess  $\underline{y}^{(0)}$  is sufficiently close to the answer  $\underline{y}$ .

---

\* A similar minimization operation can be defined for concave problems



To obtain an initial guess within the domain of convergence of a particular problem is often no trivial task. An obvious approach would be to use some type of multi-variable search or hill-climbing method to obtain an approximate result.

Another less obvious approach would be to set up an artificial problem whose solution is closer to the arbitrary initial guess. This is the approach followed in the remainder of this work.

C. Boundary Value or Data Perturbation

Let the initial guess  $\underline{y}^{(0)}$  be the solution of the following vector differential equation:

$$\frac{d\underline{y}^{(0)}}{dt} = \underline{g}(\underline{y}^{(0)}, t) \quad (\text{II-17})$$

with the initial condition  $\underline{y}^{(0)}(0) = \underline{b}$

where the constant vector  $\underline{b}$  is an intelligent guess of the actual initial condition  $\underline{y}(0)$  which is not entirely known.

Now let  $\hat{y}_{ik}$  be the given boundary value for the  $i^{\text{th}}$  element of  $\underline{y}$  at a discrete value of the independent variable  $t_k$  and let  $y_{ik}^{(0)}$  be the value of  $\hat{y}_{ik}$  predicted by equation (16).

If  $\underline{y}^{(0)}$  is within the domain of convergence for the given problem, the quasilinearization procedure may be applied

directly. However, if the initial guess  $y^{(0)}$  is outside the domain of convergence for the actual problem, it should be in the domain of convergence for another problem.

If an artificial set of boundary conditions  $y_{ik}^*$  are defined by:

$$y_{ik}^* = y_{ik}^{(0)} + \hat{R}(y_{ik} - y_{ik}^{(0)})$$

$$0 \leq \hat{R} \leq 1 \quad (\text{II-18})$$

then perhaps the quasilinearization procedure may be applied to solve the derived problem. Once the derived problem is solved, the solution  $y^*$  may be used as the initial guess  $y^{(0)}$  and the procedure may be repeated until  $y^{(0)}$  is sufficiently close to the actual solution so that the actual boundary values  $y_{ik}$  may be used in place of the pseudo-boundary conditions  $y_{ik}^*$ . This stepping, as illustrated in Figure 1 should always succeed, provided there is a domain of convergence around  $y^{(0)}$  which is sufficiently large so that the solution may be reached in a finite number of steps.

Applying this procedure to the parameter identification problem is straight forward. The only initial conditions that are not known are those for the parameter vector. Therefore, to define  $y^{(0)}$ , it is necessary only to supply a guess for each of the unknown parameters. The data is treated just as boundary values in the perturbation stepping procedure.

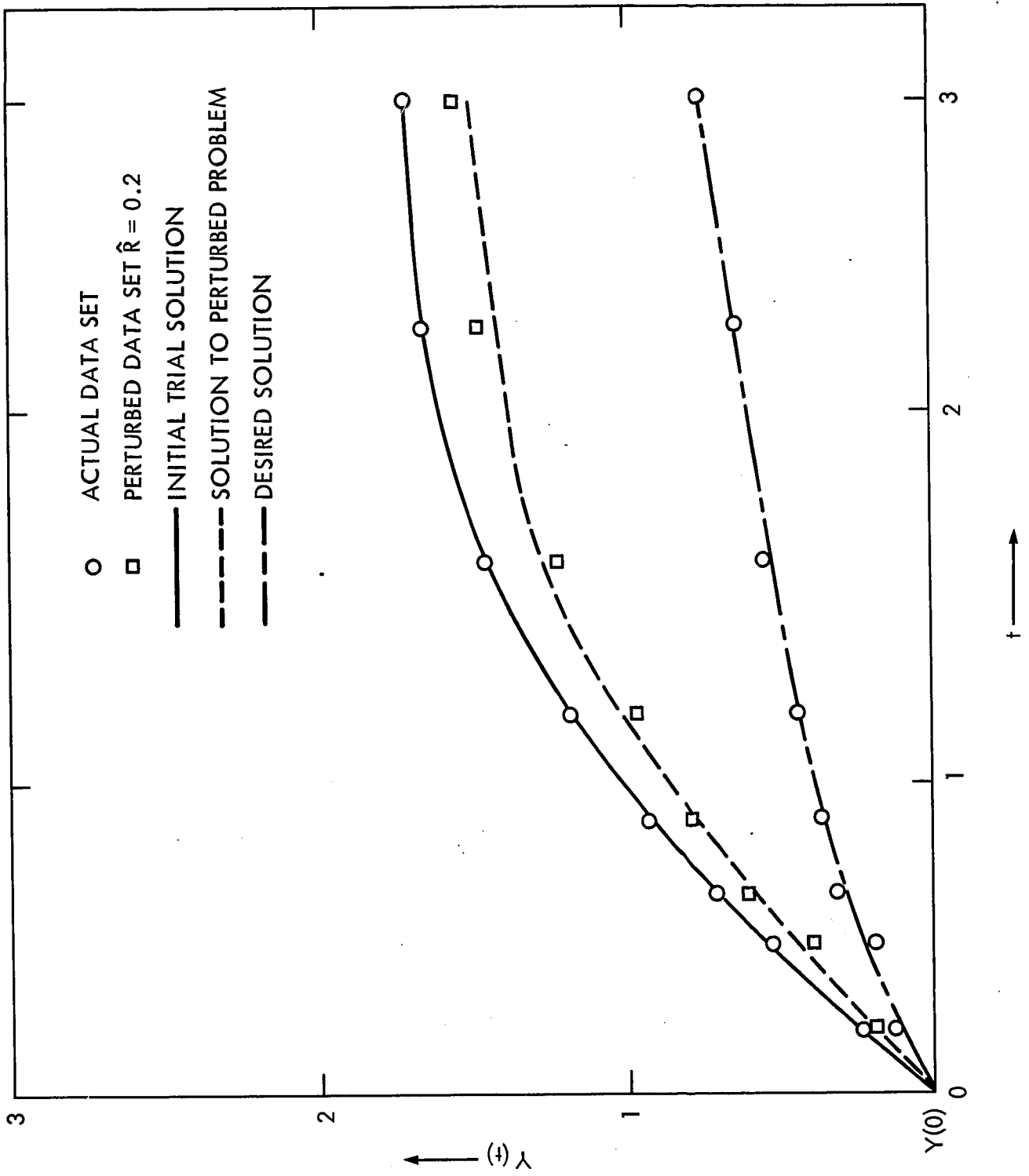


Figure 1. Illustration of Boundary Value or Data Perturbation

D. The Linear Boundary Value Problem

A systematic method for solving the successive linear boundary value problems will now be discussed.

Each of the linear boundary value problems is of the form:

$$\frac{d\underline{y}^{(m+1)}}{dt} = \underline{J}^{(m)} \underline{y}^{(m+1)} + \underline{g}^{(m)} - \underline{J}^{(m)} \underline{y}^{(m)} \quad (\text{II-18})$$

with the appropriate boundary conditions. The vectors  $\underline{g}^{(m)}$  and  $\underline{y}^{(m)}$ , and the matrix  $\underline{J}^{(m)}$  are all known functions of the independent variable  $t$ . The general solution of (II-18) is:

$$\underline{y}^{(m+1)} = \underline{y}^{(m+1)} \underline{c}^{(m+1)} + \underline{u}^{(m+1)} \quad (\text{II-19})$$

as given in Coddington and Levinson (4).  $\underline{y}^{(m+1)}(t)$  is the fundamental matrix which is the solution to the matrix differential equation:

$$\frac{d\underline{y}^{(m+1)}}{dt} = \underline{J}^{(m)} \underline{y}^{(m+1)} \quad (\text{II-20})$$

with the initial conditions  $\underline{y}^{(m+1)}(0) = \underline{I}_{(r \times r)}$

The vector  $\underline{u}^{(m+1)}(t)$  is a particular solution to the vector differential equation:

$$\frac{d\underline{u}^{(m+1)}}{dt} = \underline{J}^{(m)} \underline{u}^{(m+1)} + \underline{g}^{(m)} - \underline{J}^{(m)} \underline{y}^{(m)} \quad (\text{II-21})$$

with the initial condition  $\underline{u}_{(0)}^{(m+1)} = \underline{0}_{(rx1)}$

The constant vector  $\underline{c}_{(m+1)}^{(m+1)}$  is the vector of the initial condition of  $\underline{y}_{(0)}^{(m+1)}$  which may be determined from the boundary conditions.

In principle, the above relations may be applied directly to any boundary value problem using a numerical integration procedure to generate  $\underline{y}_{(t)}^{(m+1)}$  and  $\underline{u}_{(t)}^{(m)}$ . However, if a large number of experiments are to be considered, each with a different initial condition, and if the number of state variables is large, then the order  $r$  of the vector  $\underline{y}$ , as can be seen from equation (II-8), is quite high. The total number of differential equations that would have to be integrated numerically is  $r^2 + r$ . The value of  $r$  is  $np + q$  where  $n$  is the number of experiments,  $p$  is the number of state variables, and  $q$  is the number of parameters.

However,  $\underline{J}^{(m)}$  has a special structure, and because of this, the magnitude of the problem may be reduced considerably. The structure of  $\underline{J}^{(m)}$ , as can be seen by again referring to equation (II-8), is as follows:

$$\underline{J}^{(m)} = \begin{bmatrix} \underline{J}_{x1} & \cdot & \cdot & \underline{0} & \cdot & \cdot & \cdot & \underline{0} & \underline{J}_{a1} \\ \cdot & \cdot & & & & & & \cdot & \cdot \\ \cdot & \cdot & & & & & & \cdot & \cdot \\ \underline{0} & \cdot & \cdot & \underline{J}_{xj} & \cdot & \cdot & \cdot & \underline{0} & \underline{J}_{aj} \\ \cdot & & & \cdot & & & & \cdot & \cdot \\ \cdot & & & & \cdot & & & \cdot & \cdot \\ \underline{0} & & & & & & & \underline{J}_{xn} & \underline{J}_{an} \\ \underline{0} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \underline{0} & \underline{0} \end{bmatrix}^{(m)} \quad (\text{II-22})$$

with

$$\underline{J}_{xj}^{(m)} = \begin{bmatrix} \frac{\partial f_{1j}}{\partial x_{ij}} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \frac{\partial f_{1j}}{\partial x_{pj}} \\ \cdot & & & & & & & & \cdot \\ \cdot & & & & & & & & \cdot \\ \cdot & & & & & & & & \cdot \\ \frac{\partial f_{pj}}{\partial x_{lj}} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \frac{\partial f_{pj}}{\partial x_{pj}} \end{bmatrix}^{(m)} \quad (\text{II-23})$$

$$j = 1, 2, \dots, n$$

and

$$\underline{J}_{aj}^{(m)} = \begin{bmatrix} \frac{\partial f_{1j}}{\partial a_1} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \frac{\partial f_{1j}}{\partial a_q} \\ \cdot & & & & & & & & \cdot \\ \cdot & & & & & & & & \cdot \\ \cdot & & & & & & & & \cdot \\ \frac{\partial f_{pj}}{\partial a_1} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \frac{\partial f_{pj}}{\partial a_q} \end{bmatrix}^{(m)} \quad (\text{II-24})$$

$$j = 1, 2, \dots, n$$

The equation (II-18) may be rewritten as:

$$\frac{d}{dt} \begin{bmatrix} \underline{x}_1 \\ \cdot \\ \cdot \\ \cdot \\ \underline{x}_j \\ \cdot \\ \cdot \\ \cdot \\ \underline{x}_n \\ \underline{a} \end{bmatrix}^{(m+1)} = \underline{J}^{(m)} \begin{bmatrix} \underline{x}_1 \\ \cdot \\ \cdot \\ \cdot \\ \underline{x}_j \\ \cdot \\ \cdot \\ \cdot \\ \underline{x}_n \\ \underline{a} \end{bmatrix}^{(m+1)} + \begin{bmatrix} \underline{f}_1 \\ \cdot \\ \cdot \\ \cdot \\ \underline{f}_j \\ \cdot \\ \cdot \\ \cdot \\ \underline{f}_n \\ \underline{0} \end{bmatrix}^{(m)} - \underline{J}^{(m)} \begin{bmatrix} \underline{x}_1 \\ \cdot \\ \cdot \\ \cdot \\ \underline{x}_j \\ \cdot \\ \cdot \\ \cdot \\ \underline{x}_n \\ \underline{a} \end{bmatrix}^{(m)} \quad (\text{II-25})$$

Since each vector  $\underline{x}_j^{(m+1)}$  is coupled only with the parameter vector  $\underline{a}^{(m+1)}$ , and not with any other state variable vector from a different experiment, the general solution can be written as:

$$\begin{bmatrix} \underline{x}_1 \\ \cdot \\ \cdot \\ \cdot \\ \underline{x}_j \\ \cdot \\ \cdot \\ \cdot \\ \underline{x}_n \\ \underline{a} \end{bmatrix}^{(m+1)} = \begin{bmatrix} \underline{F}_{x1} & \cdot & \cdot & \cdot & \underline{0} & \underline{G}_{a1} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \underline{0} & \underline{F}_{xj} & \underline{0} & \underline{0} & \underline{G}_{aj} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \underline{0} & \cdot & \cdot & \cdot & \cdot & \cdot \\ \underline{0} & \underline{F}_{xn} & \underline{0} & \underline{0} & \underline{G}_{an} \\ \underline{0} & \underline{F}_a & \underline{0} & \underline{0} & \underline{0} \end{bmatrix}^{(m+1)} \begin{bmatrix} \underline{c}_1 \\ \cdot \\ \cdot \\ \cdot \\ \underline{c}_j \\ \cdot \\ \cdot \\ \cdot \\ \underline{c}_n \\ \underline{c}_a \end{bmatrix}^{-(m+1)} + \begin{bmatrix} \underline{u}_1 \\ \cdot \\ \cdot \\ \cdot \\ \underline{u}_j \\ \cdot \\ \cdot \\ \cdot \\ \underline{u}_n \\ \underline{u}_a \end{bmatrix}^{(m+1)} \quad (\text{II-26})$$

where the first term on the right hand side represents the fundamental matrix and the last term represents a particular

solution.

The block diagonal entries in the fundamental matrix  $\underline{F}_{-xj}^{(m+1)}$  ( $j = 1, 2, \dots, n$ ) and  $\underline{F}_{-a}^{(m+1)}$  are the solutions of:

$$\frac{d\underline{F}_{-xj}^{(m+1)}}{dt} = \underline{J}_{-xj}^{(m)} \underline{F}_{-xj}^{(m+1)} \quad (j = 1, 2, \dots, n) \quad (\text{II-27})$$

$$\underline{F}_{-xj}^{(m+1)}(0) = \underline{I}_{(pxp)}$$

and  $\frac{d\underline{F}_{-a}^{(m+1)}}{dt} = \underline{0}$  ;  $\underline{F}_{-a}^{(m+1)}(0) = \underline{I}_{(qxq)}$  (II-28)

From (II-28) it follows that

$$\underline{F}_{-a}^{(m+1)}(t) = \underline{I}_{(qxq)} \quad (\text{II-29})$$

The other block entries in the fundamental matrix  $\underline{G}_{-aj}^{(m+1)}$  ( $j = 1, 2, \dots, n$ ) are the solutions of:

$$\begin{aligned} \frac{d\underline{G}_{-aj}^{(m+1)}}{dt} &= \underline{J}_{-xj}^{(m)} \underline{G}_{-aj}^{(m+1)} + \underline{J}_{-aj}^{(m)} \underline{F}_{-a}^{(m+1)} \\ &= \underline{J}_{-xj}^{(m)} \underline{G}_{-aj}^{(m+1)} + \underline{J}_{-aj}^{(m)} \end{aligned} \quad (\text{II-30})$$

with the initial condition

$$\underline{G}_{-aj}^{(m+1)}(0) = \underline{0}_{(pxq)}$$

The entries in the particular solution  $\underline{u}_j$  ( $j = 1, 2, \dots, n$ ) and  $\underline{u}_a$  are the solutions of:



$$\frac{d\underline{u}_j^{(m+1)}}{dt} = \underline{J}_{-x_j}^{(m)} \underline{u}_j^{(m+1)} + \underline{J}_{-a_j}^{(m)} \underline{u}_a^{(m+1)} + \underline{f}_j - \underline{J}_{-x_j}^{(m)} \underline{x}_j^{(m)} - \underline{J}_{-a_j}^{(m)} \underline{a}^{(m)} \quad (\text{II-31})$$

with the initial condition  $\underline{u}_j^{(m+1)}(0) = \underline{0}_{(px1)}$

$$\text{and } \frac{d\underline{u}_a^{(m+1)}}{dt} = \underline{0} \quad (\text{II-32})$$

with the initial condition  $\underline{u}_a^{(m+1)}(0) = \underline{0}_{(qx1)}$  (II-33)

and, therefore, equation (II-31) may be rewritten as:

$$\frac{d\underline{u}_j^{(m+1)}}{dt} = \underline{J}_{-x_j}^{(m)} \underline{u}_j^{(m+1)} + \underline{f}_j - \underline{J}_{-x_j}^{(m)} \underline{x}_j^{(m)} - \underline{J}_{-a_j}^{(m)} \underline{a}^{(m)} \quad (\text{II-34})$$

with the initial condition  $\underline{u}_j^{(m+1)}(0) = \underline{0}_{(px1)}$ .

Thus, the number of differential equations to be integrated has been reduced to  $(np^2 + npq + np)$  from  $(np + q)^2 + (np + q)$ . This is a considerable reduction in the memory and computation requirements for this method.

Equation (II-26) may be expanded in terms of each state variable vectors  $\underline{x}_j^{(m+1)}$  as follows:

$$\underline{x}_j^{(m+1)} = \underline{F}_{-x_j}^{(m+1)} \underline{c}_j^{(m+1)} + \underline{G}_{-a_j}^{(m+1)} \underline{c}_a^{(m+1)} + \underline{u}_j^{(m+1)} \quad (\text{II-35})$$

It is known from the formulation of the problem that:

$$\begin{aligned} \underline{c}_j^{(m+1)} &= \underline{x}_j^{(m+1)} \quad (0) \\ \underline{c}_a^{(m+1)} &= \underline{a}^{(m+1)} \quad (0) \\ &= \underline{a}^{(m+1)} \end{aligned} \quad (\text{II-36})$$

In a large number of problems,  $\underline{x}_j(0)$  is known, and therefore can be assumed to be exact. This assumption further simplifies the problem.

Let  $\underline{v}_j^{(m+1)}$  be defined by:

$$\underline{v}_j^{(m+1)} = \underline{F}_{-x_j}^{(m+1)} \underline{c}_j^{(m+1)} + \underline{u}_j^{(m+1)} \quad (\text{II-37})$$

Using this definition, equation (II-35) becomes:

$$\underline{x}_j^{(m+1)} = \underline{v}_j^{(m+1)} + \underline{G}_{-a_j}^{(m+1)} \underline{a}^{(m+1)} \quad (\text{II-38})$$

With the assumption that  $\underline{x}_j(0)$  is exact, the integration of equation (II-27) and (II-31) may be replaced with  $\underline{v}_j^{(m+1)}$  which is the solution to:

$$\frac{d\underline{v}_j^{(m+1)}}{dt} = \underline{J}_{-x_j}^{(m)} \left[ \underline{v}_j^{(m+1)} - \underline{x}_j^{(m)} \right] - \underline{J}_{-a_j}^{(m)} \underline{a}^{(m)} + \underline{f}_j^{(m)} \quad (\text{II-39})$$

with the initial condition  $\underline{v}_j^{(m+1)}(0) = \underline{x}_j(0)$  ( $j = 1, 2 \dots n$ ).

The matrix  $\underline{G}_{-a_j}^{(m+1)}$  must still be evaluated as before, with equation (II-30). Thus, all the vectors  $\underline{x}_j^{(m+1)}$  ( $j = 1, 2 \dots n$ ) can be expressed linearly in terms of  $\underline{a}^{(m+1)}$  alone

and the least squares analysis may be carried out.

This simplification means that the number of differential equations per iteration is only  $(np + npq)$  as compared to  $(np^2 + npq + np)$  for the case where the initial conditions are treated as unknown. The number of variables to be considered in the least squares analysis has also been decreased from  $(np + q)$  to  $(q)$ . This is important because of the inherent ill-conditioning problems associated with the least squares analysis. This problem can also be avoided by using the Chebyshev criteria.

### III. PRACTICAL APPLICATION

The theoretical concepts presented in the previous section can be incorporated into a practical algorithm. To do this, a step by step procedure must be outlined in an organized way, which may be programmed for the digital computer.

#### A. Data Perturbation and a Stepping Procedure

An empirical procedure was devised for the purpose of controlling the step size. Perhaps a more efficient method could be devised. However, this one has been successfully implemented. The procedure is outlined below.

Step 1: The maximum step size  $S_{\max}$ , the maximum allowable relative change in the parameters for one iteration  $C_{\max}$ , and the minimum allowable change in the parameters for one step  $C_{\min}$  are all specified. The initial guess for the parameter vector  $\underline{a}^{(0)}$  is supplied.

Step 2: The maximum element in the error vector  $(\max_{ijk} |\epsilon_{i,j,k}|)$  is computed using the current value of  $\underline{a}^{(0)}$ .

Step 3: If  $\max_{i,j,k} |\epsilon_{ijk}| > S_{\max}$

$\hat{R}$  is defined by the equation

$$\hat{R} = 1 - \frac{S_{\max}}{\max_{i,j,k} |\epsilon_{i,j,k}|}$$

If  $\max_{i,j,k} |\epsilon_{i,j,k}| \leq S_{\max}$

then  $\hat{R} = 0$

Step 4: Define the pseudo-data set as

$$x_{i,j,k}^* = \hat{x}_{i,j,k} + \hat{R} (x_{i,j,k} - \hat{x}_{i,j,k})$$

for all values of  $i, j, k$

Note that if  $\hat{R} = 0$  then the pseudo-data set is equal to the real data set.

Step 5: The quasilinearization procedure is initiated with  $\underline{a}^{(0)}$  being the initial guess for the parameter vector and the data set  $x_{i,j,k}^*$  (for all  $i, j,$  and  $k$ ) being the required boundary conditions. Normally, this STEP is terminated if some convergence criteria is met or if a specified number of iterations has been completed. If during the procedure

$$\sum_{i=1}^q |a_i^{m+1} - a_i^m| / |a_i^{m+1}| > C_{\max}$$

for any  $m$  ( $m=1, 2, \dots$ ) then the procedure is terminated,  $S_{\max}$  is halved and STEP 2 is re-initiated.

Step 6: If  $\hat{R} = 0$  and STEP 5 is successfully completed, the problem is solved and the perturbation procedure may be terminated.

Step 7: If

$$\sum_{i=1}^q | a_i^{(M)} - a_i^{(O)} | / | a_i^{(M)} | \leq C_{\min}$$

then  $S_{\max}$  is tripled.

Step 8:  $\underline{a}^{(0)}$  is defined as being equal to  $\underline{a}^{(m)}$  and Step 2 is re-initiated.

The above outline covers the basic steps used in attempts to solve the indentifications problem. Many of the finer details are not included here for the sake of simplicity. The complete algorithm is listed in the form of a Fortram IV program in Appendix A.

## B. Quasilinearization

In principle, the data perturbation procedure does not require the use of quasilinearization. It does, however, require a rapidly converging method for the solution of the nonlinear boundary value problems encountered with each step. As the perturbation insures that the initial guess is quite close to the solution for each step, quasilinearization is ideally suited.

Assuming the initial conditions to be exact is not essential to data perturbation. This assumption is made solely to reduce the computational load in the evaluation

of the fundamental matrix and in the subsequent least squares analysis.

To solve each of the successive nonlinear boundary value problems, the following equations must be integrated simultaneously for each iteration.

$$\frac{dx_j^{(0)}}{dt} = f_j(x_j^{(0)}, a^{(0)}, t) \quad \text{(III-1)}$$

$$j = 1, 2, \dots, n$$

$$\frac{dx_j^{(k)}}{dt} = J_j^{(k-1)} [x_j^{(k)} - x_j^{(k-1)}] + f_j(x_j^{(k)}, a^{(k)}, t) \quad \text{(III-2)}$$

$$j = 1, 2, \dots, n$$

$$k = 1, 2, \dots, m$$

$$\frac{dv_j^{(m+1)}}{dt} = J_{x_j}^{(m)} [v_j^{(m+1)} - x_j^{(m)}] - J_{a_j}^{(m)} a^{(m)} + f_j^{(m+1)}(x_j^{(m)}, a^{(m)}, t) \quad \text{(III-3)}$$

$$j = 1, 2, \dots, n$$

$$\frac{dG_{a_j}^{(m+1)}}{dt} = J_{x_j}^{(m)} G_{a_j}^{(m+1)} + J_{a_j}^{(m)} \quad \text{(III-4)}$$

$$j = 1, 2, \dots, n$$

with the initial conditions

$$x_j^{(0)}(0) = x_j(0) \quad j = 1, 2, \dots, n$$

$$x_j^{(k)}(0) = x_j(0) \quad j = 1, 2, \dots, n$$

$$k = 1, 2, \dots, m$$

$$\underline{v}_j^{(m+1)}(0) = \underline{x}_j(0) \quad j = 1, 2, \dots, n$$

$$\underline{G}_{-aj}^{(m+1)}(0) = 0 \quad j = 1, 2, \dots, n$$

Equation (III-1) is used to generate the initial guess; equation (III-2) is used to generate the previous  $m$  solutions; and equations (III-3) and (III-4) are required to determine  $\underline{a}^{(m+1)}$ .

All the parameter vectors  $\underline{a}^{(0)}$ ,  $\underline{a}^{(1)}$ ,  $\dots$ ,  $\underline{a}^m$  must be stored to be used in the evaluation of the above system of differential equations.

Once the above system is solved, the following relationship

$$\underline{G}_{-aj}^{(m+1)} \underline{a} + \underline{v}_j^{(m+1)} - \underline{x}_j^{(m+1)} = 0 \quad (\text{III-5})$$

may be used to form the linear constraints required for the solution of the least squares problem. In general these constraints may not always be linear.

To extend the algorithm to include nonlinear boundary conditions would not be difficult in principle. However, it was decided to leave the consideration of more complex boundary conditions to be studied in future work.



#### IV. APPLICATION IN CHEMICAL REACTION KINETICS

At the heart of almost any major chemical process is the reactor. Reactor engineering and design is thus of unquestionable importance to the chemical industry.

To design a reactor effectively requires an intimate knowledge of the chemical kinetics, and it is highly desirable to have some type of reliable mechanistic rate equation. The determination of kinetic rate parameters has, justifiably, been of prime concern in the analysis of kinetic data.

E.S. Lee (18, 19) has suggested the application of quasilinearization to the identification of kinetic rate parameters. He has illustrated this approach by considering the difficult problem of analyzing the kinetic data obtained from a tubular reactor in which axial diffusion was important. He considered both nonlinear boundary conditions and the analysis of non-isothermal data. Unfortunately, however, quasilinearization is unstable for many problems.

If this is the case for a particular problem, either the problem must be modified, or some way must be found to extend the domain of convergence. Boundary value or data perturbation is one hope for doing the latter.

##### A. A Nonlinear Example

A hypothetical reaction described by the following differential equations was studied.

$$\begin{aligned}\frac{dx_1}{dt} &= -a_1(x_1^2 - k_{e1}x_2) - a_2(x_1 - k_{e2}x_3) \\ \frac{dx_2}{dt} &= a_1(x_1^2 - k_{e1}x_2) - a_3(x_2 - k_{e3}x_3)\end{aligned}\quad (\text{IV-1})$$

Following the conventions set forth earlier, the state vector is

$$\underline{x} = \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} \quad (\text{IV-2})$$

with  $x_1$  and  $x_2$  being the composition of components one and two. The composition of component three is given by the following linear relationship:

$$x_3 = 1 - x_1 - x_2 \quad (\text{IV-3})$$

The unknown parameter vector is

$$\underline{a} = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix} \quad (\text{IV-4})$$

The other parameters  $k_{e1}$ ,  $k_{e2}$ , and  $k_{e3}$  are equilibrium constants which are assumed to be known.

The purpose for considering this example was to test out the algorithm and to examine the convergence rates. To do this, values were chosen for the parameter vector and the equilibrium constants and exact data was generated for three different initial conditions as given in Table 1. The parameter

and equilibrium constants used to generate this data were:

$$\begin{array}{ll}
 a_1 = 2.0 & k_{e1} = 1.8 \\
 a_2 = 3.5 & k_{e2} = 3.0 \\
 a_3 = 5.0 & k_{e3} = 1.0
 \end{array} \quad (\text{IV-5})$$

Using the algorithm developed in the previous section, the parameter vector was then determined from the data in Table 1.

In order to evaluate the equations (III-2), (III-3), and (III-4), the following relations are used together with an initial guess.

$$\begin{array}{l}
 \underline{J}_{-xj} = \left[ \begin{array}{cc}
 - \left[ 2a_1x_1 + a_2(1 + k_{e2}) \right] & \left[ a_1k_{e1} - a_2k_{e2} \right] \\
 \left[ 2a_1x_1 - a_3k_{e3} \right] & - \left[ a_1k_{e1} + a_3(1 + k_{e3}) \right]
 \end{array} \right] \\
 j = 1, 2, 3 \quad \quad \quad (\text{IV-6})
 \end{array}$$

$$\begin{array}{l}
 \underline{J}_{-aj} = \left[ \begin{array}{cc}
 - \left[ x_1^2 - k_{e1}x_2 \right] & - \left[ x_1 + k_{e2}(1 - x_1 - x_2) \right] \left[ 0 \right] \\
 \left[ x_1^2 - k_{e1}x_2 \right] \left[ 0 \right] & - \left[ x_2 + k_{e3}(1 - x_1 - x_2) \right]
 \end{array} \right] \\
 j = 1, 2, 3 \quad \quad \quad (\text{IV-7})
 \end{array}$$

TABLE 1

Data for the Nonlinear Example

Data Set Number 1			Data Set Number 2			Data Set Number 3		
t	$x_1$	$x_2$	t	$x_1$	$x_2$	t	$x_1$	$x_2$
0	1.0000	0.0000	0	0.0000	1.0000	0	0.0000	0.0000
0.1	0.7113	0.1259	0.06	0.2102	0.6238	0.18	0.5710	0.2034
0.2	0.6350	0.1732	0.18	-	0.3205	0.32	0.5960	0.2020
0.3	0.6117	0.1905	0.26	-	0.2520	0.46	0.5993	0.2005
0.4	0.6040	0.1967	0.34	-	0.2224	0.60	0.5998	0.2002
0.5	0.6014	0.1988	0.48	0.5940	0.2051	0.72	0.6000	0.2000
0.8	0.6001	0.2000	0.60	0.5983	0.2014			
			0.76	0.5997	0.2003			
			0.90	0.5999	-			

$$\underline{f}_j = \begin{bmatrix} -a_1(x_1^2 - k_{e1}x_2) - a_3(x_2 - k_{e3}x_3) \\ a_1(x_1^2 - k_{e1}x_2) - a_3(x_2 - k_{e3}x_3) \end{bmatrix} \quad (\text{IV-8})$$

$$j = 1, 2, 3$$

$$\underline{x}_1(0) = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad \underline{x}_2(0) = \begin{bmatrix} 0 \\ 1 \end{bmatrix}, \quad \underline{x}_3(0) = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \quad (\text{IV-9})$$

The first guess vector considered was

$$\underline{a}(0) = \begin{bmatrix} 0.0000001 \\ 0.0000001 \\ 0.0000001 \end{bmatrix} \quad (\text{IV-10})$$

From this initial guess, the quasilinearization procedure could be used directly without the aid of data perturbation. The successive parameter vectors are given in Table 2. The convergence of the corresponding concentration profiles is shown in Figures 2, 3, and 4. The rapid convergence of the quasilinearization procedure is verified. However, as mentioned before, the domain of convergence is often quite small.

TABLE 2

Convergence of the Nonlinear Example  
Without Data Perturbation

Iteration	$a_1$	$a_2$	$a_3$
0	0.00	0.00	0.00
1	0.48	0.36	0.51
2	1.16	1.01	1.68
3	2.01	1.92	3.08
4	2.26	2.75	4.13
5	2.06	3.33	4.83
6	2.00	3.49	5.00

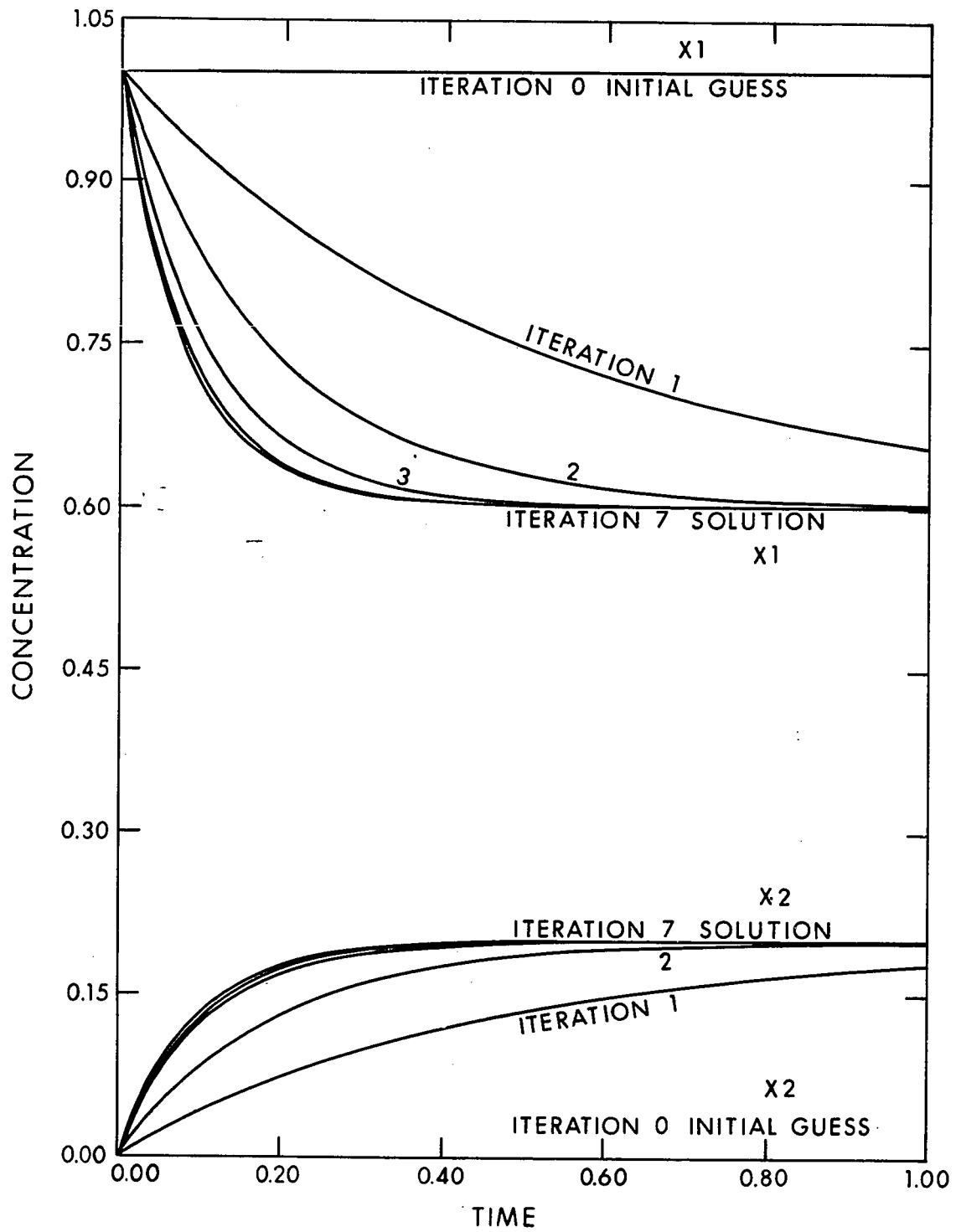


Figure 2 Convergence of nonlinear example using Quasilinearization (data set one)

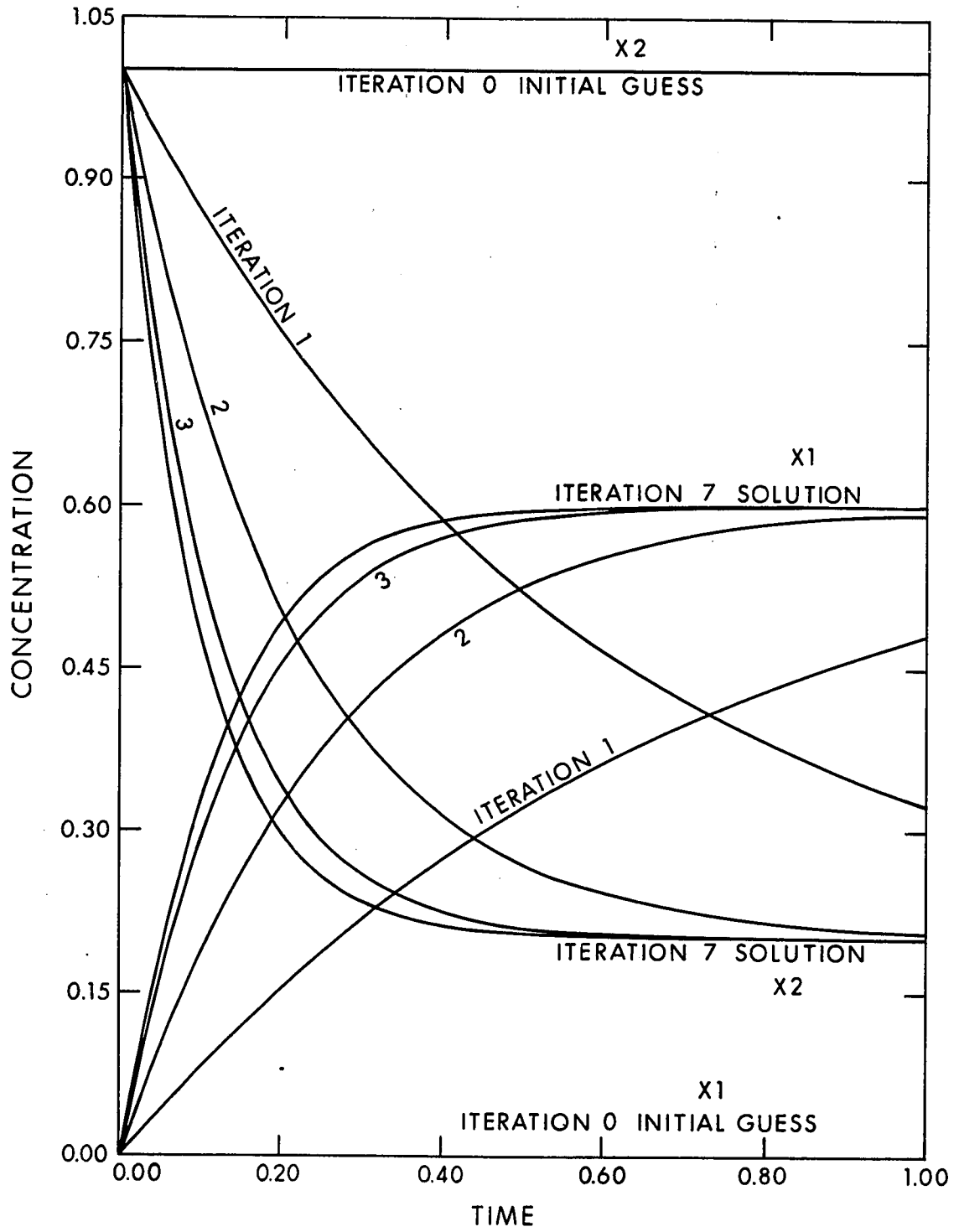


Figure 3 Convergence of nonlinear example using Quasilinearization (data set two)



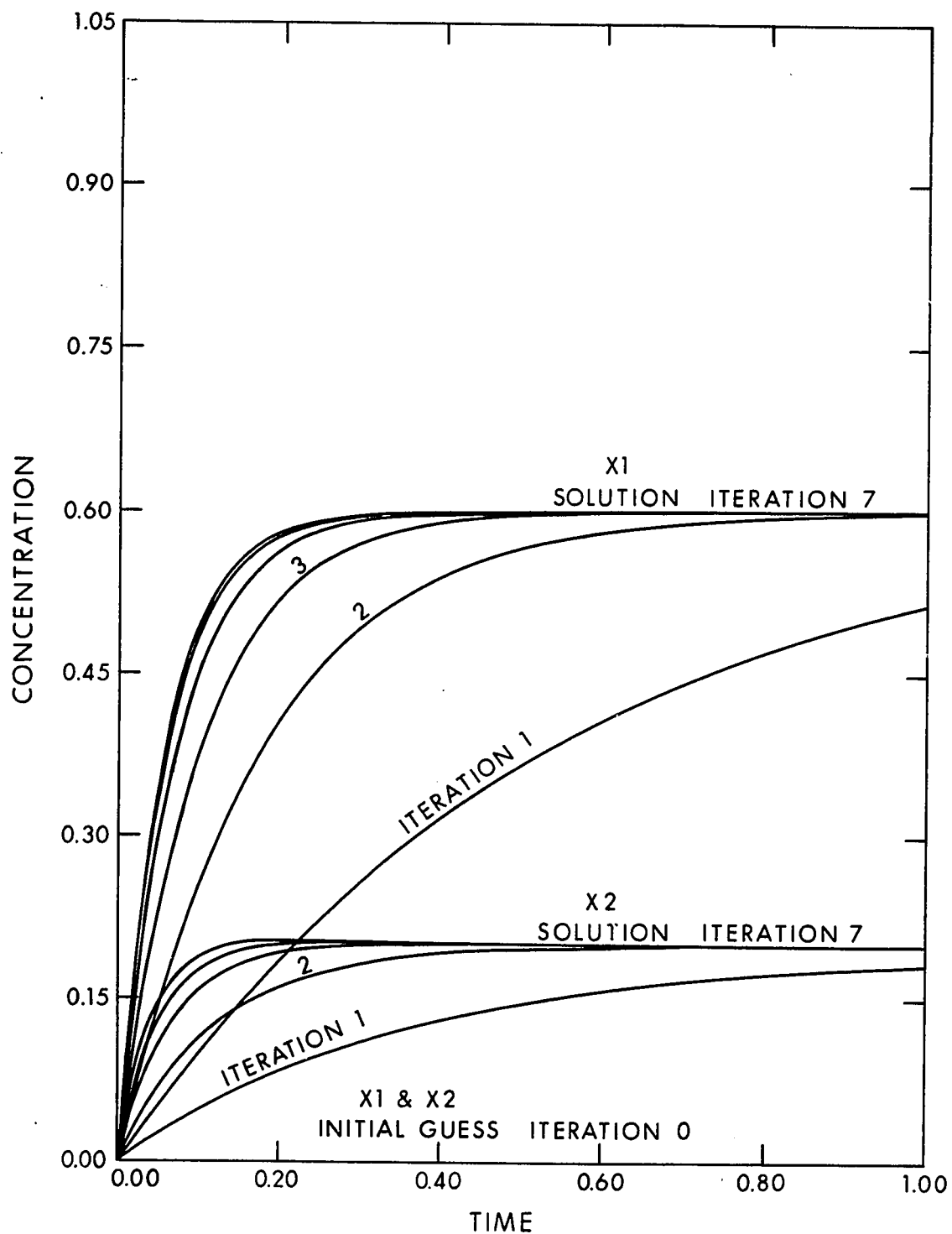


Figure 4 Convergence of nonlinear example using Quasilinearization (data set three)

With another initial guess,

$$\underline{a}^{(0)} = \begin{bmatrix} 10 \\ 10 \\ 10 \end{bmatrix} \quad (\text{IV-11})$$

attempts to find the solution using the quasilinearization directly were frustrated. In one iteration, the parameter vector changed from the values given in (IV-11) to

$$\underline{a}^{(1)} = \begin{bmatrix} -2.74 \\ -73.88 \\ -17.12 \end{bmatrix} \quad (\text{IV-12})$$

With the values in (IV-12) the integration of the fundamental matrix becomes unstable and further progress was not possible.

However, by perturbing the data to within ten percent of the concentration profiled generated from the initial guess, a solution can be obtained through the stepping procedure combined with quasilinearization. After five steps, the derived initial guess is within the domain of convergence for the direct application of the quasilinearization procedure. The stepping procedure produced the sequence of derived initial guess given in Table 3. For each step, a maximum of three quasilinearization iterations were applied to determine the next initial guess. If convergence to three significant figures was obtained, the step was considered completed.

The successive profiles yielded by the stepping procedure are shown in Figures 5, 6, and 7.

TABLE 3

Convergence of the Nonlinear Example with  
Data Perturbation

Step No.	$a_1$	$a_2$	$a_3$
0	10	10	10
1	9.61	7.96	9.32
2	8.36	5.64	8.27
3	7.28	4.76	7.65
4	4.83	3.83	6.40
5	3.12	3.58	5.54

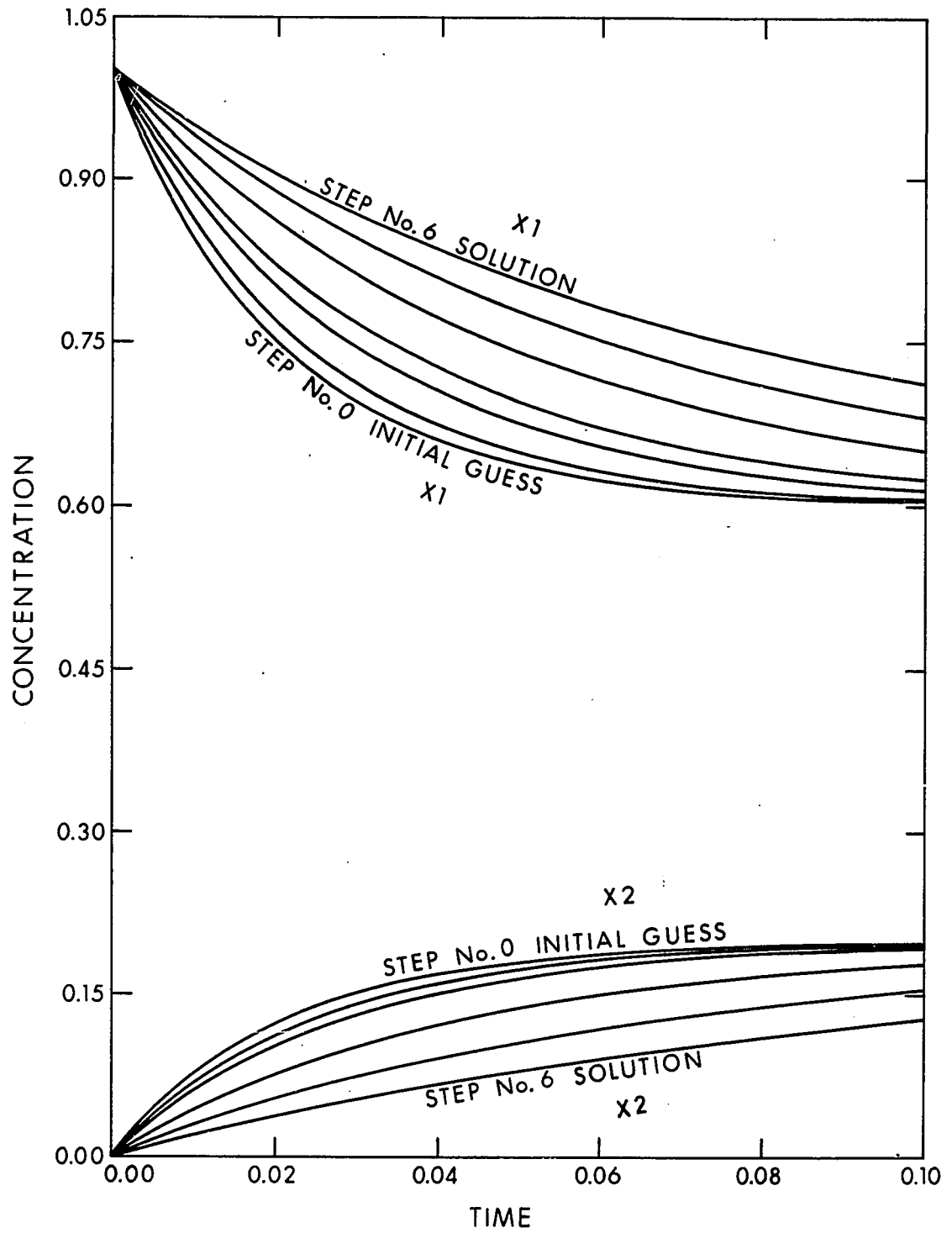


Figure 5 Convergence of nonlinear example using Data Perturbation (data set one)

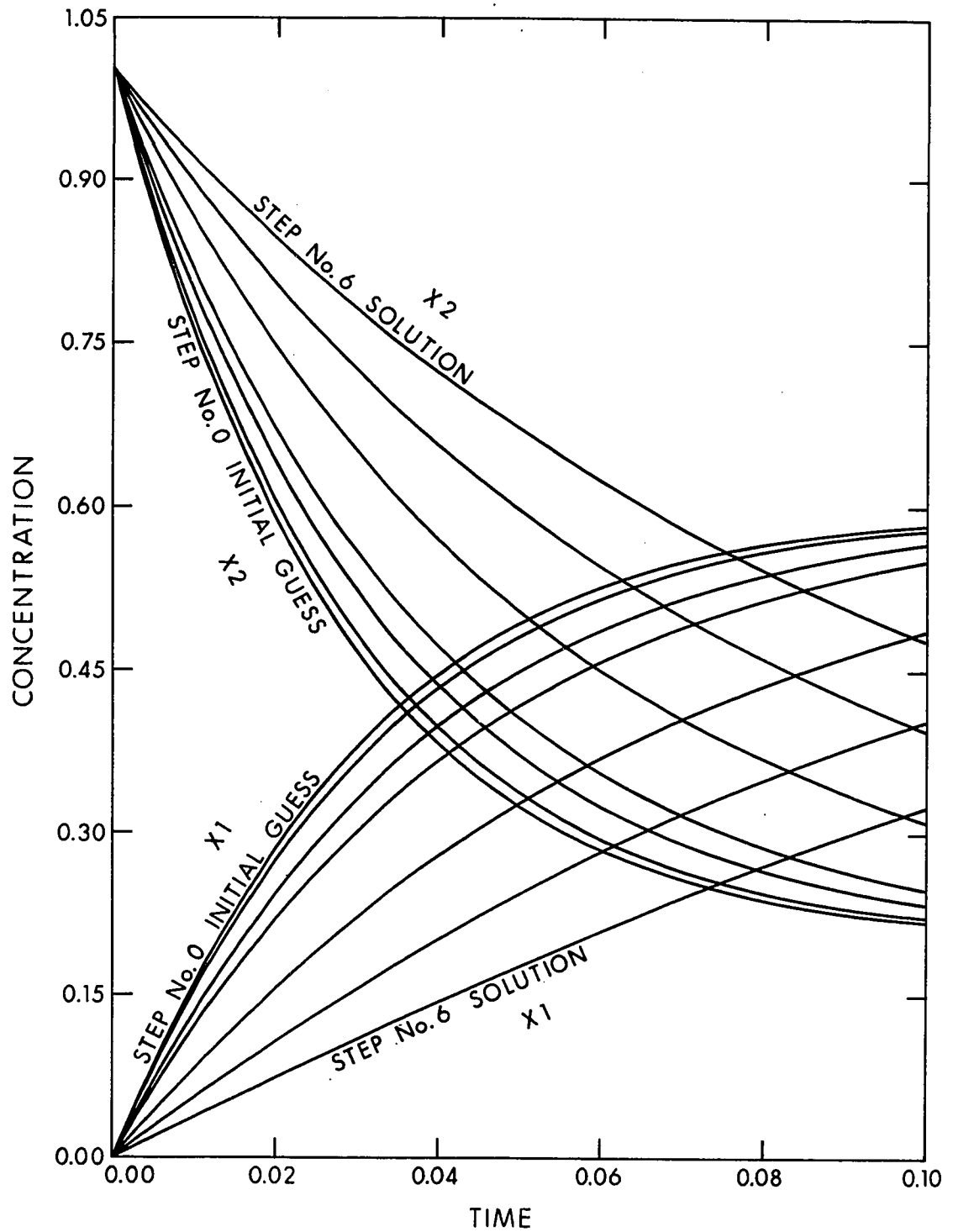


Figure 6 Convergence of nonlinear example using Data Perturbation (data set two)

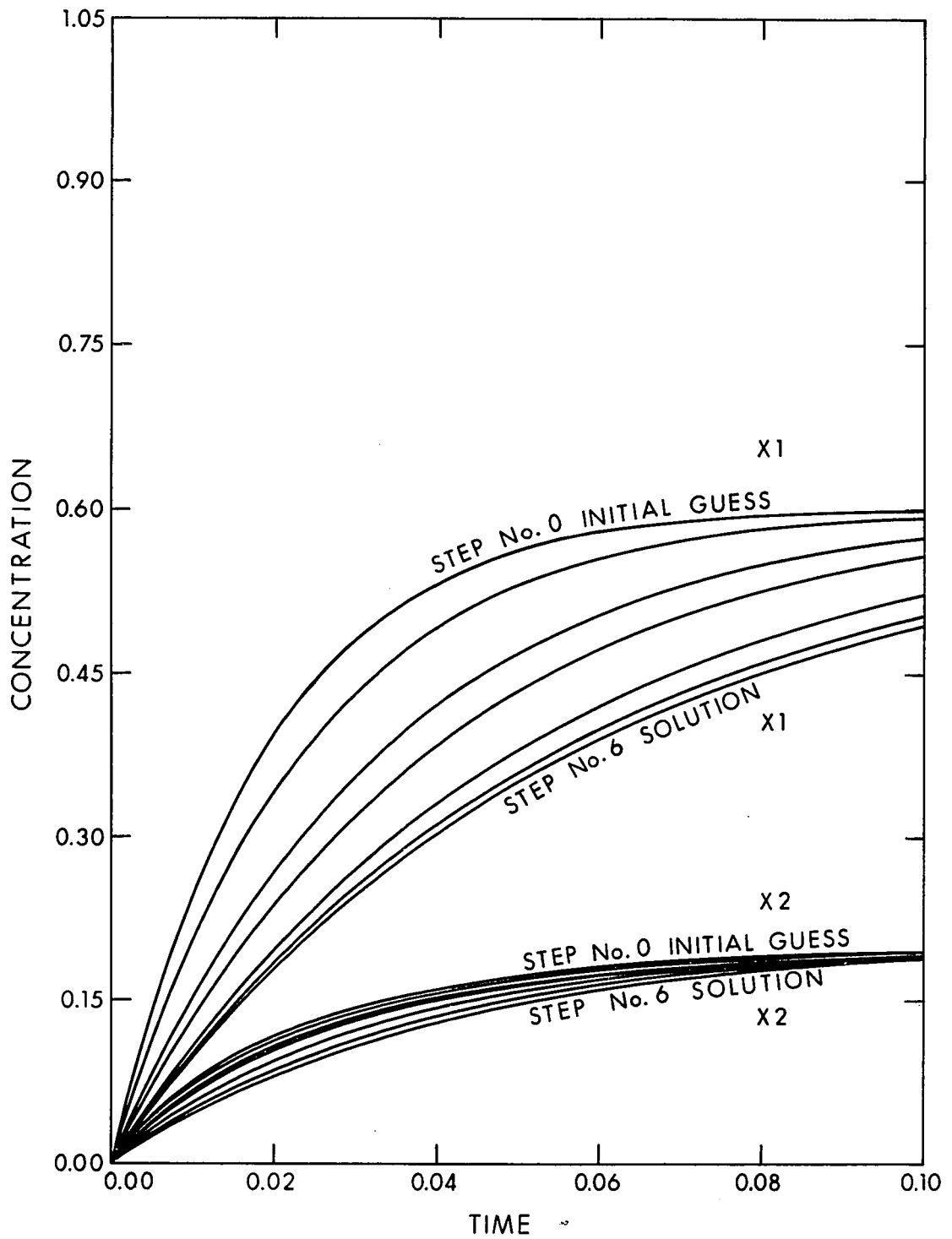


Figure 7 Convergence of nonlinear example using Data Perturbation (data set three)

With the completion of the stepping procedure, the initial guess is

$$\underline{a}^{(0)} = \begin{bmatrix} 3.12 \\ 3.58 \\ 5.54 \end{bmatrix} \quad (\text{IV-13})$$

From this guess, the direct application of the quasilinearization procedure yielded the answer quite rapidly as shown in Table 4.

TABLE 4

Convergence of the Last Step  
for the Nonlinear Example

Iteration No.	$a_1$	$a_2$	$a_3$
0	3.12	3.58	5.54
1	1.81	3.45	4.89
2	2.002	3.498	5.000
3	2.000	3.500	5.000

From this, it is evident that data perturbation, together with quasilinearization, can be a powerful tool in the solution of this type of problem. The main disadvantage, at present, is that there is no way that the optimum step size can be determined in advance. Choosing it too small will waste a large amount of computational time, but it must be chosen small enough to ensure convergence. At present, the empirical procedure for changing the step size mentioned in the previous chapter, is used. This procedure has proven satisfactory in this problem as well as the others in this work. It is recommended, but there is room for a considerable amount of improvement.

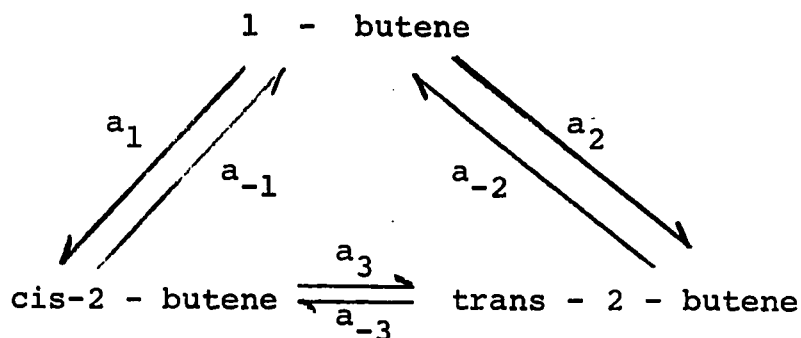
B. Sensitivity to the Choice of Experiments and to Experimental Error

Wei and Prater (27) presented a method for identifying the kinetic rate constants in a linear kinetic model. This method involved choosing experiments in an organized manner so that the eigenvector directions characteristic of the system could be determined. Once all the eigenvector directions are determined, the rate constants may be calculated directly. If some of the eigenvector directions are not known, the rate constants can not be uniquely determined. Logically, it follows that the experiments, from which the data sets are taken, must have strong components in each of



the eigenvector directions if the parameter vector is to be uniquely determined. It would also seem probable that an analogous situation would exist with nonlinear systems.

To test these principles, an example, which was used by Wei and Prater (27), was chosen.



The above mechanistic diagram may be represented by the following system of differential equations.

$$\frac{dx_1}{dt} = -a_1 (x_1 - k_{31}x_2) - a_2 (x_1 - k_{e2}x_3) \quad (\text{IV-14})$$

$$\frac{dx_2}{dt} = a_1 (x_1 - k_{e1}x_2) - a_3 (x_2 - k_{e3}x_3)$$

with  $x_1$  and  $x_2$  being the concentration of 1-butene and cis - 2 - butene respectively. The concentration of trans - 2 - butene which is  $x_3$  is given by the relationship

$$x_3 = 1 - x_1 - x_2 \quad (\text{IV-15})$$

The equilibrium constants are:

$$\begin{aligned}k_{e1} &= \frac{a_{-1}}{a_1} = 0.4469 \\k_{e2} &= \frac{a_{-2}}{a_2} = 0.2685 \\k_{e3} &= \frac{a_{-3}}{a_3} = 0.6002\end{aligned}\tag{IV-16}$$

The actual parameter vector determined by Wei and Prater is:

$$\underline{a} = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix} = \begin{bmatrix} 10.344 \\ 3.724 \\ 5.616 \end{bmatrix}\tag{IV-17}$$

Using the parameters given in (IV-17) data was generated from seven different initial conditions. This data was then perturbed with the use of a random number generator in order that the effects of experimental error could also be observed.

It is interesting to note that this is a linear system, but when the parameter determination problem is formulated as a boundary value problem, the problem is nonlinear because of the cross terms between the state vector and the parameter vector. This means that the Jacobians for this problem are not constant matrices as shown below:

$$J_{xj} = \begin{bmatrix} \bar{a}_1 + a_2 (1+k_{e2}) & \bar{a}_1 k_{e1} - a_2 k_{e2} \\ \bar{a}_1 - a_3 k_{e3} & \bar{a}_1 k_{e1} + a_3 (1+k_{e3}) \end{bmatrix} \quad (IV-18)$$

$j = 1, 2 \dots 7$

$$J_{aj} = \begin{bmatrix} \bar{k}_{e2} x_2 - x_1 & \bar{k}_{e2} (1-x_2 - x_1) & [0] \\ \bar{x}_1 - k_{e1} x_2 & [0] & \bar{k}_{e3} (k - x_2 - x_1) - x_2 \end{bmatrix} \quad (IV-19)$$

$j = 1, 2 \dots 7$

Data were generated for the seven different initial conditions given in Table 5. This data was then perturbed with a random relative error with a normal distribution. These errors were generated using the IBM 360 scientific subroutine package (10) with a mean of zero and standard deviations of 0.001, 0.01, 0.1.

TABLE 5

Initial Conditions for 1-Butene Problem

Data Set No.	$x_1(0)$	$x_2(0)$
1	1.0	0.0
2	0.0	1.0
3	0.0	0.0
4	0.24	0.76
5	0.3492	0.6508
6	0.0	0.4937
7	0.413	0.0

The phase plane diagram shown in Figure 8 shows the relative trajectories of  $x_1(t)$  and  $x_2(t)$ . The straight line trajectories represent eigenvector directions.

Using the initial guess parameter vector:

$$\underline{a}^{(0)} = \begin{bmatrix} 1.0 \\ 1.0 \\ 1.0 \end{bmatrix} \quad (\text{IV-20})$$

and all the data sets, the solutions in Table 6 were obtained using quasilinearization directly without the aid of data perturbation.

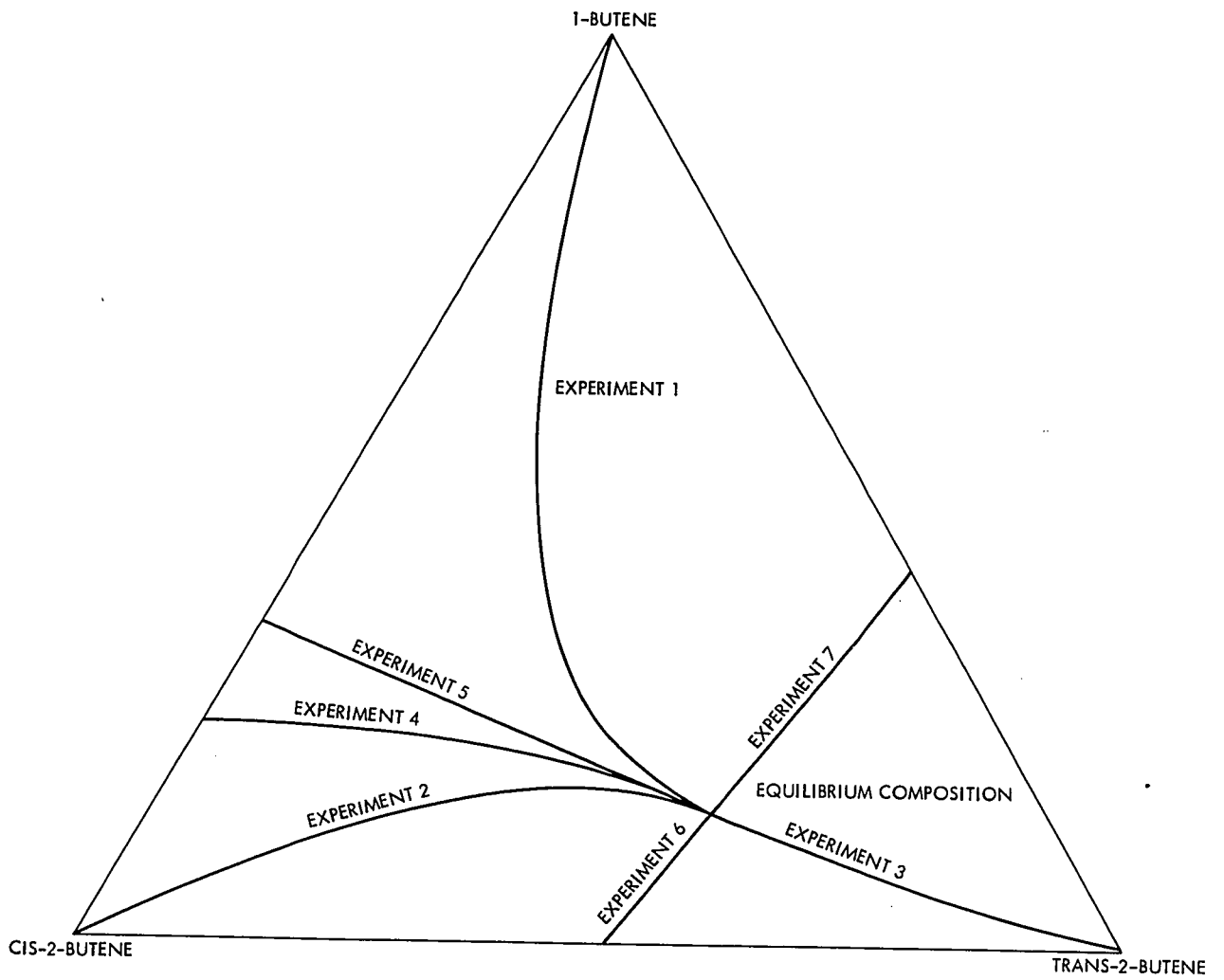


Figure 8. Phase Plane Diagram for 1-Butene Problem (These Trajectories were Produced by the True Parameters.)

TABLE 6

Solutions Using All Available Data  
for 1-Butene Problem

Standard Deviation	No. of Iterations	$a_1$	$a_2$	$a_3$	Sum of Errors Squared
0.1	7	10.930	3.619	5.540	0.09481
0.01	6	10.404	3.713	5.609	0.00095
0.001	5	10.350	3.722	5.615	0.00009
actual values		10.344	3.724	5.616	-

From the results in Table 6, it can be seen that when all the data is considered together, the quasilinearization procedure is relatively insensitive to experimental error.

In order to established the relative importance of each of the data sets, several additional runs were made. The results of these numerical experiments verified the logical conclusions made earlier in this section.

Data sets five and six were generated from the initial conditions:

$$\underline{x}_5(0) = \begin{bmatrix} 0.3492 \\ 0.6508 \end{bmatrix}$$

and 
$$\underline{x}_6(0) = \begin{bmatrix} 0.0 \\ 0.4937 \end{bmatrix}$$

(IV-21)

respectively. These initial conditions are in the two different eigenvector directions. Attempts to find the parameter vector using only one of these two data sets proved fruitless, no matter how close the initial guess. In other words, a solution could not be found.

However, by using both of these data sets, a solution was easily found as shown in Table 7. The initial guess vector was the same as before.

TABLE 7

Solutions Using Data from the  
Eigenvector Directions

Standard Deviations	No. of Iterations	$a_1$	$a_2$	$a_3$	Sum of Errors Squared
0.1	9	12.227	2.242	6.146	0.02946
0.01	6	10.513	3.588	5.658	0.00030
0.001	5	10.361	3.710	5.620	0.000003
actual values		10.344	3.724	5.616	-

This confirms that data must be taken in a manner such that all the different eigenvector directions are adequately defined.

It would seem possible that one experiment, if properly chosen, could be used to find a solution. This experiment would have to be chosen so that its data set contained sufficiently strong components in each of the eigenvector directions. Data sets one and two, with the initial conditions:

$$\underline{x}_1(0) = \begin{bmatrix} 1.0 \\ 0.0 \end{bmatrix}; \quad \underline{x}_2(0) = \begin{bmatrix} 0.0 \\ 1.0 \end{bmatrix} \quad (\text{IV-22})$$

satisfied this requirement. Using the same initial guess for the parameter vector, the results listed in Tables 8 and 9 were obtained for data sets one and two respectively.

TABLE 8

Solutions Using Data Set One

Standard Deviation	No. of Iterations	$a_1$	$a_2$	$a_3$	Sum of Errors Squared
0.1	oscillating without convergence	~9.6	~4.9	~3.2	~0.013
0.01	7	10.167	3.932	5.189	0.001226
0.001	6	10.324	3.746	5.569	0.0000012
actual values		10.344	3.724	5.616	-



TABLE 9

Solutions for Data Set Two

Standard Deviation	No. of Iterations	$a_1$	$a_2$	$a_3$	Sum of Errors Squared
0.1	No Convergence			Obtained	
0.01	7	10.473	4.129	5.575	0.0001856
0.001	6	10.355	3.758	5.614	0.00000186
actual values		10.344	3.724	5.616	-

The remaining data sets were all too close to one or the other of the two eigenvector directions to get any meaningful results.

From the results obtained in Tables 8 and 9, it is evident that one experiment, if properly chosen can be used to find the parameters. However, it is also evident that when one such experiment is used, that the results as well as the convergence may be quite sensitive to any experimental error. In general, it was observed that the more experiments that are included in the analysis, the less sensitive is the procedure to experimental error.

As the proposed method depends on having accurate initial conditions for each experiment, it would seem advisable to check the sensitivity of the results to this assumption. To do this, the first three data sets were used with exact and perturbed initial conditions. The perturbed initial

conditions were

$$\underline{x}_1(0) = \begin{bmatrix} 1.0 - \gamma \\ 0.0 + \gamma \end{bmatrix}; \quad \underline{x}_2(0) = \begin{bmatrix} 0.0 + \gamma \\ 1.0 - \gamma \end{bmatrix}; \quad \text{and} \quad \underline{x}_3(0) = \begin{bmatrix} 0.0 + \gamma \\ 0.0 + \gamma \end{bmatrix}$$

The results for a standard deviation of 0.001 and 0.1 are presented in Tables 10 and 11.

TABLE 10

Solution for 1-Butene Problem Using Perturbated  
Initial Conditions ( $\sigma = 0.001$ )

$\gamma$	$a_1$	$a_2$	$a_3$
0.00	10.346	3.727	5.631
0.01	10.177	3.724	5.545
0.10	8.487	3.968	4.876

TABLE 11

Solutions for 1-Butene Problem Using Perturbated  
Initial Conditions ( $\sigma = 0.1$ )

$\gamma$	$a_1$	$a_2$	$a_3$
0.00	10.638	3.930	5.471
0.01	10.479	3.921	5.389
0.10	8.866	4.143	4.749

From these results it is evident that small inaccuracies can be tolerated. However, if a large discrepancy exists, the solution may be strongly affected.

In conclusion, it may be said, that the design and execution of the experiments may determine whether or not a unique solution can be found. Further, if a solution is found, the dependability of the results will be reflected by the design of the experiment. Experimental design is an extensive topic in itself and it will not be discussed further here.

### C. A Non-Isothermal Reaction

The two previous examples were somewhat artificial in that actual experimental data was not used. The example presented in this section uses data for the non-isothermal pyrolysis of propane obtained by Kershenbaum and Martin (14, 15). They suggested the following rate expression:

$$\frac{df}{dL} = \frac{S}{F} A' \exp\left(-\frac{E}{RT(L)}\right) \left[\frac{P(L)}{R'T(L)}\right]^\alpha \left[\frac{1-f}{1 + \frac{N_0}{F} + f}\right]^\alpha$$

$$P(L) = P_i - \frac{L}{L_m} (P_i - P_e) \quad (\text{IV-23})$$

f	=	fractional conversion
L	=	distance from reactor entrance (cm)
L <sub>m</sub>	=	total length of reactor (cm)
S	=	reactor cross-sectional area (cm <sup>2</sup> )
T(L)	=	temperature along reactor (°K)
P(L)	=	pressure along reactor (mmHg)
P <sub>i</sub>	=	inlet pressure (mmHg)
P <sub>e</sub>	=	exit pressure (mmHg)
F	=	feed rate of propane (g-moles/sec)
N <sub>o</sub>	=	feed rate of inerts (g-moles/sec)
R	=	ideal gas constant (1.987 x 10 <sup>-3</sup> $\frac{\text{Kcal}}{(\text{g-mole})(\text{°K})}$ )
R'	=	ideal gas constant (62361 $\frac{\text{cm}^2 \text{ mmHg}}{(\text{g-mole})(\text{°K})}$ )
A'	=	kinetic rate constant (g-mole/cc) <sup>1-α</sup> sec <sup>-1</sup>
E	=	activation energy (Kcal/g-mole)
α	=	order of reaction

The temperature was measured at twenty-seven equally spaced points along the reactor; T(L) could thus be accurately established. Conversion was measured only at the outlet. Data for sixteen different experiments were used in the analysis.

Using the notation given before, the state vector is

$$\underline{x} = f \quad (\text{IV-24})$$

and the parameter vector is

$$\underline{a} = \begin{bmatrix} A' \\ E \\ \alpha \end{bmatrix} \quad (\text{IV-25})$$

When the problem is formulated as in equation (IV-23), certain computational problems arise. These problems were also reported by Lee (19) who suggested that double precision arithmetic is needed. However, it was found that if  $A'$  and  $E$  are normalized to the same approximate order of magnitude, that higher precision was not necessary. This was done by letting

$$A' = 10^{-4} \exp(A) \quad (\text{IV-26})$$

and substituting into equation (IV-23)

$$\frac{df}{dL} = \frac{S}{F \times 10^4} \exp\left(A - \frac{E}{RT(L)}\right) \left[\frac{P(L)}{R'T(L)}\right]^\alpha \left[\frac{1-f}{1 + \frac{N_o + f}{F}}\right]^\alpha \quad (\text{IV-27})$$

With this formulation, no computational problems were encountered. The parameter vector now is

$$\underline{a} = \begin{bmatrix} A \\ E \\ \alpha \end{bmatrix} \quad (\text{IV-28})$$

and the parameter vector is

$$\underline{a} = \begin{bmatrix} A' \\ E \\ \alpha \end{bmatrix} \quad (\text{IV-25})$$

When the problem is formulated as in equation (IV-23), certain computational problems arise. These problems were also reported by Lee (19) who suggested that double precision arithmetic is needed. However, it was found that if A' and E are normalized to the same approximate order of magnitude, that higher precision was not necessary. This was done by letting

$$A' = 10^{-4} \exp(A) \quad (\text{IV-26})$$

and substituting into equation (IV-23)

$$\frac{df}{dL} = \frac{S}{F \times 10^4} \exp\left(A - \frac{E}{RT(L)}\right) \left[\frac{P(L)}{R'T(L)}\right]^\alpha \left[\frac{1-f}{1 + \frac{N_O}{F} + f}\right]^\alpha \quad (\text{IV-27})$$

With this formulation, no computational problems were encountered. The parameter vector now is

$$\underline{a} = \begin{bmatrix} A \\ E \\ \alpha \end{bmatrix} \quad (\text{IV-28})$$

This problem was broken into two parts by first considering it with the order of the reaction fixed at unity, and then considering the effects of allowing the third parameter  $\alpha$  to be free.

With the first problem, the unknown parameter vector is reduced to

$$\underline{a} = \begin{bmatrix} A \\ E \end{bmatrix} \quad (\text{IV-29})$$

Several indirect methods were used by Kershenbaum and Martin (14, 15) in attempts to find suitable values for  $A'$  and  $E$ . All of these methods took advantage of the fact that equation (IV-23) is separable and an explicit expression for  $A'$  in terms of  $E$  could be found. This yielded a set of algebraic expressions of the form

$$A' = \phi_i (E) \quad (\text{IV-30})$$

$$i = 1, 2 \dots n$$

with one equation being for each of the  $n$  different experiments.

An attempt to find  $A'$  and  $E$  by minimizing

$$Z = \sum_{i=1}^n \left[ \phi_i (E) - A' \right]^2 \quad (\text{IV-31})$$

by using steepest descent required an excessive amount of digital computer time and this method was abandoned.

They finally resorted to a method which took advantage of the approximate relation given below

$$\log \phi_i(E) \approx v_i E + u_i \quad (\text{IV-32})$$

$$i=1, 2 \dots n$$

A straight line could be plotted for each experiment. The slope and intercept could be measured and then A' and E could be determined by a linear least squares analysis.

This ingenious approach will give a reasonable approximation to A' and E. However, it will not necessarily give the best unbiased estimate of the parameters in a least squares sense.

Using the algorithm proposed in this work, a direct solution to this problem can be obtained. With the least squares criterion, the objective function to be minimized is

$$Z = \sum_{i=1}^n \left[ f_i(L_m) - \hat{f}_i(L_m) \right]^2 \quad (\text{IV-33})$$

with  $f_i(L_m)$  and  $\hat{f}_i(L_m)$  being the predicted and experimental conversions for the reactor.

The solution obtained was

$$\begin{bmatrix} A' \\ E \end{bmatrix} = \begin{bmatrix} 6.3 \times 10^8 \\ 37.2 \end{bmatrix} \quad (\text{IV-34})$$

with  $Z = 0.034$



This is somewhat better than the solution obtained by the indirect approach which was

$$\begin{bmatrix} A' \\ E \end{bmatrix} = \begin{bmatrix} 2.4 \times 10^{11} \\ 52.1 \end{bmatrix} \quad (\text{IV-35})$$

with  $Z = 0.27$

Quasilinearization combined with data perturbation was used to obtain the solution given in equation (IV-34). The same solution was obtained with several different initial guesses.

TABLE 12  
Convergence Rates for the First  
Propane Problem

Initial Guess		No. of Steps	IBM 360/67 time (min)
A	E/R		
35	26	8	3.90
10	10	17	4.56
30	30	16	4.34
40	40	16	4.44
0	0	36	7.73
50	50	16	4.03
35.40	26.22	15	3.98

From Table 12, it is evident that the solution can be obtained in a reasonable amount of computational time. However, it is not a trivial problem. When the third parameter  $\alpha$  was allowed to be free, the computational task becomes larger.

The solution obtained for the second problem was

$$\begin{bmatrix} A' \\ E \\ \alpha \end{bmatrix} = \begin{bmatrix} 2.13 \times 10^9 \\ 42.68 \\ 1.109 \end{bmatrix} \quad (\text{IV-36})$$

with  $Z = 0.0303$

This solution was obtained from each of the initial guess listed in Table 13.

TABLE 13

Convergence Rates for the Second  
Propane Problem

Initial Guess			No. of Steps	IBM 360/67 time (min)
A	E/R	$\alpha$		
18	15	1.0	9	6.94
18	15	0.5	12	8.35

It was found that if the initial guess for  $\alpha$  was greater than 1.5, a very small step size was required and thus an excessive amount of computational time was needed.

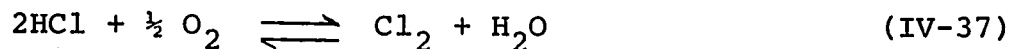
Allowing  $\alpha$  to be free yielded only a small improvement in the objective function. From this, it could be concluded that the first order model is sufficient to represent the data from the given sixteen experiments.

From this example, it is evident that reasonably small non-isothermal kinetic systems can be handled with the proposed algorithm. For larger systems, with several different unknown activation energies, a large amount of computational time may be required due to the extreme behavior of the exponential function.

As the computational time is directly proportional to the number of experiments considered, it would seem desirable to use the minimum number of experiments needed to define the parameter vector uniquely. Then once an approximate solution is obtained, the additional experiments could be used to improve the initial result.

#### D. A Catalytic Reaction

Solid catalyzed gas reactions such as:



in the presence of a chromic oxide catalyst, normally can be modeled with a Langmuir-Hinshelwood type rate expressions such as the equation

$$R_{O_2} = \frac{a_1 (P_{O_2}^{1/2} - \frac{P_{H_2O} P_{Cl_2}}{K_e P_{HCl}^2})}{1 + a_2 P_{HCl} + a_3 P_{H_2O} + a_4 \frac{P_{H_2O} P_{Cl_2}}{K_e P_{HCl}^2}} \quad (IV-38)$$

$R_{O_2}$  = rate of reaction (g-mole of oxygen/g-catalyst) / (min)

$K_e$  = known equilibrium constant ( $\text{atm}^{-1/2}$ )

$P_{H_2O}$  = partial pressure of water (atm)

$P_{O_2}$  = partial pressure of oxygen (atm)

$P_{Cl_2}$  = partial pressure of chlorine (atm)

$P_{HCl}$  = partial pressure of hydrogen chloride (atm)

Equation (IV-38) was proposed by Jones, Bliss and Walker (11) to model the above reaction with a fourth order unknown parameter vector.

$$\underline{a} = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} \quad (IV-39)$$

For this type of problem, although the nonlinear differential equation modeling the system is of first order the parameter vector is of high order. Models with up to seven constants are not unusual. An extensive experimental and analytical research program is required if such a model is to be identified properly. For this reason, Levenspiel (21) suggests that simpler empirical expressions could be satisfactorily fitted to the data for the purpose of design. However, if the data is to be extrapolated, a mechanistic model is desirable.

Extrapolation is at best a dangerous procedure. But, a mechanistic equation does give some qualitative insight into what may be expected under other conditions, and may be used to design further experimental studies. For these reasons, the application of the proposed algorithm to this type of equation was considered.

The analysis of this type of problem for the most part has been limited to the least squares analysis of algebraic relations similar to equation (IV-38). The rates are measured and the parameters are determined by nonlinear least squares. Frequently, the relations may be manipulated to form a linear system with respect to the parameters. Rewriting equation (IV-38) as

$$\begin{aligned}
 & 1/a_1 \left( 1 + a_2 P_{\text{HCl}} + a_3 P_{\text{H}_2\text{O}} + a_4 \frac{P_{\text{H}_2\text{O}} P_{\text{Cl}_2}}{K_e P_{\text{HCl}}^2} \right) \\
 &= \frac{1}{R_{\text{O}_2}} \left( P_{\text{O}_2}^{\frac{1}{2}} - \frac{P_{\text{H}_2\text{O}} P_{\text{Cl}_2}}{K_e P_{\text{HCl}}^2} \right) \quad (\text{IV-40})
 \end{aligned}$$

produces such a linear system, but with the sacrifice of the desired fitting criterion.

If the rates cannot be measured directly, they must be obtained by numerically differentiating the integrated data, thus introducing a large amount of error. Under these circumstances, it would seem desirable to attack the integrated data directly. Such an approach leads to the inevitable boundary value problem to which quasilinearization and data perturbation may be applied.

As an example, the problem presented in the equation (IV-37) and (IV-39) was considered. Taking the partial pressure of oxygen to be the dependent variable

$$R_{\text{O}_2} = - \frac{N_B}{W' P_i} \frac{d P_{\text{O}_2}}{dt} \quad (\text{IV-41})$$

with

$N_B$  = total number of gm-moles initially present in the reactor

$W'$  = weight of catalyst present in the reactor (gm)

$P_i$  = the initial pressure in the reactor (atm)

If the system were free from external interference, the total pressure and the partial pressure of each of the other components in the reactor would be a function of  $P_{O_2}$ . Presuming this, the total pressure would be given by

$$P_{tot} = \frac{P_i}{N_B} \left[ N_B - (N_{O_2} - \frac{N_B}{P_i} P_{O_2}) \right] \quad (IV-42)$$

However, the pressure measurements throughout the experiment did not follow this relation too closely, indicating some external interference, probably stemming from the operation of the recirculation pump. It was found that the pressure data could be better represented by a relation of the form

$$P_{tot} = \frac{P_i}{N_B} \left[ N_B - (N_{O_2} - \frac{N_B}{P_i} P_{O_2}) \right] B(t) \quad (IV-43)$$

where  $B(t)$  is a correction factor correlated from the actual pressure data. The correction factor never exceeded 15% and was correlated to be within one and a half percent with polynomials of up to the third order. The error in the correction factors was small compared with the experimental error in the data.

The partial pressures of the other components are given by the relations

$$P_{\text{HCl}} = \left[ \frac{N_{\text{HCl}} - 4 \left( N_{\text{O}_2} - \frac{N_{\text{B}}}{P_i} P_{\text{O}_2} \right)}{N_{\text{B}} - \left( N_{\text{O}_2} - \frac{N_{\text{B}}}{P_i} P_{\text{O}_2} \right)} \right] P_{\text{tot}} \quad (\text{IV-44})$$

$$P_{\text{Cl}_2} = \left[ \frac{N_{\text{Cl}_2} + 2 \left( N_{\text{O}_2} - \frac{N_{\text{B}}}{P_i} P_{\text{O}_2} \right)}{N_{\text{B}} - \left( N_{\text{O}_2} - \frac{N_{\text{B}}}{P_i} P_{\text{O}_2} \right)} \right] P_{\text{tot}} \quad (\text{IV-45})$$

$$P_{\text{H}_2\text{O}} = \left[ \frac{N_{\text{H}_2\text{O}} + 2 \left( N_{\text{O}_2} - \frac{N_{\text{B}}}{P_i} P_{\text{O}_2} \right)}{N_{\text{B}} - \left( N_{\text{O}_2} - \frac{N_{\text{B}}}{P_i} P_{\text{O}_2} \right)} \right] P_{\text{tot}} \quad (\text{IV-46})$$

with  $N_{\text{O}_2}$  = no. of moles of  $\text{O}_2$  initially in the reactor  
 $N_{\text{HCl}}$  = no. of moles of  $\text{HCl}$  initially in the reactor  
 $N_{\text{Cl}_2}$  = no. of moles of  $\text{Cl}_2$  initially in the reactor  
 $N_{\text{H}_2\text{O}}$  = no. of moles of  $\text{H}_2\text{O}$  initially in the reactor

The total number of moles initially present in the reactor is given by

$$N_{\text{B}} = N_{\text{O}_2} + N_{\text{HCl}} + N_{\text{Cl}_2} + N_{\text{H}_2\text{O}} + N_{\text{I}}$$

where  $N_{\text{I}}$  = the number of moles of inerts initially present in the reactor.



Combining equations (IV-44), (IV-45), and (IV-46) with (IV-43) produces

$$P_{\text{HCl}} = \left[ N_{\text{HCl}} - 4(N_{\text{O}_2} - \frac{N_{\text{B}}}{P_{\text{i}}} P_{\text{O}_2}) \right] \frac{P_{\text{i}}}{N_{\text{B}}} B(t) \quad (\text{IV-47})$$

$$P_{\text{Cl}_2} = \left[ N_{\text{Cl}_2} - 2(N_{\text{O}_2} - \frac{N_{\text{B}}}{P_{\text{i}}} P_{\text{O}_2}) \right] \frac{P_{\text{i}}}{N_{\text{B}}} B(t) \quad (\text{IV-48})$$

$$P_{\text{H}_2\text{O}} = \left[ N_{\text{H}_2\text{O}} + 2(N_{\text{O}_2} - \frac{N_{\text{B}}}{P_{\text{i}}} P_{\text{O}_2}) \right] \frac{P_{\text{i}}}{N_{\text{B}}} B(t) \quad (\text{IV-49})$$

Partial pressure data was made available for nine experiments at 355°C, eleven experiments at 340°C, and nine experiments at 325°C.\*

Jones, Bliss and Walker (11) determined the rate parameters for each temperature by using linear least squares with equation (IV-40). The rates were obtained by plotting the data and estimating the slope. Subsequently Mezaki and Bliss (23) fitted the data for all three temperatures using nonlinear least squares.

Both of these correlations made use of numerical differentiation of the observed data and therefore suffered from the inevitable loss of accuracy.

\* Data was taken by A M. Jones and was kindly supplied by Professor Harding Bliss of Yale University.

Attempts to solve for the parameters for each temperature separately using quasilinearization and data perturbation yielded mixed results.

For the data at 355°C, the following results were obtained.

$$\underline{a} = \begin{bmatrix} 9.8 \times 10^{-4} \\ 13.2 \\ 47.9 \\ 762 \end{bmatrix} \quad (\text{IV-50})$$

with a least square error of 0.000747. The parameter vector reported by Jones, Bliss, and Walker (11) was

$$\underline{a} = \begin{bmatrix} 2.4 \times 10^{-4} \\ 3.1 \\ 25 \\ 230 \end{bmatrix} \quad (\text{IV-51})$$

with a least square error of 0.00315.

Using the data given for 340°C, the results were

$$\underline{a} = \begin{bmatrix} 5.57 \times 10^{-4} \\ 0.791 \\ 121.3 \\ -34.8 \end{bmatrix} \quad (\text{IV-52})$$

with a least square error of 0.00144. Jones, Bliss and Walker (11) found

$$\underline{a} = \begin{bmatrix} 0.92 \times 10^{-4} \\ 0.22 \\ 21 \\ 142 \end{bmatrix} \quad (\text{IV-53})$$

with a least square error of 0.00708. The results given in equation (IV-52) contain a negative rate constant. This is inconsistent with kinetic theory. However, given this set of data, this model and the unweighted least square criteria, the parameter vector given in equation (IV-52) is an optimum for reproducing the experimental data.

For the data given at 325°C, the parameters tended to grow, seemingly without bound, with each successive step. Using the parameters found by Jones, Bliss, and Walker (11) as an initial guess, the results of several different steps are presented in Table 14.

TABLE 14

Hydrogen Chloride Problem Results for 325°C Data

Step No.	$a_1$	$a_2$	$a_3$	$a_4$	Sum of Errors Squared
0	$0.26 \times 10^{-4}$	0.01	11.0	18.0	0.0183
4	$0.68 \times 10^{-4}$	1.71	24.5	672	0.0135
5	$3.11 \times 10^{-4}$	10.7	101	2,259	0.0097
7	$34 \times 10^{-4}$	124	1076	19,964	0.0083

It can be seen from Table 14, that there are at least several parameter vectors which will reproduce the data better by the least square criteria than those given by Jones, Bliss, and Walker (11). However, most of these other parameter vectors are physically inconsistent with the results obtained at the other temperatures.

From this, it appears that the integrated rate data is taken over a domain which is insufficient to excite all modes of the system. A similar situation may exist with the data given at 340°C, producing the inconsistent negative rate constant. If this is so, the parameters cannot be properly identified.

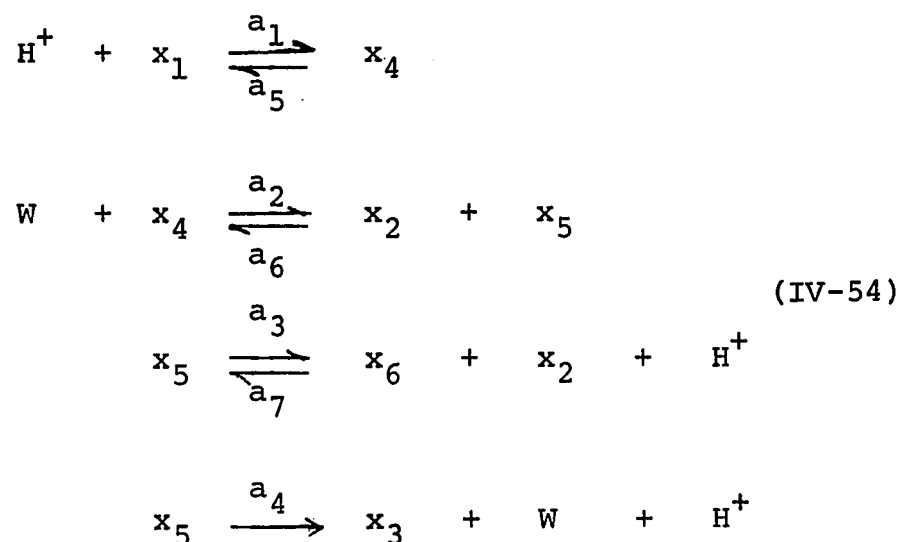
The convergence for the data at 355°C and 340°C was quite rapid when an order of magnitude guess was supplied. There is then good reason to suppose that the proposed

procedure will be quite useful in the analysis of Langmuir-Hinshelwood models when integrated rate data is obtained. However, the discouraging results obtained from the data given at 325°C and 340°C indicates that a considerable amount of caution should be exercised when attempting to correlate with this type of model.

In principle, it would not be too difficult to modify the proposed procedure so that constraints on the parameter vector could be incorporated. If this were done, rates obtained by direct measurement could be incorporated so that all integrated and differential data could be fitted by the same correlation technique. This would be of considerable advantage in attacking problems such as the one above.

#### E. A Complex Nonlinear Reaction

To identify the parameters in a complex reaction model is at best a very difficult problem. This will be illustrated by the problems encountered in attempts to identify a system with the proposed mechanistic model.



Several experiments were performed at each of the two temperatures 80°C and 100°C in a batch reactor. The concentrations of  $x_1$ ,  $x_2$ , and  $x_3$  were measured at several different times during the reaction. The components  $x_4$  and  $x_5$  were unmeasurable intermediates and  $x_6$  was given by the following linear relation derived from the stoichiometry

$$x_6 = C_0 - (x_1 + x_3 + x_4 + x_5) \tag{IV-55}$$

Hydrogen ion concentration ( $\text{H}^+$ ), water concentration (W) and the constant  $C_0$  remained fixed throughout any one experiment. At the request of Chemcell, who generously supplied the data for this example, the other components will not be identified.

From the proposed mechanistics model, the system of ordinary differential equations may be written:

$$\frac{dx_1}{dt} = - a_1 H^+ x_1 + a_5 x_4 \quad (\text{IV-56})$$

$$\frac{dx_2}{dt} = a_2 W x_4 + a_3 x_5 - a_6 x_2 x_5 - a_7 H^+ x_6 x_2 \quad (\text{IV-57})$$

$$\frac{dx_3}{dt} = a_4 x_5 \quad (\text{IV-58})$$

$$\frac{dx_4}{dt} = a_1 H^+ x_1 - a_5 x_4 - a_2 W x_4 + a_6 x_2 x_5 \quad (\text{IV-59})$$

$$\frac{dx_5}{dt} = a_2 W x_4 - a_6 x_3 x_5 - a_3 x_5 + a_7 H^+ x_6 x_2 - a_4 x_5 \quad (\text{IV-60})$$

with the unknown parameter vector being

$$\underline{a} = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \\ a_5 \\ a_6 \\ a_7 \end{bmatrix} \quad (\text{IV-61})$$

and the state vector being:

$$\underline{x} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \end{bmatrix} \quad (\text{IV-62})$$

Attempts to solve this system directly met with difficulties, as the system of ordinary differential equations was unstable to numerical integration. This was caused by the tremendous difference in magnitude of the time constants associated with the different compounds. To avoid this problem, the stationary state approximation was employed by setting

$$\frac{dx_4}{dt} = 0 \quad (\text{IV-63})$$

and

$$\frac{dx_5}{dt} = 0 \quad (\text{IV-64})$$

and using the resultant system of algebraic equations to obtain the following relations.



$$x_5 = \frac{(a_7 H^+ x_2 - a_2 W) a_1 H^+ x_1 - a_7 H^+ x_2 (C_0 - x_1 - x_3) (a_1 + a_2)}{(a_2 W - a_7 H^+ x_2) a_6 x_2 - (a_6 x_2 + a_3 + a_4 + a_7 H^+ x_2) (a_5 + a_2 W)} \quad (\text{IV-65})$$

$$x_4 = \frac{a_1 H^+ x_1}{a_5 + a_2 W} + \frac{a_6 x_2}{a_5 + a_2 W} x_5 \quad (\text{IV-66})$$

Substituting (IV-65) and (IV-66) into the differential equations (IV-56), (IV-57), and (IV-58) produced a stable system with the state vector being reduced to order three

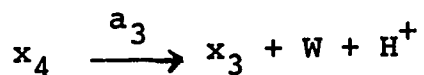
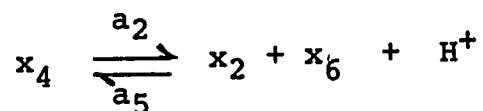
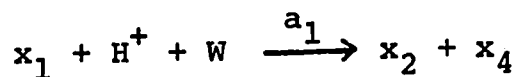
$$\underline{x} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} \quad (\text{IV-67})$$

Although, with this modification, no integration stability problems were encountered, attempts to find all seven parameters were not successful. If the data sets are examined, it will be found that all the initial conditions are of the form:

$$\underline{x}(0) = \begin{bmatrix} C_0 \\ 0 \\ 0 \end{bmatrix} \quad (\text{IV-68})$$

It was suspected that data taken from this initial condition alone, was not sufficient to identify distinctly the various forward and backward rate parameters in the first two steps in the mechanistic model.

A simplified model was then proposed:



which may be described mathematically by the differential equations:

$$\frac{dx_1}{dt} = - a_1 H^+ W x_1 \quad (\text{IV-69})$$

$$\frac{dx_2}{dt} = a_2 x_4 - a_5 H^+ x_2 x_6 + a_1 H^+ W x_1 \quad (\text{IV-70})$$

$$\frac{dx_3}{dt} = a_3 x_4 \quad (\text{IV-71})$$

and the algebraic relations

$$x_6 = C_0 - (x_1 + x_3 + x_4) \quad (\text{IV-72})$$

$$x_4 = \frac{a_1 x_1 H^+ W + a_5 x_2 (C_0 - x_1 - x_3)}{a_2 + a_3 + a_5 H^+ x_2} \quad (\text{IV-73})$$

The relation (IV-72) comes from the stoichiometry and the expression for  $x_4$  (IV-73) again comes from the stationary state approximation. The parameter vector has now been reduced to

$$\underline{a} = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_5 \end{bmatrix} \quad (\text{IV-74})$$

In attempts to identify the parameters in the vector (IV-74), an interesting phenomenon was encountered. The parameters  $a_1$  and  $a_5$  were accurately identified for the data given at the two different temperatures. For the parameters  $a_2$  and  $a_3$  a large number of different solutions could be obtained. Each yielded the same least squares minimum.

On closer examination of the model, it will be found that the following relation is approximately true

$$x_4 \propto \frac{1}{a_2 + a_3} \quad (\text{IV-75})$$

and  $x_4$  only appears in two terms where is is dominant. The first is the term  $a_2x_4$  in equation (IV-70) and the second is  $a_3x_4$  in equation (IV-71).

From the above:

$$a_2x_4 \quad \alpha \quad \frac{a_2}{a_2 + a_3} \quad \text{(IV-76)}$$

and

$$a_3x_4 \quad \alpha \quad \frac{a_3}{a_2 + a_3} \quad \text{(IV-77)}$$

Since the concentration of  $x_4$  is not specified, other than being several orders of magnitude smaller than the principal components, as long as the terms on the right hand sides of equations (IV-76) and (IV-77) remain constant, the model will reproduce the data equally well. The constant  $a_2$  was found to be much larger than  $a_3$ . Therefore the approximations

$$\frac{a_2}{a_2 + a_3} \approx 1 \quad \text{(IV-78)}$$

and

$$\frac{a_3}{a_2 + a_3} \approx \frac{a_3}{a_2} \quad \text{(IV-79)}$$

may be made. So, if the ratio of  $a_3$  to  $a_2$  is the same, different parameter vectors will produce the same solution profiles. This is what was observed.

To verify these observations, examine the following table of solutions for the data at  $100^{\circ}\text{C}$ . The concentration profiles produced by any one of the three parameter vectors given in Table 15 are shown in Figures 9, 10, 11, 12, 13 and 14.

TABLE 15

Chemcell Problem  
Various Solutions for  $100^{\circ}\text{C}$  Data

$a_1$	$a_2$	$a_3$	$a_5$	$a_3/a_2$	Sum of Errors Squared
0.0815	0.982	0.151	7.15	0.154	0.00023
0.0815	2.11	0.323	7.11	0.153	0.00023
0.0815	0.174	0.027	7.47	0.155	0.00023

Similarly, the results for the data given at  $80^{\circ}\text{C}$  verified the above as shown in Table 16.

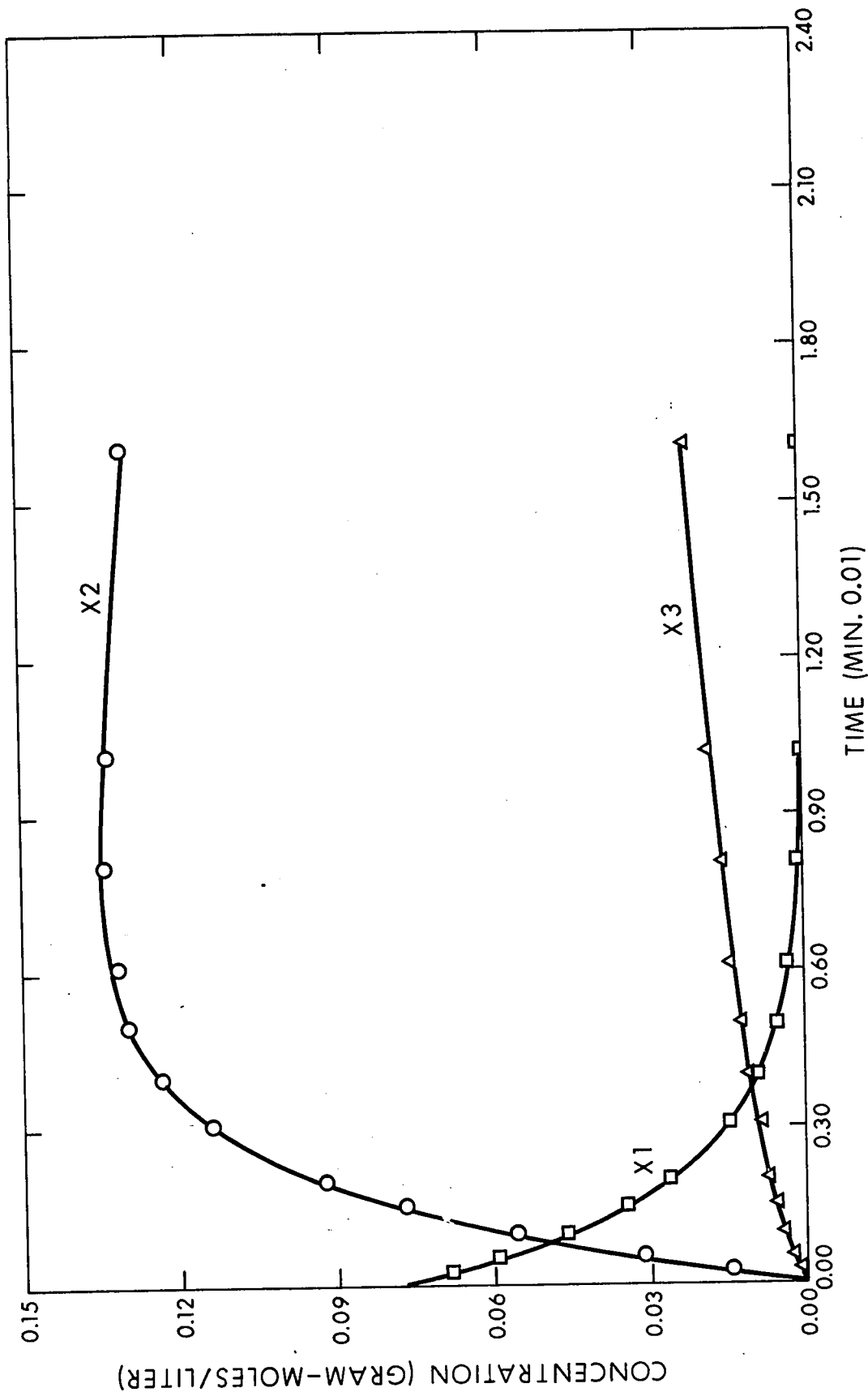


Figure 9 Solution to Chemcell problem 100°C (data set one)  
[H<sup>+</sup>] = 0.012 g-mole/l C<sub>0</sub> = 0.0759 g-mole/l

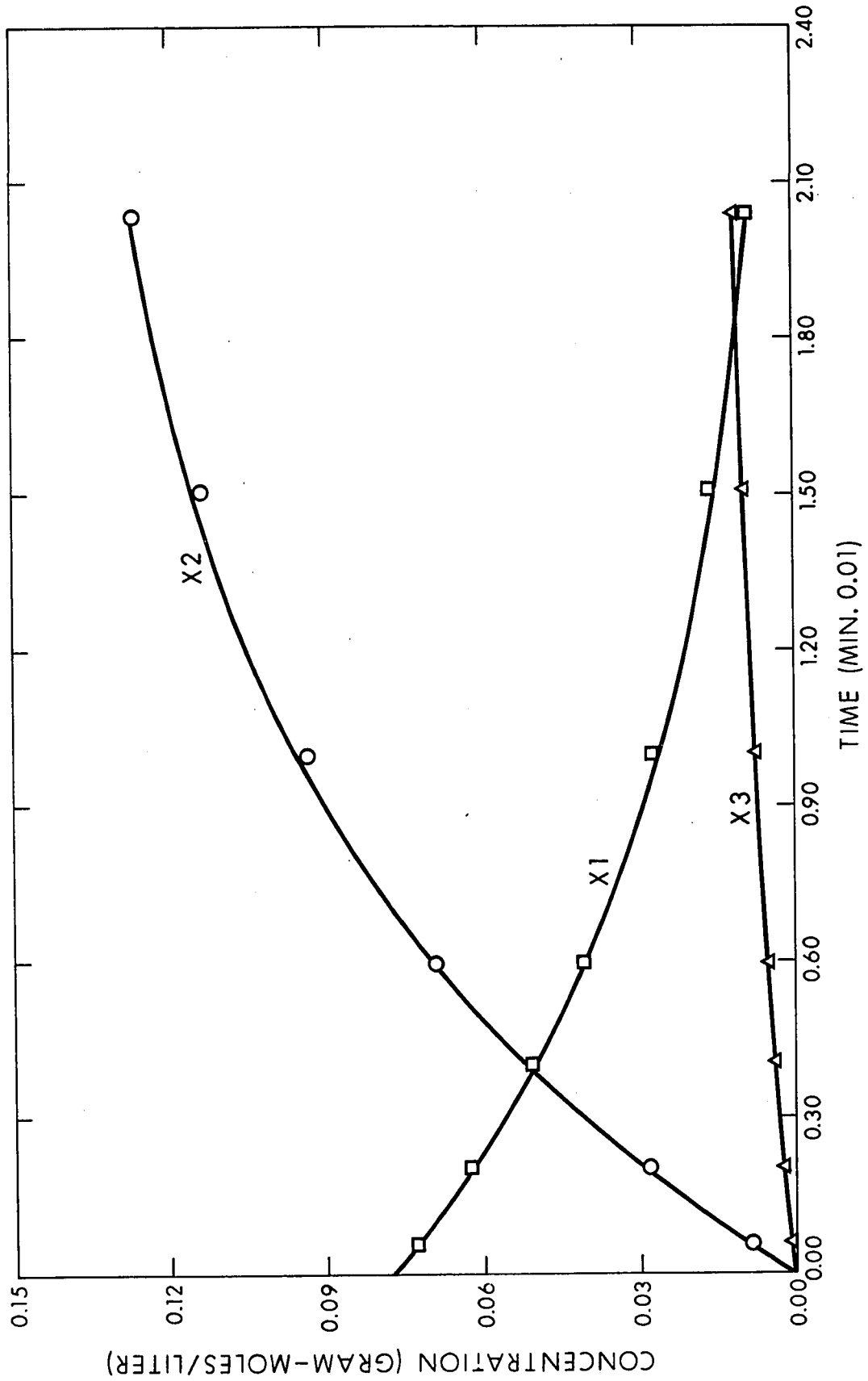


Figure 10 Solution to Chemcell problem 100°C (data set two)  
[H<sup>+</sup>] = 0.00241 g-mole/l C<sub>0</sub> = 0.0774 g-mole/l

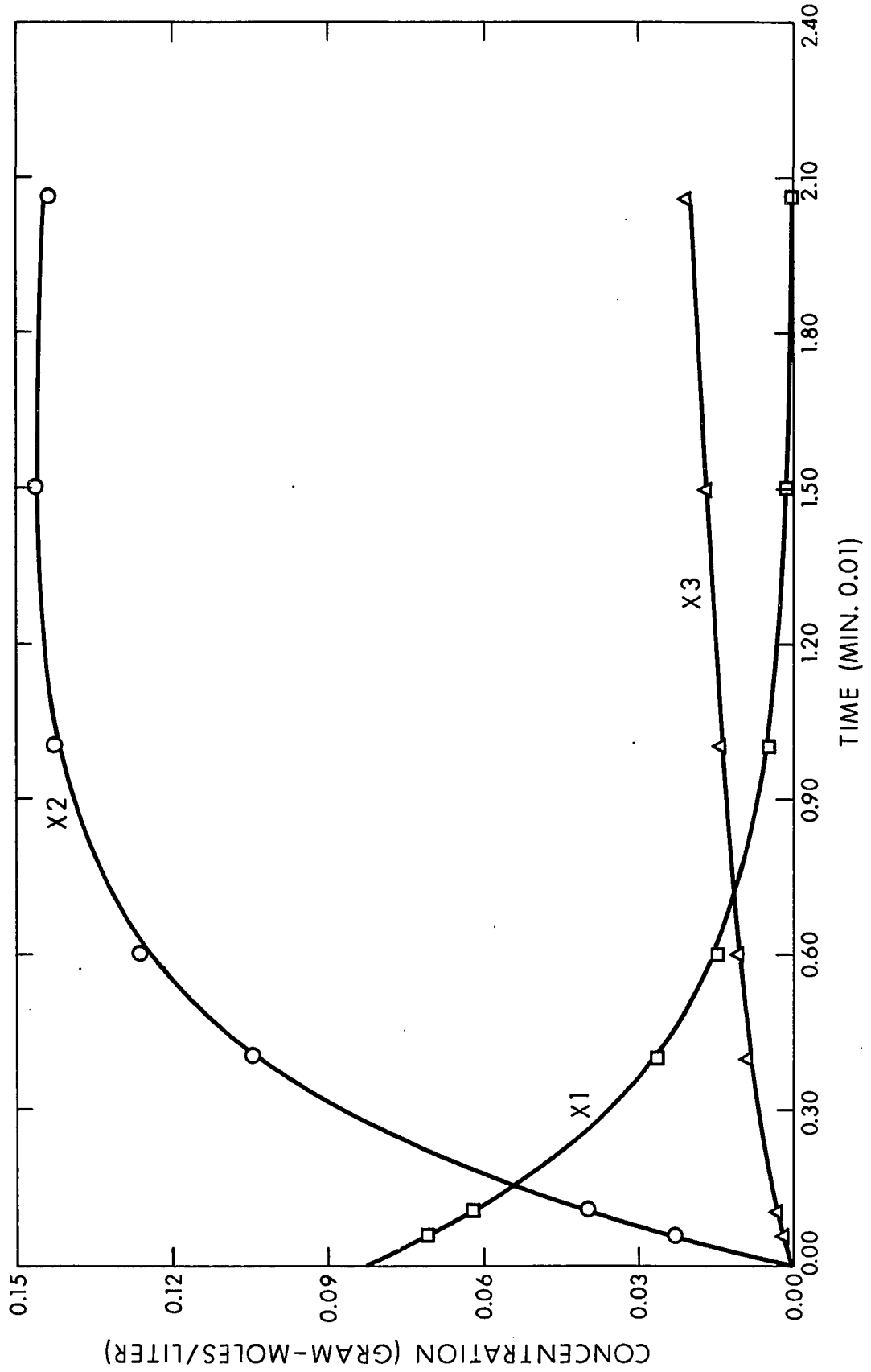


Figure 11 Solution to Chemcell problem 100°C (data set three)  
[H<sup>+</sup>] = 0.00614 g-mole/l C<sub>0</sub> = 0.0828 g-mole/l



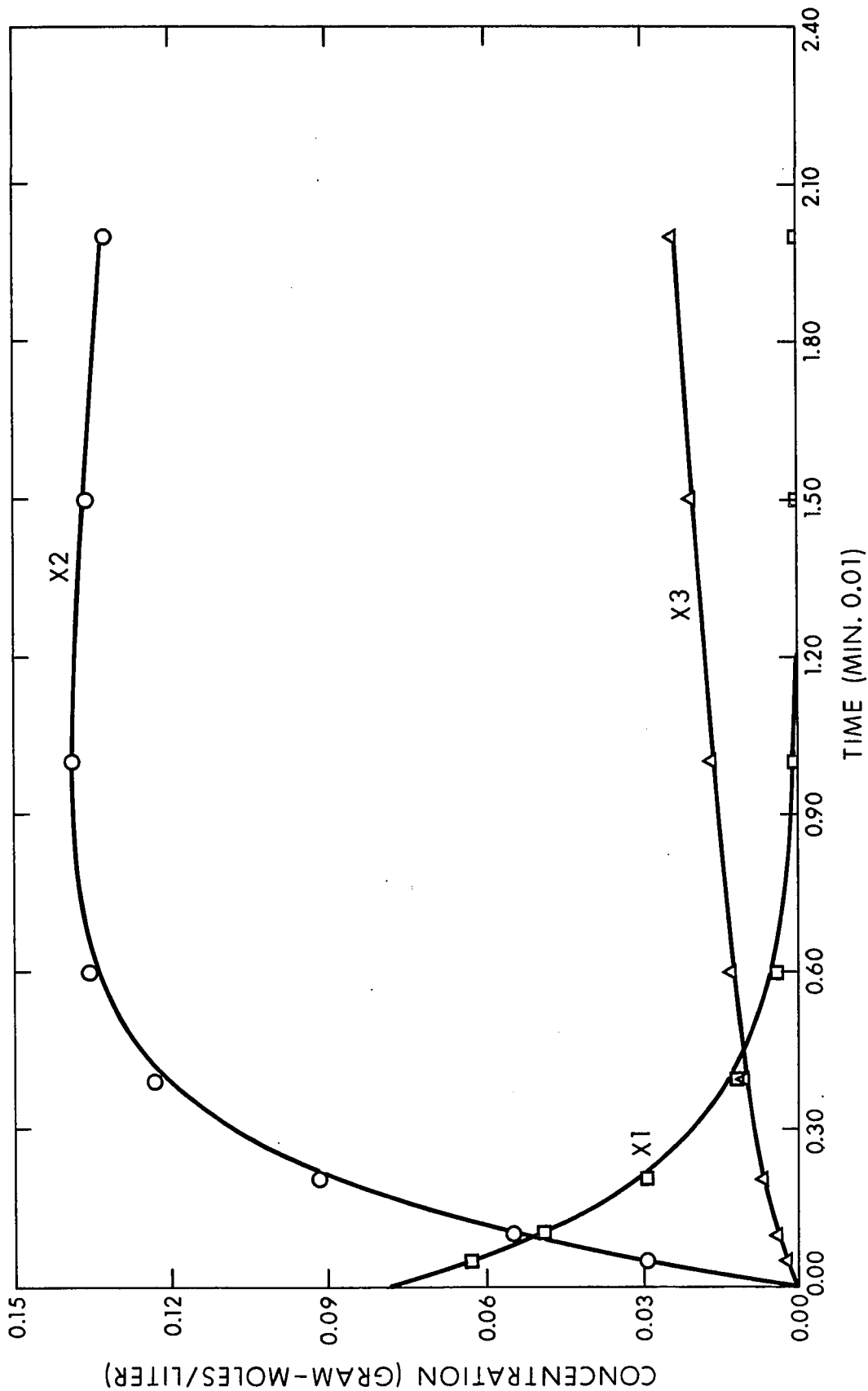


Figure 12 Solution to Chemcell problem 100°C (data set four)  
[H<sup>+</sup>] = 0.00986 g-mole/l C<sub>0</sub> = 0.0784 g-mole/l

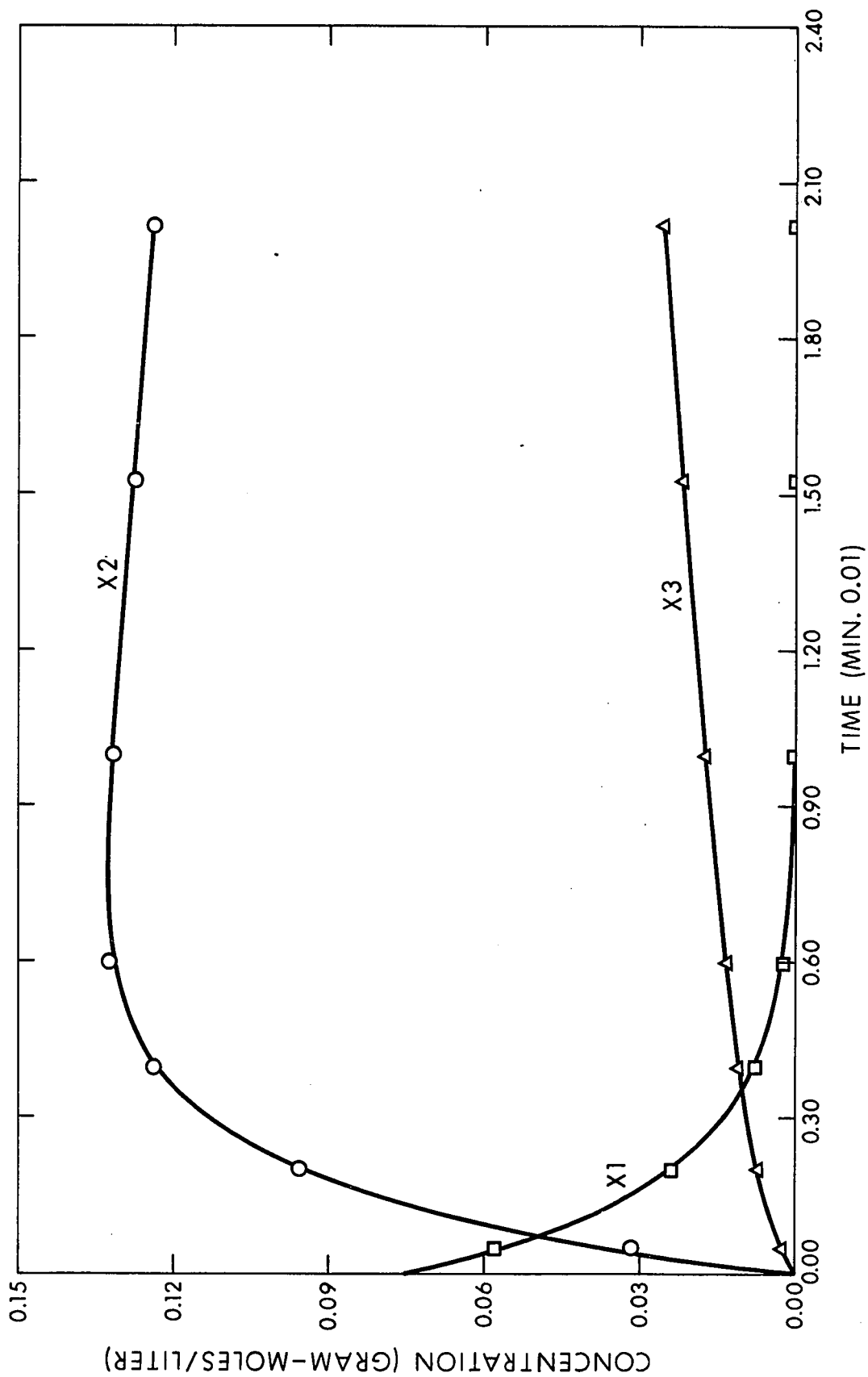


Figure 13 Solution to Chemcell problem 100°C (data set five)  
[H<sup>+</sup>] = 0.0125 g-mole/l C<sub>0</sub> = 0.0749 g-mole/l

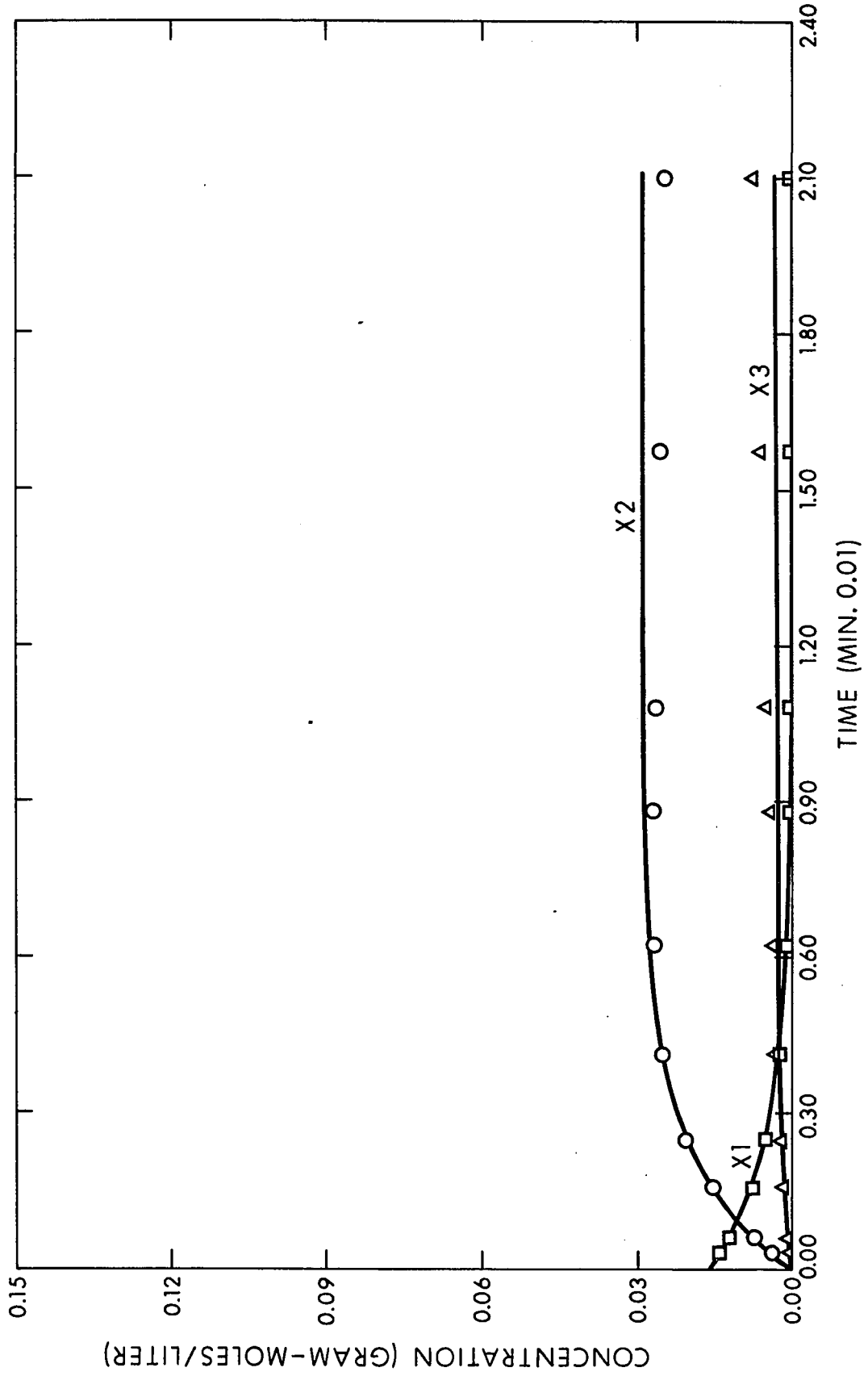


Figure 14 Solution to Chemcell problem 100°C (data set six)  
[H<sup>+</sup>] = 0.0103 g-mole/l C<sub>0</sub> = 0.01563 g-mole/l

TABLE 16  
Chemcell Problem  
Various Solutions for 80°C Data

$a_1$	$a_2$	$a_3$	$a_5$	$a_3/a_2$	Sum of Errors Squared
0.0106	0.183	0.025	1.37	0.136	0.000072
0.0106	1.02	0.138	1.30	0.135	0.000070
0.0106	2.23	0.302	1.29	0.135	0.000070

All of the parameters vectors given in Tables 15 and 16 reproduced the data equally well. When the profiles were plotted for each experiment, the different curves could not be distinguished.

For each experiment there were data points taken at 24 and 48 hours. These points were not used in the fitting procedure in order to eliminate the large amount of integration time required. However, once the parameters have been determined, these points may be used to check the results.

With each of the sets of parameters given in Table 14 for the 80°C data, the predicted values of the data at 24 and 48 hours were the same. This is shown in Figures 15, 16, 17, 18 and 19.

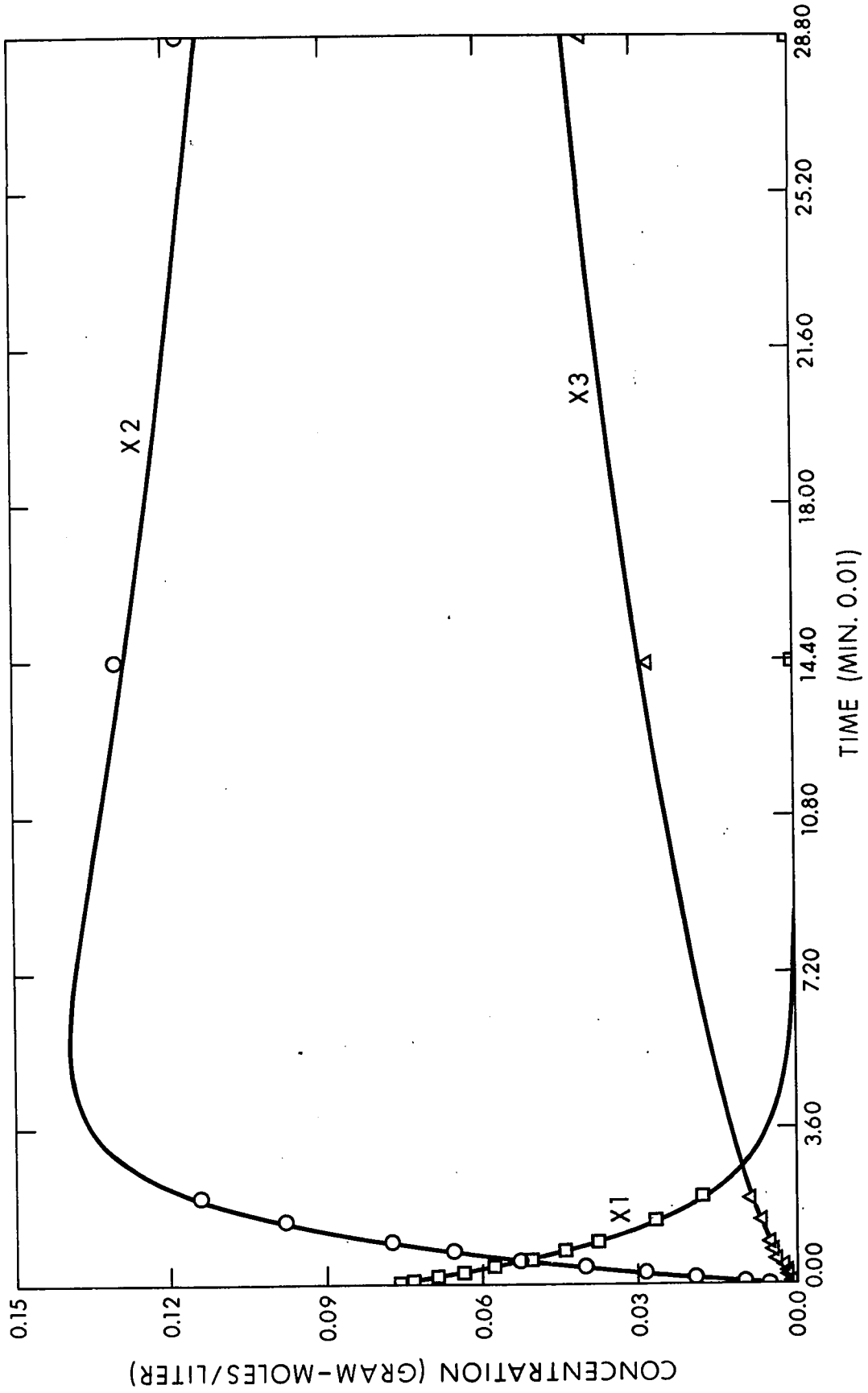


Figure 15 Solution to Chemcell problem 80°C (data set one)  
[H<sup>+</sup>] = 0.0127 g-mole/l C<sub>0</sub> = 0.0791 g-mole/l

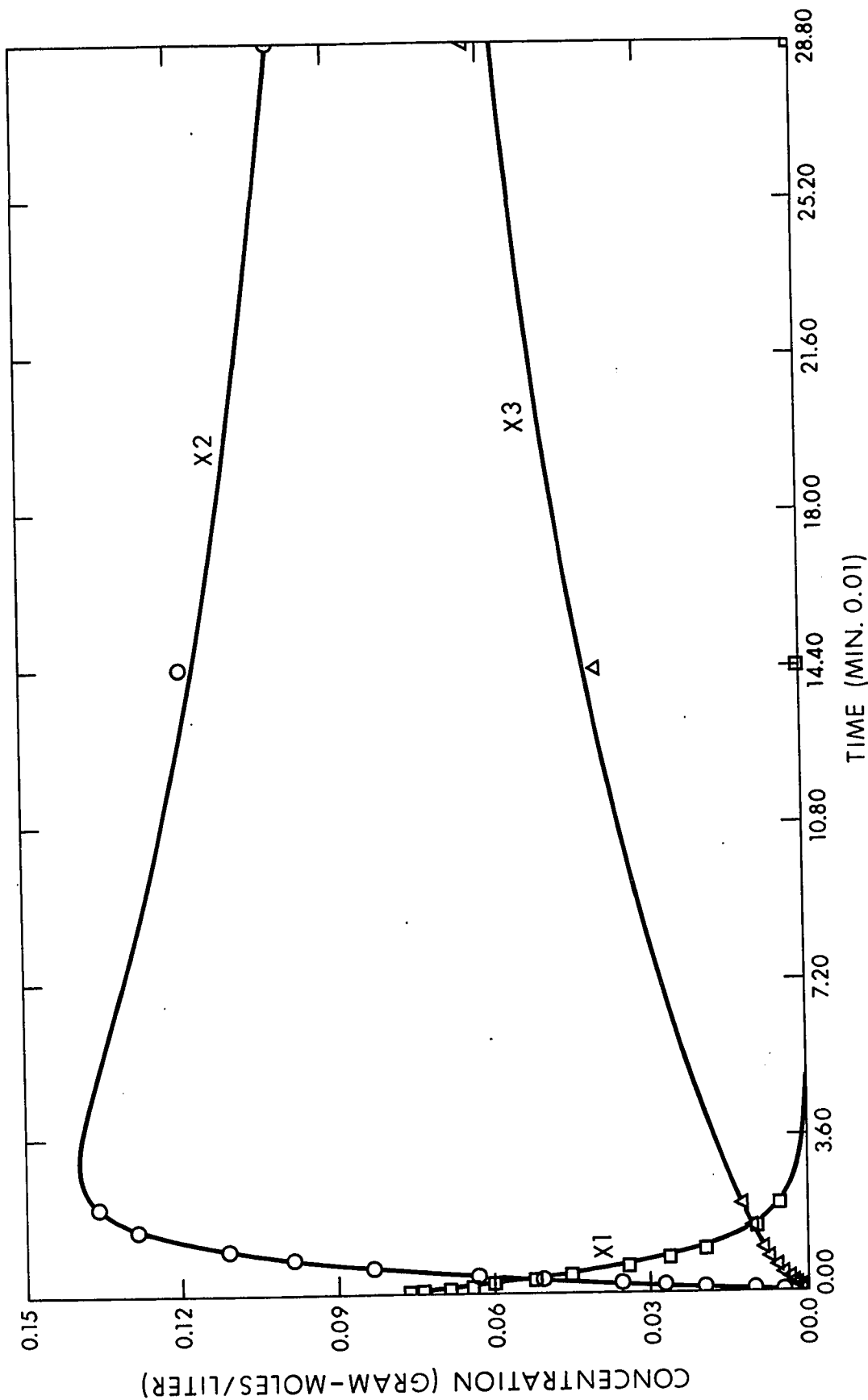


Figure 16 Solution to Chemcell problem 80°C (data set two)  
[H<sup>+</sup>] = 0.0230 g-mole/l C<sub>0</sub> = 0.0795 g-mole/l

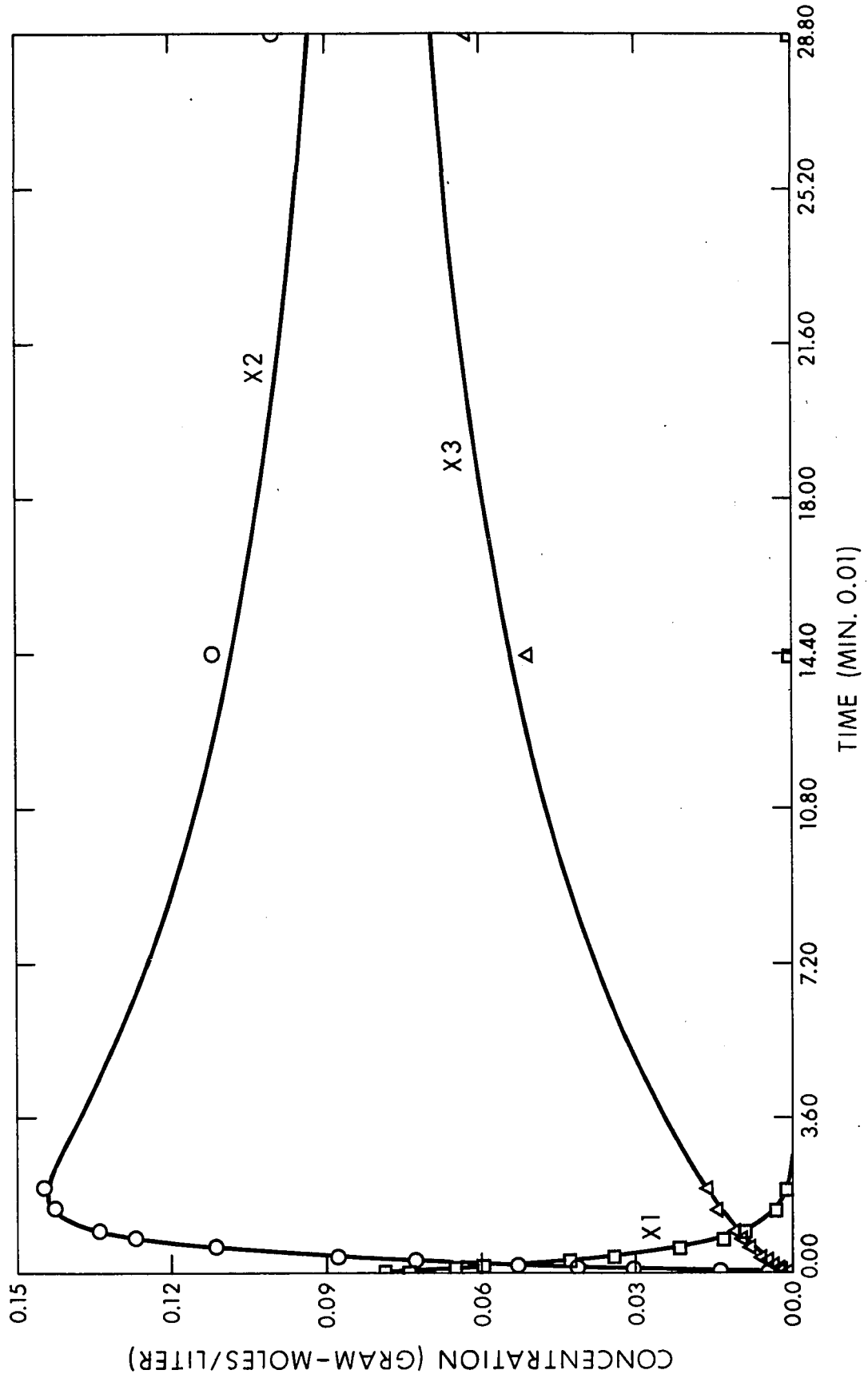


Figure 17 Solution to Chemcell problem 80°C (data set three)  
[H<sup>+</sup>] = 0.0368 g-mole/l C<sub>0</sub> = 0.0822 g-mole/l

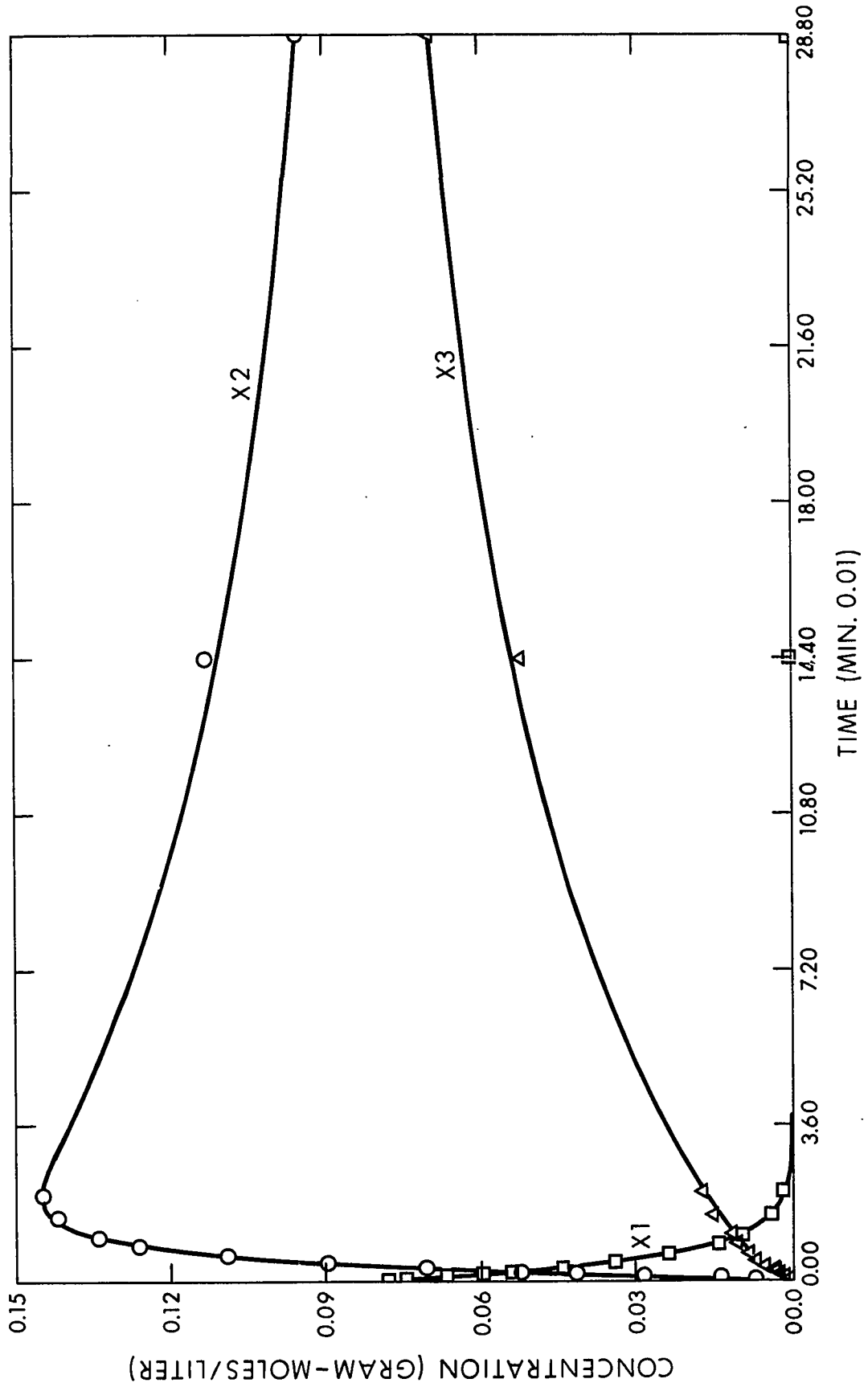


Figure 18 Solution to Chemcell problem 80°C (data set four)  
[H<sup>+</sup>] = 0.0345 g-mole/l C<sub>0</sub> = 0.0825 g-mole/l



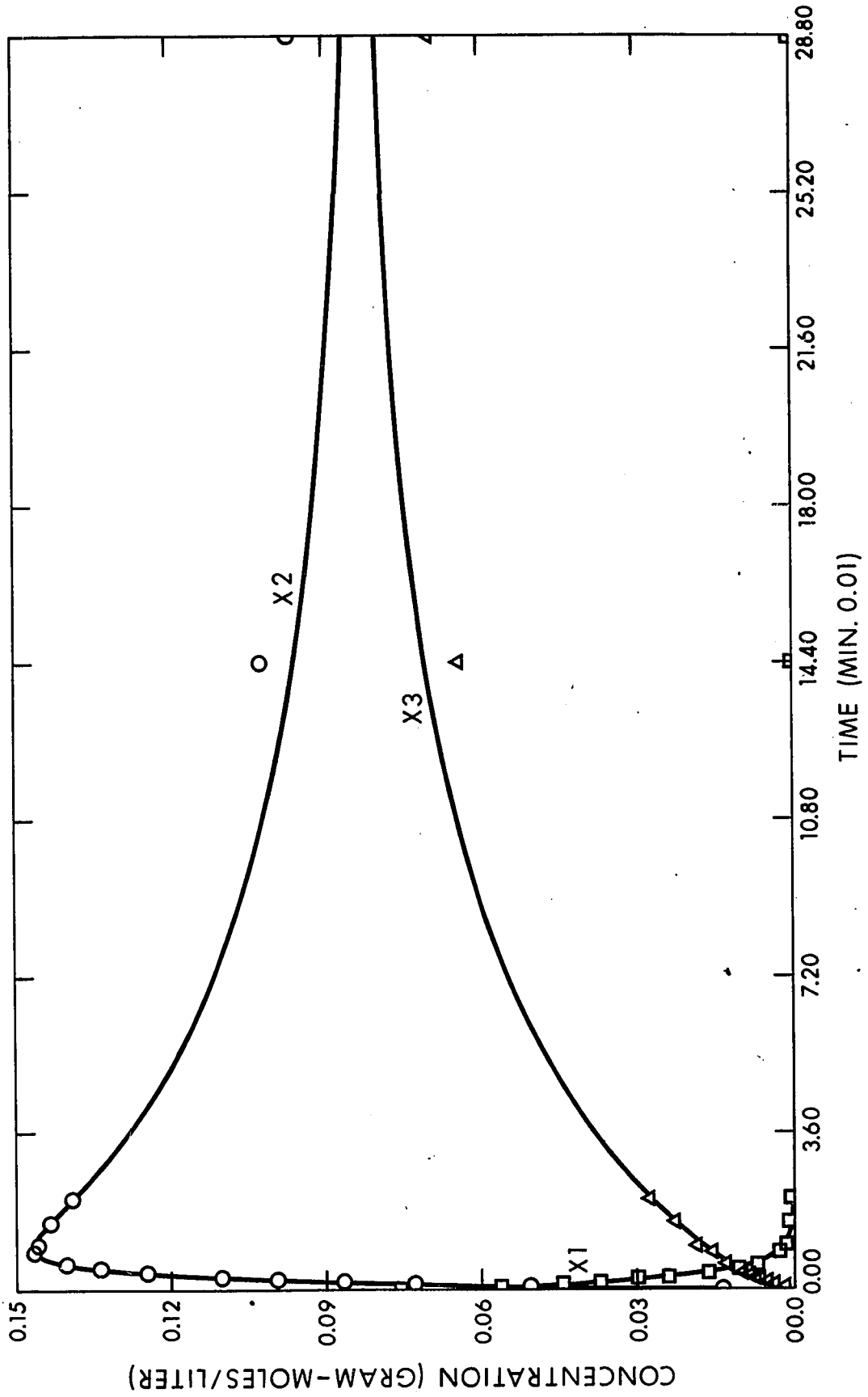


Figure 19 Solution to Chemcell problem 80°C (data set five)  
[H<sup>+</sup>] = 0.0345 g-mole/l C<sub>0</sub> = 0.0825 g-mole/l

Even though  $a_2$  and  $a_3$  could not be uniquely determined, the model has been successfully fitted to the given data, and may be used to produce information, with reasonable certainty, in the range of conditions under which the experiments were performed.

To establish  $a_2$  and  $a_3$  uniquely measurements need to be made of the intermediate  $x_4$ . This, however, is not necessary if the model is only to be used for the above purposes.

The most important conclusion that can be drawn from this example, is that identifying complex systems is not a routine operation. The analysis must be closely coupled with the design and execution of the experiments.

V. IDENTIFICATION OF SIMPLE CONTROL MODELS FOR  
COMPLEX SYSTEMS

For many complex systems, the sophisticated mathematical models that are needed to accurately simulate them require a large amount of time for solution, or they may defy solution altogether. Time is not of critical importance in most design problems as long as a solution is obtained, and the cost of obtaining that solution can be justified economically. However, for control problems with the independent variable being time itself, it is essential that solutions be obtained quickly so that the appropriate manipulations of the control variables can be made at the proper times. For these complex systems then, it is important to develop simple theoretical or correlative models which can be used over a narrow range of operating conditions.

In many cases, the initial conditions are not known for some of the state variables. This being the case, the proposed algorithm, in its simplified form, cannot be used. However, there are some cases for which this is not true. An example is given and discussed in this section.

A. Flow of a Tracer Through a Packed Bed

The analysis of flow through packed beds is of considerable importance in a number of systems, the least of which is certainly not the non-homogeneous catalytic reactor.

The partial differential equation

$$\frac{\partial x}{\partial t} = \frac{1}{N_{P_e}} \frac{\partial^2 x}{\partial L^2} - \frac{\partial x}{\partial L} \quad (V-1)$$

x - dimensionless concentration

L - dimensionless length

t - dimensionless time

$N_{P_e}$  - Peclet number

is a mathematical model which can be used to describe the unsteady state behavior of a tracer flowing through a packed bed. This model has already been simplified. The radial diffusion terms have been dropped, leaving only the axial diffusion and convective terms on the right hand side of the equation.

Equation (V-1) can be solved numerically without a great deal of difficulty. With packed bed reactors, however, the nonlinear rate expressions must be added, and the resultant nonlinear partial

differential equations are quite difficult to handle. This example was considered with the application to more complex systems being the ultimate goal.

Data was generated by H.S. Koonar (17) for the transient behavior of (V-1) with the initial condition

$$x(0,L) = 0.75 \quad (V-2)$$

and the boundary conditions

$$\frac{\partial x}{\partial L} (t,l) = 0 \quad (V-3)$$

$$\begin{aligned} x(t,0) &= f(t) \\ &= 0.75 + 0.25 \text{ SIN}(\omega t) \end{aligned} \quad (V-4)$$

It was solved by using central finite difference relations to approximate the terms on the right hand side of the equation. Doing this results in a system of linear ordinary differential equations with time being the independent variable. Eleven grid points were used and the system of linear ordinary differential equations was solved by finding the eigenvalues and eigenvectors of the coefficient matrix. In Table 17 are the outlet concentrations generated from  $\omega = 0.1, 1.0, 5.0, 10.0$ .

TABLE 17

Data for Tracer Problem  $x(t,1)$

$t/\omega$	0.1	1.0	5.0	10.0
0.0	0.7500	0.7500	0.7500	0.7500
0.5	0.7954	0.7602	0.7523	0.7888
1.0	0.7523	0.8250	0.7599	0.8423
1.5	0.7384	0.9095	0.7708	0.6853
2.0	0.7575	0.9692	0.7828	0.8100
2.5	0.7737	0.9781	0.7951	0.7404
3.0	0.7611	0.9341	0.8073	0.7188
3.5	0.7370	0.8459	0.8194	0.8204
4.0	0.7354	0.7351	0.8314	0.6784
4.5	0.7588	0.6286	0.8432	0.8041
5.0	0.7735	0.5525	0.8548	0.7447

It has been suggested that (26), (24) many complex systems can be modeled sufficiently for control purposes by a second order differential equation with a time delay such as

$$\frac{d^2x(t,1)}{dt^2} + a_1 \frac{dx(t,1)}{dt} + a_2 [x(t,1) - f(t-t_D)] = 0 \quad (V-5)$$

with  $t_D$  being the time delay. By defining

$$x_1 = x(t,1) \quad (V-6)$$

and

$$x_2 = \frac{dx(t,1)}{dt} \quad (V-7)$$

equation (V-5) can be written as a system of first order differential equations

$$\frac{dx_1}{dt} = x_2$$

$$\frac{dx_2}{dt} = -a_1x_2 - a_2 [x_1 - f(t-t_D)] \quad (V-8)$$

with the unknown parameter vector

$$\underline{a} = \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} \quad (V-9)$$

The time delay  $t_D$  cannot be treated directly by quasi-linearization and data perturbation. For small problems such as this, the time delay can be determined by a search procedure. For more complex systems with many different unknown time delays, other methods must be employed.

With several different values for  $t_D$  the parameter vector was determined with the initial guess being

$$\underline{a} = \begin{bmatrix} 1.0 \\ 1.0 \end{bmatrix} \quad (V-10)$$

Table 18 contains these values.



TABLE 18

Solutions of Tracer Problem

$t_D$	$a_1$	$a_2$	Sum of the Errors Squared
0.100	4.39	6.69	0.003203
0.150	5.40	8.59	0.000891
0.170	5.96	9.59	0.000466
0.180	6.28	10.18	0.000371
0.187	6.54	10.62	0.000350*
0.190	6.65	10.83	0.000353
0.200	7.07	11.57	0.000418
0.210	7.56	12.42	0.000560
0.230	10.68	17.79	0.001863

\* Value for optimum time delay

The parameters obtained for each of the given estimates of the time delay all reproduce the data well. This can be seen by observing Table 19 which contains the deviations from the actual solution, presented in Table 17, for the optimum time delay ( $t_D = 0.187$ ).

TABLE 19

Deviation of the Model from the Actual Values  
for Tracer Problem

$$|\hat{x}(t,1) - x(t,1)|$$

$t/\omega$	0.1	1.0	5.0	10.0
0.0	0.0000	0.0000	0.0000	0.0000
0.5	0.0007	0.0019	0.0015	0.0026
1.0	0.0022	0.0036	0.0024	0.0010
1.5	0.0062	0.0035	0.0024	0.0013
2.0	0.0042	0.0036	0.0028	0.0048
2.5	0.0001	0.0019	0.0029	0.0013
3.0	0.0002	0.0017	0.0028	0.0035
3.5	0.0041	0.0017	0.0028	0.0031
4.0	0.0074	0.0022	0.0029	0.0013
4.5	0.0035	0.0027	0.0029	0.0045
5.0	0.0004	0.0032	0.0030	0.0013

These results confirm that a second order differential equation with a time delay can be used as an adequate control model for the flow of a tracer through a packed bed.

The computational time required to solve this problem was quite small (less than one minute of 360/67 computational time). Therefore, with small problems, it is quite practical to find the unknown time delay by searching procedure.

## VI. DISCUSSION AND CONCLUSIONS

Quasilinearization and data perturbation has been shown to be a powerful tool in the solution of certain identification problems. Certain limitations, however, were evident from the experience gained in analyzing the examples given in this work.

### A. Numerical Problems

There are two major numerical operations which must be performed. Both of these operations can be a source of difficulties.

The first is the integration of the large number of initial value problems associated with each iteration of the quasilinearization procedure. In some instances, these equations may be unstable to numerical integration. If this is the case, there are three alternatives. The first is to use a small step size which will result in consuming a large amount of computer time. The second alternative is to find a better numerical integration procedure. Perhaps one of the multistep methods such as Hammings prediction corrector method (7) could be used to replace the fourth order Runge Kutta method (8) presently being used. The final alternative is to make use of a hybrid computer.

The second numerical operation is the solution of the least squares problem at the completion of each quasilinearization iteration. It is well-known that this problem is subject to ill-conditioning if the number of the unknown parameters and initial conditions becomes large (greater than seven). This problem, as has been mentioned before, can be avoided by using the Chebyshev criteria for fitting the data.

B. Experimental Design

Advances have been made recently in the theory of the design of experiments. Especially noted is the work done by Box, Hunter, and their co-workers (3), (9), and (16). It is evident from their work that if a mechanistic or correlative model is the ultimate aim of an experimental program, it is essential to determine the nature of the model early so that subsequent experimentation can be designed appropriately. With the proper design of experiments, at least some of the identification failures will be eliminated. Unfortunately, most of the work that has been done has been associated with the identification of systems which can be represented by algebraic relations or can be reduced to this form.

Until the theory of experimental design has been extended to function space, intuition and judgment must be used in the identification of systems which can be described adequately only by a system of ordinary differential equations. The theory for linear systems is more advanced (20), (27) and can be used as a guide to the solution of problems which are of a non-linear nature.

### C. Computer Time Requirements

Few of the problems presented in this work required more than five minutes of time on the IBM 360/67 computer. However, there were indications that the time requirements may be disproportionately larger for more complex systems. If this is true, then ways must be devised to improve the efficiency of this procedure or another more effective method must be found.

Two obvious ways of cutting down the time requirements are to improve the programming and to use more efficient numerical techniques. Some improvement undoubtedly could be made in this direction.

As the amount of time required is directly proportional to the number of experiments being considered, it would seem advisable to minimize the total number

used to identify the system. Once a few experiments had been used to get an approximate result, all of the experiments could then be used to find the true solution. This approach may be profitable in complex problems, if the few experiments chosen are sufficient to identify the system. The choice of these few experiments is closely coupled to the problem of experimental design discussed above.

The method for adjusting the step size for the data perturbation is completely arbitrary. If a technique were developed for choosing the optimum step size for each step, a considerable advantage would be gained.

#### D. Future Work

To extend the present work to more general systems would be of obvious advantage.

In principle, the modification of the method to handle more general boundary conditions, both linear and nonlinear, is not difficult. However, the addition of nonlinear boundary conditions and constraints will probably require larger amounts of computer time.

It has been noted that the data perturbation procedure will work satisfactorily only if reasonably

large steps may be taken. If the number of steps becomes large, the computer time required will become excessive.

To circumvent this problem, it may prove advantageous to combine this method with one of the hill climbing methods such as Rosenbrock's (25). In general, the rate of convergence of the hill climbing procedures tends to be slower as the solution is approached. This is quite the contrary to the rate of convergence of the quasilinearization procedure, which tends to accelerate as the solution is approached. A combination of these two methods may yield fruitful results.



N O M E N C L A T U R E

A	-	normalized Arrhenius rate constant
A'	-	Arrhenius pre-exponential rate constant
$\underline{a}$	-	parameter vector
B	-	pressure correction factor
C <sub>max</sub>	-	maximum allowable relative change in the parameters for one iteration
C <sub>min</sub>	-	minimum allowable relative change in the parameters for one step
c <sub>o</sub>	-	constant
$\underline{c}$	-	vector of initial conditions $\underline{y}(0)$
E	-	activation energy in the Arrhenius expression
F	-	feed rate of reactant
$\underline{F}_a$	-	block entry in the fundamental matrix contributed by the parameter vector
$\underline{F}_{xj}$	-	block entry in the fundamental matrix contributed by the jth state vector $\underline{s}_j$
f	-	fractional conversion
$f_j(\underline{x}_j; \underline{a}, t)$	-	rate of change of $\underline{x}_j$ with respect to the independent variable
$\underline{Ga}_j$	-	block entries in the fundamental matrix contributed by coupling of the state vector $\underline{x}_j$ with the parameter vector
$\underline{g}(\underline{y}, \underline{a}, t)$	-	rate of change of the total state vector $\underline{y}$ with respect to the independent variable
H <sup>+</sup>	-	concentration of hydrogen ion
$\underline{J}$	-	Jacobian of $\underline{g}(\underline{y}, \underline{a}, t)$ with respect to $\underline{y}$

$J_{\underline{a}j}$	-	Jacobian of $\underline{f}_j(\underline{x}_j, \underline{a}, t)$ with respect to $\underline{a}$
$J_{\underline{x}j}$	-	Jacobian of $\underline{f}_j(\underline{x}_j, \underline{a}, t)$ with respect to $\underline{x}_j$
$K_e$	-	equilibrium constant
$L$	-	the distance from the entrance of a tubular reactor
$L_m$	-	the total length of a tubular reactor
$m$	-	the superscript referring to the quasi-linearization iteration count
$N_{Cl_2}$	-	the number of moles of chlorine initially present in the reactor
$N_B$	-	the total number of moles initially present in the reactor
$N_{HCl}$	-	the number of moles of hydrogen chloride initially present in the reactor
$N_{H_2O}$	-	the number of moles of water initially present in the reactor
$N_I$	-	the number of moles of inerts initially present in the reactor
$N_{Pe}$	-	Peclet number
$N_O$	-	feed rate of inerts
$n$	-	the number of experiments
$P$	-	the total pressure of a point in the tubular reactor
$P_{Cl_2}$	-	the partial pressure of chlorine
$P_e$	-	the exit or final pressure
$P_{HCl}$	-	the partial pressure of hydrogen chloride
$P_{H_2O}$	-	the partial pressure of water

$P_i$	-	the inlet of initial pressure
$P_{O_2}$	-	the partial pressure of oxygen
$P_{tot}$	-	the total pressure of the reactor
$p$	-	the order state variable vector $\underline{x}_j$ ( $j = 1, 2, \dots n$ )
$q$	-	the order of the parameter vector $\underline{a}$
$R$	-	the ideal gas constant (Kcal)/(g-mole) ( $^{\circ}K$ )
$R'$	-	the ideal gas constant ( $cm^2$ ) (mmHg)/ (g-mole) ( $^{\circ}K$ )
$\hat{R}$	-	the relative step size
$R_{O_2}$	-	the rate of reaction of oxygen
$r$	-	the order of the vector $\underline{y}$
$S_{max}$	-	the initial maximum step size
$s$	-	the cross section area of a tubular reactor
$T$	-	temperature
$t$	-	the independent variable (or time)
$t_k$	-	the kth discrete value of $t$
$t_{jk}$	-	the kth discrete value of $t$ for which data is given for the jth experiment
$\underline{u}$	-	a particular solution to the system of first order linear differential equa- tions
$\underline{v}_j$	-	an intermediate solution required for the jth experiment when the initial conditions are assumed exact
$W$	-	the concentration of water
$W'$	-	the weight of catalyst present in the reactor

- $\underline{w}$  - a solution to the linear systems associated to the maximum operation
- $x_{ijk}$  - the predicted value of the  $i$ th state variable for the  $j$ th experiment for the  $k$ th discrete value of  $t$  for which data are taken
- $\hat{x}_{ijk}$  - the experimental value of  $x_{ijk}$
- $x_{ijk}^*$  - the pseudo-experimental value of  $x_{ijk}$  derived from data perturbation
- $\underline{x}_j$  - the state vector for the  $j$ th experiment
- $\underline{y}$  - the fundamental matrix
- $\underline{y}$  - the state vector which includes the states for all experiments and the parameters
- $y_{ik}$  - the predicted value of the  $i$ th element of  $\underline{y}$  for the  $k$ th discrete value of  $t$  for which data is taken
- $\hat{y}_{ik}$  - the experimental value of  $y_{ik}$
- $y_{ik}^*$  - the pseudo-experimental value of  $y_{ik}$  produced by data perturbation
- $Z$  - objective function
- $\underline{z}$  - dummy vector required for the maximum operation
- $\alpha$  - the order of the reaction
- $\gamma$  - perturbation constant for the initial conditions
- $\underline{\delta}$  - a vector which must be greater than or equal to zero for all  $t$  if the positivity requirement is to be satisfied
- $\underline{\varepsilon}$  - the vector of errors
- $\varepsilon_{ijk}$  - the deviation of  $x_{ijk}$  from  $\hat{x}_{ijk}$

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APPENDIX A

Documentation of the Basic Program and the  
Nonlinear Example

The quasilinearization and data perturbation procedure was programmed in Fortran IV to solve the problem of finding the characteristic parameter vector  $\underline{a}$  of a system described by a system of differential equations of the form:

$$\frac{d\underline{x}}{dt} = \underline{g}(\underline{x}, \underline{a}, t) \quad (A-1)$$

It was assumed that  $n$  different experiments were performed with the known initial conditions  $\underline{x}_j(0)$   $j = 1, 2, \dots, n$  and that some or all of the state variables were measured at several discrete times. Given the model and the data, the parameter vector is found such that the unweighted least squares are minimized.

The Fortran IV program, listed on the following pages, is broken up into a main line and five subroutines. The purpose of each subroutine is stated in the comment cards at its beginning. The main line program reads in the required data and controls the data perturbation stepping procedure. Comment cards in the main line program defined each variable which is read in as data. All



of the subroutines are general, except for the subroutine SLOPE which defines the functions and Jacobians required for the particular problem. The subroutine SLOPE must be supplied. A well documented example is listed with the rest of the program.

The SLOPE subroutine listed is the one required to solve the nonlinear example which was described by the differential equations:

$$\frac{dx_1}{dt} = -a_1(x_1^2 - k_{e1}x_2) - a_2 [x_1 - k_{e2}(1-x_1-x_2)]$$

$$\frac{dx_2}{dt} = a_1(x_1^2 - k_{e1}x_2) - a_3 [x_2 - k_{e3}(1-x_1-x_2)]$$

(A-2)

The input data required by the program may be broken into three blocks. With the first three read statements, the variables which control the program are defined. In the second block the data for each different experiment is read into memory. The third block of data is that which is read on the first entry into the subroutine SLOPE. This third block consists of the extra data required to define the functions and Jacobians for each experiment. In many cases, such as

with this example, the third data block is not needed. A complete description of each variable read from the data cards is given on the comment cards contained in the Fortran IV listing.

The data was obtained for this example by using equation (A-2) with the values of

$$\begin{array}{rcl} a_1 & = & 2.0 \quad k_{e1} = 1.8 \\ a_2 & = & 3.5 \quad k_{e2} = 3.0 \\ a_3 & = & 5.0 \quad k_{e3} = 1.0 \end{array} \quad (\text{A-3})$$

for the parameters and the equilibrium constants. Three different initial conditions were used.

$$\underline{x}_1(0) = \begin{bmatrix} 1 \\ 0 \end{bmatrix} ; \quad \underline{x}_2(0) = \begin{bmatrix} 0 \\ 1 \end{bmatrix} ; \quad \underline{x}_3(0) = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \quad (\text{A-4})$$

The data generated for each of these initial conditions is correct to within  $\pm 0.00005$ . It would, therefore, be expected that the parameters extracted from the data would be almost identical with those given in (A-3). This was verified with the results obtained from the first and third sets of control data cards shown immediately following the program listing and input data.

```

C      THE PURPOSE OF THIS PROGRAM IS TO IDENTIFY CERTAIN
C      UNKNOWN PARAMETERS IN A SYSTEM OF ORDINARY
C      DIFFERENTIAL EQUATIONS, WHICH MODEL A GIVEN
C      PHYSICAL SYSTEM FROM WHICH EXPERIMENTAL DATA HAS
C      BEEN OBTAINED.
C
C      THE PROBLEM IS TREATED AS A NONLINEAR MULTIPOINT
C      BOUNDARY VALUE PROBLEM AND SOLVED USING A
C      COMBINATION OF QUASILINEARIZATION AND BOUNDARY
C      VALUE PERTUBATION.
C
C      REAL UB(10,10),C(11,10),XU(30,10),TC(30,15),XB(30,15,10
1),H,XBAR(30
1,15,10),XB1(30,15,10),RP,RATIO,RMAXI,CO(10),X(10,10),CH
1MAX,
1P(10),T,SUMA,SUMB
      INTEGER NE,NK,RMAX,NDSLL,ICUTM,ICUTI,NO,NPTOT,NP(30),NP
1IJ(30,15),N
1C(30,15),NPITOT(30),KSI(30,15,10),M1,M2,NCJ,J,I,II,JJ,K
1,S,LL
1,LKJM,LKJI,ICHECK,LKJS,RMAXS,ICUTS
      COMMON /AB8/XO,I,NDS/AB3/C,NE,NK,NO/AB4/UB,X,P,H,T,NCJ,
1LL/AB10/TC,
1XB,ERROR,CHMAX,RMAXI,KSI,NPIJ,NC,NP,NPITOT,RMAX,NPTOT,R
1,J,M1,M2,II
1,JJ,S,ICHECK/AB4/LKJM,LKJI/AB6/CO
C
C
C      TO USE THIS PROGRAM THE DIFFERENTIAL EQUATIONS MUST
C      BE NORMALIZED SUCH THAT:
C
C          1 NONE OF THE STATE VARIABLES EXCEEDS 10.
C
C          2 THE INDEPENDENT VARIABLE VARRIES FROM ZERO
C          TO A VALUE NOT EXCEEDING 100, WITH THE INITIAL
C          CONDITION BEING GIVEN AT ZERO.
C
C          3 THE ELEMENTS OF THE PARAMETER VECTOR ARE OF
C          THE SAME APPROXIMATE ORDER OF MAGNITUDE.
C
C
C      THE MAIN LINE PROGAM HAS THE FUNCTIONS OF READING
C      IN THE DATA SETS AND CONTROLLING THE PERTURBED DATA
C      STEPPING PROCEEDURE. THE DATA ARE WRITTEN EXACTLY
C      AS THEY ARE READ. 'BEGIN PHASE I' IS THEN WRITTEN
C      OUT SIGNIFYING THE BEGINING OF THE STEPPING
C      PROCEEDURE. IT IS ALSO WRITTEN OUT EACH TIME THE
C      STEP SIZE IS DECREASED AND THE PROCEEDURE IS

```

C RE-INITIATED. AT THE BEGINING OF EACH STEP THE STEP  
C NO. IS WRITTEN ALONG WITH THE CURRENT ESTIMATES OF  
C THE PARAMETERS AND THE SUM OF THE ERRORS SQUARED.  
C 'BEGIN PHASE II' IS WRITTEN WHEN THE ACTUAL DATA  
C POINTS ARE USED. PHASE II IS TERMINATED WHEN  
C CONVERGENCE IS OBTAINED OR WHEN TEN SUCCESSIVE  
C ITERATIONS HAVE BEEN COMPLETED WITHOUT CONVERGENCE  
C OR WHEN PHASE I HAS BEEN RE-ENTERED BECAUSE OF AN  
C EXCESSIVELY LARGE CHANGE IN THE PARAMETERS IN  
C SUCCESSIVE ITERATIONS. IN THE LATER CASE 'BEGIN  
C PHASE I' IS AGAIN WRITTEN OUT.

C  
C

C AUXILIARY SUBROUTINES REQUIRED ARE:

C

C 1 GENER - USED TO GENERATE THE SOLUTIONS FOR  
C APPROXIMATE PARAMETERS NEEDED FOR THE STEPPING  
C PROCEEDURE AND FOR GENERATING THE FINAL SOLUTION  
C SO THAT THE SUM OF THE ERRORS SQUARED MAY BE  
C CALCULATED.

C

C 2 QUASI - USED TO CONTROL THE QUASILINEARIZATION  
C ITERATIVE PROCEEDURE.

C

C 3 INTE - CALLED FROM QUASI AND USED TO INTEGRATE  
C THE SYSTEMS OF DIFFERENTIAL EQUATIONS ENCOUNTERED  
C WITH THE QUASILINEARIZATION PROCEEDURE.

C

C 4 LEAST - CALLED FROM QUASI AND USED TO DETERMINE  
C THE LEAST SQUARE MATRIX EQUATION WHICH IS SOLVED  
C IN THE GAUSS ELIMINATION SUBROUTINE.

C

C 5 GAUSS - CALLED FROM LEAST AND IS USED AS  
C DESCRIBED ABOVE.

C

C 6 SLOPE - CALLED FROM GENER AND INTE AND IS USED TO  
C EVALUATE THE FUNCTIONS AND JACOBIANS. THIS  
C SUBROUTINE MUST BE SUPPLIED ALONG WITH THE DATA.  
C THE FORMAT OF THIS SUBROUTINE IS EXPLAINED IN THE  
C SAMPLE GIVEN IN THIS LISTING.

C

C

C THE FOLLOWING INTEGERS ARE READ IN ON A 16I5 FORMAT.

C

C NE THE NO. OF STATE VARIABLES. NE<11

C

C NK THE NO. OF PARAMATERS. NK<11

C

C RMAX THE MAXIMUM NO. OF COMPLETE ITERATIONS TO BE  
C MADE AT EACH STEP. RMAX<11

C

```

C
C   NDS  THE NO. OF DATA SETS. NDS<31
C
C   LL   PRINT OUT CONTROL FOR STATE VARIABLE PROFILES;
C        FOR EXAMPLE IF LL=2, THEN EVERY SECOND
C        INTEGRATION STEP IS PRINTED. A * IS PRINTED TO
C        THE LEFT OF EVERY VALUE OF THE INDEPENDENT
C        VARIABLE FOR WHICH DATA ARE GIVEN.
C
C   ICUTM THE MAXIMUM NO. OF STEPS.
C
C   LKJM PRINT SUPPRESSION CONTROL.
C        LKJM=0 PRINTING OF STATE VARIABLE PROFILES IS
C        SUPRESSED.
C        LKJM=K STATE VARIABLE PROFILES ARE PRINTED
C        IN PHASE I AND II FOR EVERY K TH ITERATION.
C        LKJM=-K STATE VARIABLE PROFILES ARE PRINTED
C        FOR EVERY K TH ITERATION IN PHASE II ONLY.
C
C   READ(5,1) NE,NK,RMAX,NDS,LL,ICUTM,LKJM
C   WRITE(6,1) NE,NK,RMAX,NDS,LL,ICUTM,LKJM
C   LKJS=LKJM
C   RMAXS=RMAX
C   ICUTS=ICUTM
C   NO=1
C
C
C   CO   THE INITIAL GUESS FOR THE PARAMETER VECTOR IS
C        READ IN ON A 5E16.6 FORMAT.
C
C   READ(5,11) (CO(II),II=1,NK)
C   WRITE(6,11)(CO(II),II=1,NK)
C
C
C   THE FOLLOWING CONTROL VARIABLES ARE READ IN ON A
C   4E16.6 FORMAT.
C
C   ERROR THE MAXIMUM AMOUNT OF RELATIVE ERROR ALLOWED
C   IN THE DESIRED PARAMETERS.
C
C   RMAXI THE INITIAL STEP SIZE.
C
C   CHMAX THE MAXIMUM ALLOWABLE RELATIVE CHANGE IN THE
C   PARAMETERS FOR ONE ITERATION. IF CHMAX IS
C   EXCEEDED RMAXI IS HALVED AND PHASE I IS
C   RE-INITIATED.
C
C   CHMIN THE MINIMUM ALLOWABLE RELATIVE CHANGE IN THE

```

```

C           PARAMETERS FOR ONE STEP BEFORE RMAXI IS
C           TRIPLED.
C
C
C           READ(5,11) ERRRCR,RMAXI,CHMAX,CHMIN
C           WRITE(6,11)ERROR,RMAXI,CHMAX,CHMIN
11 FORMAT(5E16.6)
C           NPTOT=0
C
C
C           THE DATA FOR EACH EXPERIMENT ARE READ IN
C           SEQUENTIALLY AS GIVEN BELOW. ALL INTEGERS ARE READ
C           IN ON A I6I5 FORMAT AND ALL OTHER DATA ON A 8F10.6
C           FORMAT. THE DATA IS PRINTED OUT EXACTLY AS IT IS
C           READ IN.
C
C           I IS THE INDEPENDENT VARIABLE.
C
C
C           DO 101 I=1,NDS
C
C           XC(I,J) THE INTIAL CONDITION FOR THE J TH STATE
C           VARIABLE FOR THE I TH EXPERIMENT.
C
C           READ(5,2) (XC(I,J),J=1,NE)
C           WRITE(6,2)(XC(I,J),J=1,NE)
C
C           NP(I) THE NO. OF VALUES OF T FOR WHICH DATA ARE
C           GIVEN IN THE I TH EXPERIMENT.
C
C           READ(5,1) NP(I)
C           WRITE(6,1)NP(I)
C           M1=NP(I)
C
C           NPIJ(I,J) THE NO. OF DATA POINTS WHICH ARE GIVEN
C           FOR THE J TH VALUE OF T FOR WHICH DATA ARE
C           GIVEN FOR THE I TH EXPERIMENT.
C
C           READ(5,1) (NPIJ(I,J),J=1,M1)
C           WRITE(6,1)(NPIJ(I,J),J=1,M1)
C
C           TC(I,J) THE VALUE OF THE J TH VALUE OF T FOR WHICH
C           DATA ARE GIVEN FOR THE I TH EXPERIMENT.
C
C           READ(5,2) (TC(I,J),J=1,M1)
C           WRITE(6,2)(TC(I,J),J=1,M1)
C
C           NC(I,J) THE NO. OF INTEGRATION POINTS REQUIRED
C           BETWEEN TC(I,J) AND TC(I-1,J) WITH TC(0,J)
C           BEING TAKEN AS ZERO.

```

```

C
  READ(5,1) (NC(I,J),J=1,M1)
  WRITE(6,1)(NC(I,J),J=1,M1)
  NPITOT(I)=0
  DO 100 J=1,M1
  M2=NP1J(I,J)
  NPITOT(I)=NPITOT(I)+M2
C
C      KSI(I,J,K) THE STATE VARIABLE INDEX OF THE K TH
C      DATA POINT AT TC(I,J).
C
  READ(5,1) (KSI(I,J,K),K=1,M2)
  WRITE(6,1)(KSI(I,J,K),K=1,M2)
C
C      XB1(I,J,K) THE VALUE OF THE K TH DATA POINT AT
C      TC(I,J) WITH THE INDEX KSI(I,J,K).
C
  READ(5,2) (XB1(I,J,K),K=1,M2)
  100 WRITE(6,2)(XB1(I,J,K),K=1,M2)
  101 NPTOT=NPTOT+NPITOT(I)
C
C
C      THE TOTAL NO. OF DATA POINTS IS WRITEN OUT.
C
C
  WRITE(6,22) NPTOT
  22 FORMAT('0THE TOTAL NO. OF DATA POINTS IS ',I5)
  1 FORMAT(16(1X,I4))
  2 FORMAT(8(1X,F9.6))
C
C
C      IF THE TOTAL NO. OF DATA POINTS EXCEEDS 500 THEN
C      THE PROGRAM IS TERMINATED.
C
C
  IF(NPTOT.LE.500) GOTO 120
  WRITE(6,21)
  21 FORMAT('0NO. OF DATA POINTS EXCEEDS 500')
  STOP
C
C
C      PHASE I IS INITIATED.
C
C
  120 ICUTI=0
  114 ICHECK=1
  WRITE(6,18)
  18 FORMAT('0BEGIN PHASE I')
  LKJM=LKJS
  RMAX=RMAXS

```

```

      ICUTM=ICUTS
C
C
C      GENERATE THE SOLUTION FROM THE APPROXIMATE
C      PARAMETERS.
C
C
110 RP=0.0
      DO 107 I=1,NK
107 C(1,I)=CO(I)
      SUMB=0.0
      DO 103 I=1,NDS
          T=0.0
          DO 104 II=1,NE
104 X(1,II)=XO(I,II)
          M1=NP(I)
          DO 103 J=1,M1
              NCJ=NC(I,J)
              H=(TC(I,J)-T)/NCJ
              CALL GENER
              M2=NPIJ(I,J)
              DO 103 K=1,M2
                  S=KSI(I,J,K)
                  XBAR(I,J,K)=X(1,S)
                  SUMA=ABS(XB1(I,J,K)-XBAR(I,J,K))
                  SUMB=SUMB+SUMA**2
103 IF(SUMA.GT.RP) RP=SUMA
          ICUTI=ICUTI+1
C
C
C      START STEP ICUTI AND CHECK TO SEE IF ICUTM HAS BEEN
C      EXCEEDED.
C
C
      WRITE(6,14) ICUTI
14 FORMAT('0',10X,'BEGIN STEP',15)
      WRITE(6,25) (I,CO(I),I=1,NK)
      WRITE(6,19) SUMB
      IF(ICUTI.LT.ICUTM) GOTO 119
      WRITE(6,20)
20 FORMAT('0STEP COUNT EXCEEDED')
      STOP
119 RATIO=1.0-RMAXI/RP
C
C
C      CHECK TO DETERMINE IF PHASE II MAY BE ENTERED.
C
C
      IF(RP.GT.RMAXI) GOTO 111
      WRITE(6,17)

```



```
17 FORMAT('1BEGIN PHASE II')
```

```
RMAX=10
```

```
RATIC=0.0
```

```
LKJM=IABS(LKJM)
```

```
ICUTM=-ICUTM
```

```
C
```

```
C
```

```
C
```

```
DETERMINE PSEUDO DATA SETS.
```

```
C
```

```
C
```

```
111 DO 106 I=1,NCS
```

```
M1=NP(I)
```

```
DO 106 J=1,M1
```

```
M2=NPIJ(I,J)
```

```
DO 106 K=1,M2
```

```
XB(I,J,K)=XB1(I,J,K)+RATIC*(XBAR(I,J,K)-XB1(I,J,K))
```

```
106 CONTINUE
```

```
C
```

```
C
```

```
C
```

```
ENTER QUASILINEARIZATION ITERATIVE PROCEEDURE.
```

```
C
```

```
C
```

```
CALL QUASI
```

```
C
```

```
C
```

```
CHECK FOR PHASE I RE-ENTRY.
```

```
C
```

```
C
```

```
IF(ICHECK.LT.0) GOTO 114
```

```
C
```

```
C
```

```
C
```

```
CHECK FOR PROGRAM COMPLETION.
```

```
C
```

```
C
```

```
IF(ICUTM.LT.0) GOTO 112
```

```
SUMA=0.0
```

```
DO 118 I=1,NK
```

```
118 SUMA=SUMA+ABS((C(1,I)-CO(I))/C(1,I))
```

```
C
```

```
C
```

```
C
```

```
CHECK TO DETERMINE IF STEP SIZE SHOULD BE INCREASED.
```

```
C
```

```
C
```

```
IF(SUMA.LT.CHMIN) RMAXI=3.0*RMAXI
```

```
GOTO 110
```

```
C
```

```
C
```

```
C
```

```
THE FINAL PARAMETERS ARE USED TO DETERMINE THE SUM  
OF THE ERRORS SQUARED AND THE SOLUTION IS WRITTEN.
```

```
C
```

```
C
```

```
C
```

```
112 DO 115 I=1,NK
115 C(1,I)=CC(I)
    SUMB=0.0
    DO 116 I=1,NCS
    T=0.0
    DO 117 II=1,NE
117 X(1,II)=XC(I,II)
    M1=NP(I)
    DO 116 J=1,M1
    NCJ=NC(I,J)
    H=(TC(I,J)-T)/NCJ
    CALL GENER
    M2=NPIJ(I,J)
    DO 116 K=1,M2
    S=KSI(I,J,K)
116 SUMB=SUMB+(XB1(I,J,K)-X(1,S))**2
    IF(ICHECK.EQ.0) WRITE(6,23)
23 FORMAT('CONVERGENCE TO THE DESIRED ACCURACY WAS NOT ',
1OBTAINED AFTER 10 ITERATIONS IN PHASE II')
    WRITE(6,24)
24 FORMAT('THE FINAL SOLUTION OBTAINED')
    WRITE(6,25) (I,CO(I),I=1,NK)
25 FORMAT('O      K',I2,' =',E16.6)
    WRITE(6,19) SUMB
19 FORMAT('O',9X,'THE SUM OF THE SQUARES OF THE ERRORS IS'
1,E14.4)
16 FORMAT('O AFTER',I5,' STEPS')
    STOP
    END
```

```

SUBROUTINE QUASI
  INTEGER KSI(30,15,10),NPIJ(30,15),NC(30,15),NP(30),NPIT
  1CT(30),NE,
  1NK,RMAX,NDS,NPTOT,R,I,J,M1,M2,INDEX,ICOUNT,II,JJ,S,LL,N
  1C
  1,LKJM,LKJI,ICHECK
  REAL UB(10,10),X(10,10),P(10),TC(30,15),XO(30,10),XB(30
  1,15,10),T,H
  1,C(11,10),CR(10)
  REAL*8 B(500,10),Q(500)
  COMMON /AB6/CR/AB1/B,Q /AB8/XO,I,NDS/AB3/C,NE,NK,NO/AB4
  1/UB,X,P,H,
  1T,NCJ,LL/AB10/TC,XB,ERROR,CHMAX,RMAXI,KSI,NPIJ,NC,NP,NP
  1ITOT,RMAX,
  1NPTOT,R,J,M1,M2,II,JJ,S,ICHECK/AB4/LKJM,LKJI
C
C
C   THE PURPOSE OF THIS SUBROUTINE IS TO CONTROL THE
C   QUASILINEARIZATION ITERATIVE PROCEEDURE.
C
C
  LKJI=0
  DO 103 R=1,RMAX
  LKJI=LKJI+1
  INDEX=0
  DO 104 I=1,NDS
  S=R-1
  1F(LKJI.NE.LKJM) GOTO 113
  WRITE(6,5) S,I,NPITOT(I)
  DO 112 II=1,NE
112 WRITE(6,6) II,XO(I,II)
  WRITE(6,8) (C(R,II),II=1,NK)
  WRITE(6,7)
  5 FORMAT(15H1FGR ITERATION ,I4,11H DATA SET ,I4,' WITH '
  1,I4,' POINTS '/O THE INITIAL CONDITION IS'/)
  6 FORMAT(10X,1HX,I2,2H =,F10.6)
  71FORMAT(1H0,14X,1HT,8X,2HX1,8X,2HX2,8X,2HX3,8X,2HX4,8X,
  12HX5,8X,2HX6,8X,2HX7,8X,2HX8,8X,2HX9,8X,3HX10/)
  8 FORMAT(19H0THE CONSTANTS ARE /10X,8E16.6)
C
C
C   THE INITIAL CONDITIONS FOR THE I TH DATA SET ARE
C   INITIALIZED AND T IS SET TO ZERO.
C
C
113 T=0.0
  DO 105 II=1,NE
  DO 106 JJ=1,NK
106 UB(II,JJ)=0.0
  DO 107 JJ=1,R

```

```

107 X(JJ,II)=XO(I,II)
105 P(II)=XO(I,II)
      M1=NP(I)
      DO 104 J=1,M1
      NCJ=NC(I,J)
      H=(TC(I,J)-T)/FLOAT(NCJ)

```

```

C
C
C
C
C
C

```

THE SUBROUTINE INTE IS CALLED TO INTEGRATE THE MATRIX DIFFERENTIAL EQUATIONS FROM T TO TC(I,J), UPON RETURN T=TC(I,J).

```

      CALL INTE(R)
      IF(LKJI.NE.LKJM) GOTO 114
      WRITE(6,9) T,(X(R,II),II=1,NE)
9  FORMAT(7X,1H*,10F10.6)

```

```

C
C
C
C
C
C

```

SET UP THE LINEAR EQUATIONS AND CALL SUBROUTINE LEAST TO DETERMINE THE IMPROVED ESTIMATE OF THE PARAMETER VECTOR.

```

114 M2=NPIJ(I,J)
      DO 110 K=1,M2
      ICOUNT=K+INDEX
      S=KSI(I,J,K)
      Q(ICOUNT)=XB(I,J,K)-P(S)
      DO 110 JJ=1,NK
110 B(ICOUNT,JJ)=UB(S,JJ)
104 INDEX=INDEX+M2
      IF(LKJM.EQ.LKJI) LKJI=0
      CALL LEAST(NK,NPTOT)
      SUMA=0.0
      DO 108 II=1,NK
      SUMA=SUMA+ABS(C(R,II)-CR(II))/(ABS(C(R,II))+0.1)
108 C(R+1,II)=CR(II)
      IF(SUMA.GT.CHMAX) GOTO 116
      IF(SUMA.LT.ERROR) GOTO 115
      IF(R.EQ.10) ICHECK=0
      IF(R.EQ.10) GOTO 118
103 CONTINUE

```

```

C
C
C
C
C
C

```

THE PARAMETERS ARE WRITTEN OUT AT THE END OF THE STEP IF RMAX IS EXCEEDED. THIS OCCURS WHEN THE ERROR SPECIFICATION IS NOT MET IN RMAX ITERATIONS. THIS IS NOT TOO CRITICAL IN MOST CASES AS ACCURATE SOLUTIONS TO EACH STEP ARE NOT NECESSARY.

C  
C

```
R=RMAX+1
WRITE(6,10) RMAX
WRITE(6,8) (C(R,II),II=1,NK)
10 FORMAT(7H0AFTER ,15,12H ITERATIONS)
115 RETURN
116 RMAXI=RMAXI*0.5
DO 117 II=1,NK
117 CR(II)=C(1,II)
ICHECK=-1
118 RETURN
END
```

```

SUBROUTINE GENER
REAL UB(10,10),P(10),X(10,10),XA(10,10),KP(4,10),G(10),
1I,IA,H
1,JX(10,10),JK(10,10),C(11,10)
INTEGER NCJ,NE,NK,LL,NO,N,II,I
COMMON /AB3/C,NE,NK,NO/AB4/UB,X,P,H,T,NCJ,LL/AB5/JX,JK,
1XA,G
C
C
C   THE PURPOSE OF THIS SUBROUTINE IS TO GENERATE THE
C   SOLUTION OF THE SYSTEM OF DIFFERENTIAL EQUATIONS
C   GIVEN A SET OF PARAMETERS. THE 4 TH ORDER RUNGE
C   KUTTA PROCEEDURE IS USED.
C
C
DO 100 N=1,NCJ
DO 101 II=1,4
GOTO(102,103,104,105),II
102 TA=T
DO 106 I=1,NE
106 XA(1,I)=X(1,I)
GOTO 107
103 TA=T+0.5*H
DO 108 I=1,NE
108 XA(1,I)=X(1,I)+0.5*KP(1,I)
GOTO 107
104 DO 109 I=1,NE
109 XA(1,I)=X(1,I)+0.5*KP(2,I)
GOTO 107
105 TA=T+H
DO 110 I=1,NE
110 XA(1,I)=X(1,I)+KP(3,I)
107 CALL SLOPE(1,TA,-1)
DO 101 I=1,NE
101 KP(II,I)=H*G(I)
T=TA
DO 100 I=1,NE
100 X(1,I)=X(1,I)+(KP(1,I)+2.0*(KP(2,I)+KP(3,I))+KP(4,I))/6
1.0
RETURN
END

```

```

SUBROUTINE INTE(R)
REAL UB(10,10),P(10),X(10,10),UBA(10,10),PA(10),XA(10,1
10),KX(4,10,
110),KUB(4,10,10),KP(4,10),G(10),T,TA,H,SUMA,SUMB,JX(10,
110),
1JK(10,10),C(11,10)
INTEGER NCJ,R,I,J,II,NE,NK,L,LL,S,N,NO,LKJM,LKJI
COMMON /AB3/C,NE,NK,NO/AB4/UB,X,P,H,T,NCJ,LL/AB5/JX,JK,
1XA,G
1/AB4/LKJM,LKJI

```

C  
C  
C  
C  
C  
C  
C  
C  
C  
C  
C  
C  
C

```

THE PURPOSE OF THIS SUBROUTINE IS TO GENERATE THE
SOLUTION OF THE SYSTEMS OF MATRIX DIFFERENTIAL
EQUATIONS REQUIRED FOR THE SOLUTION OF THE LINEAR
BOUNDARY VALUE PROBLEMS ENCOUNTERED IN EACH
ITERATION OF THE QUASILINEARIZATION PROCEEDURE. THE
INITIAL GUESS IS ALSO GENERATED. THE 4 TH ORDER
RUNGE KUTTA PROCEEDURE IS USED.

```

```

L=0
DO 100 N=1,NCJ
DO 101 II=1,4
GOTC(102,103,104,105),II
102 TA=T
DO 109 I=1,NE
PA(I)=P(I)
DO 108 J=1,R
108 XA(J,I)=X(J,I)
DO 109 J=1,NK
109 UBA(I,J)=UB(I,J)
GOTC 110
103 TA=T+0.5*H
DO 113 I=1,NE
PA(I)=P(I)+0.5*KP(1,I)
DO 112 J=1,R
112 XA(J,I)=X(J,I)+0.5*KX(1,J,I)
DO 113 J=1,NK
113 UBA(I,J)=UB(I,J)+0.5*KUB(1,I,J)
GOTC 110
104 DO 114 I=1,NE
PA(I)=P(I)+0.5*KP(2,I)
DO 116 J=1,R
116 XA(J,I)=X(J,I)+0.5*KX(2,J,I)
DO 114 J=1,NK
114 UBA(I,J)=UB(I,J)+0.5*KUB(2,I,J)
GOTC 110
105 TA=T+H
DO 117 I=1,NE

```

```

      PA(I)=P(I)+KP(3,I)
      DO 119 J=1,R
119  XA(J,I)=X(J,I)+KX(3,J,I)
      DO 117 J=1,NK
117  UBA(I,J)=UB(I,J)+KUB(3,I,J)
110  CALL SLOPE(R,TA,1)
      IF(R.NE.1) GOTO 118
      DO 115 I=1,NE
      SUMA=G(I)
115  KX(II,1,I)=H*SUMA
118  DO 120 I=1,NE
      SUMA=G(I)
      DO 121 J=1,NK
      SUMB=JK(I,J)
      SUMA=SUMA-JK(I,J)*C(R,J)
      DO 122 S=1,NE
122  SUMB=SUMB+JX(I,S)*UBA(S,J)
121  KUB(II,I,J)=H*SUMB
      DO 130 J=1,NE
130  SUMA=SUMA+JX(I,J)*(PA(J)-XA(R,J))
120  KP(II,I)=H*SUMA
      IF(R.EQ.1) GOTO 101
      DO 124 S=2,R
      CALL SLOPE(S-1,TA,1)
      IF(S.NE.2) GOTO 107
      DO 111 I=1,NE
      SUMA=G(I)
      KX(II,1,I)=H*SUMA
111  CONTINUE
107  DO 124 I=1,NE
      SUMA=G(I)
      DO 125 J=1,NE
125  SUMA=SUMA+JX(I,J)*(XA(S,J)-XA(S-1,J))
      DO 126 J=1,NK
126  SUMA=SUMA+JK(I,J)*(C(S,J)-C(S-1,J))
124  KX(II,S,I)=H*SUMA
101  CONTINUE
      DO 127 I=1,NE
      P(I)=P(I)+(KP(1,I)+2.0*(KP(2,I)+KP(3,I))+KP(4,I))/6.0
      DO 127 J=1,NK
      UB(I,J)=UB(I,J)+(KUB(1,I,J)+2.0*(KUB(2,I,J)+KUB(3,I,J))
1+KUB(4,I,J)
1)/6.0

```

C  
C  
C  
C  
C  
C

CHECK TO DETERMINE IF THE FUNDAMENTAL MATRIX IS  
BOUNDED, IF NOT EXECUTION IS TERMINATED. IF THERE  
IS A FAILURE AT THIS POINT, IT IS LIKELY THAT THE  
INTEGRATION PROCEEDURE IS UNSTABLE FOR THIS SYSTEM  
WITH THE GIVEN NO. OF INTEGRATION POINTS NC(I,J)



```
C      AND WITH THE CURRENT ESTIMENT OF THE PARAMETER
C      VECTOR.
C
C      IF (ABS(UB(I,J)).LT.1.0E 50) GOTO 127
      WRITE(6,2)
      2 FORMAT('OTHE INTEGRATION OF THE FUNDAMENTAL MATRIX IS',
      1 ' UNBOUNDED')
      STOP
      127 CONTINUE
      DO 129 S=1,R
      DO 129 I=1,NE
      129 X(S,I)=X(S,I)+(KX(1,S,I)+2.0*(KX(2,S,I)+KX(3,S,I))+KX(4
      1,S,I))/6.0
      T=TA
      L=L+1
      IF(L.NE.LL) GOTO 100
      L=0
      IF(LKJ1.NE.LKJM)GCTO 100
      IF(N.EQ.NCJ) GOTO 100
      WRITE(6,1) T,(X(R,I),I=1,NE)
      1 FORMAT(8X,10F10.6)
      100 CONTINUE
      RETURN
      END
```

```

SUBROUTINE GAUSS(N)
INTEGER II(10),I,J,K,N,L,M,H,MM,T
REAL*8 A(10,10),R(10),X(10),S,U
REAL XX(10)
COMMON /AB2/A,R/AB6/XX

```

```

C
C
C   THE PURPOSE OF THIS SUBROUTINE IS TO SOLVE THE
C   SYSTEM OF LINEAR ALGEBRAIC EQUATIONS ASSOCIATED
C   WITH THE LINEAR LEAST SQUARES PROBLEM.  THE GAUSS
C   ELIMINATION PROCEEDURE IS USED WITH THE PIVOT
C   ELEMENT BEING THE LARGEST IN THE UNREDUCED PART
C   OF THE MATRIX.
C
C

```

```

C
      M=N-1
      DO 10 I=1,N
10    II(I)=I
      DO 11 J=1,M
      S=0.0
      DO 12 I=J,N
      DO 12 K=J,N
      U=DABS(A(I,J))
      IF(U.LE.S) GOTO 12
      S=U
      L=I
      T=K
12    CONTINUE
      IF(L.EQ.J) GOTO 19
      DO 14 I=J,N
      S=A(L,I)
      A(L,I)=A(J,I)
14    A(J,I)=S
      S=R(L)
      R(L)=R(J)
      R(J)=S
19    IF(K.EQ.J) GOTO 13
      DO 20 I=J,N
      S=A(I,T)
      A(I,T)=A(I,J)
20    A(I,J)=S
      I=II(T)
      II(T)=II(J)
      II(J)=I
13    IF(DABS(A(J,J)).GT.1.00-35) GOTO 15
      IF(J.EQ.1) GOTO 15
      WRITE(6,3)
      STOP
15    MM=J+1
      DO 11 I=MM,N

```

```
IF(DABS(A(I,J)).LT.1.0D-35) GOTO 11
S=A(J,J)/A(I,J)
A(I,J)=0.0
DO 16 K=MM,N
16 A(I,K)=A(J,K)-S*A(I,K)
R(I)=R(J)-S*R(I)
11 CONTINUE
DO 17 K=1,N
I=N+1-K
S=0.0
IF(I.EQ.N) GOTO 17
MM=I+1
DO 18 J=MM,N
18 S=S+A(I,J)*X(J)
17 X(I)=(R(I)-S)/A(I,I)
DO 21 I=1,N
K=II(I)
IF(I.EQ.K) GOTO 21
S=X(K)
X(K)=X(I)
X(I)=S
II(I)=II(K)
II(K)=K
21 CONTINUE
DO 23 I=1,N
23 XX(I)=X(I)
3 FORMAT(16HJMATRIX SINGULAR)
RETURN
END
```

```
SUBROUTINE LEAST(N,M)
INTEGER I,J,N,M,S
REAL*8 A(500,10),B(10,10),R(500),C(10),SLMA,SUMB
REAL X(10)
COMMON /AB2/B,C/AB6/X/AB1/A,R
```

```
C
C
C
C
C
C
C
```

```
THE PURPOSE OF THIS SUBROUTINE IS TO REDUCE THE
LEAST SQUARE PROBLEM TO A SYSTEM OF LINEAR
ALGEBRAIC EQUATIONS.
```

```
IF(M.GT.N) GOTO 14
IF(M.EQ.N)GOTO 17
WRITE(6,2)
2 FORMAT(18HJINSUFFICIENT DATA)
STOP
17 DO 15 I=1,N
C(I)=R(I)
DO 15 J=1,N
15 B(I,J)=A(I,J)
GOTO 16
14 DO 10 I=1,N
DO 12 J=I,N
SUMA=0.0
DO 11 S=1,M
11 SUMA=SUMA+A(S,I)*A(S,J)
B(I,J)=SUMA
12 B(J,I)=SUMA
SUMA=0.0
DO 13 S=1,M
13 SUMA=SUMA+A(S,I)*R(S)
10 C(I)=SUMA
16 CALL GAUSS(N)
RETURN
END
```



C THE I TH ELEMENT OF THE STATE VECTOR IS TRANSFERED  
C THROUGH X(R,1) AS SHOWN BELOW.

C  
C

X1=X(R,1)  
X2=X(R,2)

C  
C

C THE I TH ELEMENT OF THE PARAMETER VECTOR IS  
C TRANSFERED THROUGH C(R,I) AS SHOWN BELOW.

C  
C

K1=C(R,1)  
K2=C(R,2)  
K3=C(R,3)

C  
C

C THE STATEMENTS 11 UP TO 12 INCLUDE ALL OPERATIONS  
C THAT ARE TO BE EXECUTED ONLY ONCE ON THE FIRST  
C CALLING OF THIS SUBROUTINE SUCH AS: INITIALIZING  
C CONSTANTS AND VARIABLES AND READING IN DATA.

C  
C

C IF DATA IS TO BE READ IT IS PLACED IMMEDIATELY  
C AFTER THE DATA READ IN THE MAIN LINE PROGRAM.

C  
C

GOTC(11,12),NC  
11 DO 13 I=1,NE  
G(1)=0.0  
DO 14 J=1,NE  
14 JX(I,J)=C.0  
DO 13 J=1,NK  
13 JK(I,J)=0.0  
NO=2  
KE1=1.8  
KE2=3.0  
KE3=1.0

C  
C

C THE FUNCTIONS ARE EVALUATED IN THE FOLLOWING  
C STATEMENTS BEGINING WITH STATEMENT 12.

C  
C

12 G(1)=-K1\*(X1\*\*2-KE1\*X2)-K2\*(X1-KE2\*(1.0-X1-X2))  
G(2)=K1\*(X1\*\*2-KE1\*X2)-K3\*(X2-KE3\*(1.0-X1-X2))

C  
C

C IF THIS SUBROUTINE HAS BEEN CALLED FROM GENER, THE  
C FOLLOWING IF STATEMENT WILL CAUSE A RETURN.

C  
C

```
C      IF THIS SUBROUTINE HAS BEEN CALLED FROM INTE, THE
C      JACOBIANS JX AND JK WILL BE EVALUATED IN THE
C      STATEMENTS FOLLOWING THE IF STATEMENT BEFORE A
C      RETURN IS MADE.
C
```

```
      IF(IJACK.LT.0) GOTO 15
      JX(1,1)=-2.0*K1*X1-K2-K2*KE2
      JX(1,2)=K1*KE1-K2*KE2
      JX(2,1)=2.0*K1*X1-K3*KE3
      JX(2,2)=-K1*KE1-K3*KE3-K3
      JK(1,1)=- (X1**2-KE1*X2)
      JK(1,2)=- (X1-KE2*(1.0-X1-X2))
      JK(2,1)=X1**2-KE1*X2
      JK(2,3)=- (X2-KE3*(1.0-X1-X2))
15 RETURN
END
```





0.320500

2

0.252000

2

0.222400

1

0.554000

2

0.265100

1

0.598300

2

0.201400

1

0.559700

2

0.200300

1

0.555900

2

0.000000

0.000000

5

0.180000

36

28

28

0.320000

2

0.460000

28

0.000000

24

0.720000

0.571000

1

0.203400

2

0.556000

1

0.202000

2

0.559300

1

0.200500

2

0.559800

1

0.200200

2

0.600000

1

0.200000

2

WITH THE FIRST SET OF CONTROL DATA CARDS, THE INITIAL GUESS FOR EACH OF THE ELEMENTS IN THE PARAMETER VECTOR IS C.000001. THE CONTROL VARIABLES ON THE THIRD CARD WERE CHOSEN SO THAT THE QUASILINEARIZATION PROCEDURE WOULD BE USED DIRECTLY.

2 3 3 4 10 -1  
0.100000E-06 0.100000E-06 0.100000E-06  
0.500000E-03 0.100000E 01 0.150000E 03 0.500000E 00

THE ABOVE CONTROL DATA CARDS PRODUCED A CONVERGENT SEQUENCE.

THE SECOND SET OF CONTROL DATA CARDS IS THE SAME AS THE FIRST EXCEPT THAT THE INITIAL GUESS FOR EACH OF THE ELEMENTS IN THE PARAMETER VECTOR IS CHANGED TO 10.0.

2 3 3 4 10 -1  
0.100000E 02 0.100000E 02 0.100000E 02  
0.500000E-03 0.100000E 01 0.150000E 03 0.500000E 00

THE ABOVE CONTROL DATA CARDS DID NOT PRODUCE A CONVERGENT SEQUENCE.

WITH THE THIRD SET OF CONTROL DATA CARDS THE INITIAL GUESS WAS THE SAME AS WITH THE SECOND BUT THE CONTROL VARIABLES ON THE THIRD CARD WERE CHANGED TO MAKE USE OF THE DATA PERTURBATION FACILITY.

2 3 3 4 10 -1  
0.100000E 02 0.100000E 02 0.100000E 02  
0.500000E-03 0.100000E 01 0.150000E 03 0.500000E 00

THESE CONTROL DATA CARDS PRODUCED A CONVERGENT SEQUENCE.

APPENDIX B

The 1-Butene Problem

For Example Two, exact data was generated from the model

$$\frac{dx_1}{dt} = -a_1(x_1 - k_{e1}x_2) - a_2 \left[ \bar{a}_1 - k_{e2}(1-x_1-x_2) \right]$$

$$\frac{dx_2}{dt} = a_1(x_1 - k_{e1}x_2) - a_3 \left[ x_2 - k_{e3}(1-x_1-x_2) \right]$$

(B-1)

A normally distributed error was then obtained from a random number generator. Then each exact data point was perturbed by setting

$$\hat{x}_{ijk} = x_{ijk} (1 + \sigma \epsilon_{ijk})$$

$$i = 1, 2 \dots j = 1, 2 \dots k = 1, 2 \dots$$

with  $\hat{x}_{ijk}$  representing an experimental observation of  $x_{ijk}$  which is the actual value of the  $i$ th state variable for the  $j$ th experiment at the  $k$ th discrete value of time. The relative error  $\sigma \epsilon_{ijk}$  for this point has a standard deviation of  $\sigma$ . Three values of  $\sigma$  (0.1, 0.01, 0.001) were used to perturbate the data generated from equation B-1

with the parameters and equilibrium constants listed below

$$\begin{aligned} a_1 &= 10.344 & k_{e1} &= 0.4469 \\ a_2 &= 3.724 & k_{e2} &= 0.2685 \\ a_3 &= 5.616 & k_{e3} &= 0.6002 \end{aligned} \quad (B-3)$$

and the initial conditions as given in Table B-1.

TABLE B-1

Initial Conditions for Example Two

Experiment Number	$x_1(0)$	$x_2(0)$
1	1.0000	0.0000
2	0.0000	1.0000
3	0.0000	0.0000
4	0.2400	0.7600
5	0.3492	0.6508
6	0.0000	0.4937
7	0.4130	0.0000

Several different attempts were made to determine the parameter vector from the data. Different combinations of experiments were used to test the sensitivity of the method to the choice of experiment as well as to experimental error. The results of these attempts are presented in the following tables. Each attempt was made

with the initial guess of

$$\underline{a}^{(0)} = \begin{bmatrix} 1.0 \\ 1.0 \\ 1.0 \end{bmatrix} \quad (\text{B-4})$$

for the parameter vector. This guess was sufficiently close to the answer to use quasilinearization directly.

Tables B-2, B-3, and B-4 contain the convergent sequences of parameters when all the seven experiments are included.

TABLE B-2

1-Butene Problem

All Seven Data Sets  $\sigma = 0.1$

Iteration	$a_1$	$a_2$	$a_3$
0	1.000	1.000	1.000
1	2.389	2.417	2.523
2	5.820	3.727	4.449
3	9.937	3.790	5.380
4	10.845	3.662	5.512
5	10.943	3.616	5.540
6	10.929	3.619	5.540
7	10.930	3.619	5.540

TABLE B-3

1-Butene Problem

All Seven Data Sets  $\sigma = 0.01$

Iteration	$a_1$	$a_2$	$a_3$
0	1.000	1.000	1.000
1	2.383	2.448	2.546
2	5.584	3.885	4.532
3	0.409	3.885	5.482
4	10.381	3.721	5.605
5	10.404	3.713	5.609
6	10.404	3.713	5.609

TABLE B-4

1-Butene Problem

All Seven Data Sets  $\sigma = 0.001$

Iteration	$a_1$	$a_2$	$a_3$
0	1.000	1.000	1.000
1	2.383	2.451	2.549
2	t.t60	3.901	4.541
3	0.357	3.894	5.491
4	10.331	3.728	5.613
5	10.350	3.722	5.615

In the following three tables, the results of using the data given in the two eigenvector directions are presented. Experiments five and six are in the two respective eigenvector directions.

TABLE B-5

1-Butene Problem

Data Sets Five and Six  $\sigma = 0.1$

Iteration	$a_1$	$a_2$	$a_3$
0	1.000	1.000	1.000
1	2.608	2.407	2.515
2	6.801	3.515	4.424
3	10.751	2.948	5.615
4	12.464	2.293	6.088
5	12.111	2.225	6.135
6	12.247	2.242	6.146
7	12.222	2.242	6.146
8	12.223	2.242	6.146
9	12.223	2.242	6.146

TABLE B-6

1-Butene Problem  
Data Sets Five and Six  $\sigma = 0.01$ .

Iterations	$a_1$	$a_2$	$a_3$
0	1.000	1.000	1.000
1	2.407	2.434	2.547
2	5.682	3.844	4.537
3	9.540	3.789	5.523
4	10.504	3.598	5.653
5	10.513	3.588	5.658
6	10.513	3.588	5.658

TABLE B-7

1-Butene Problem  
Data Sets Five and Six  $\sigma = 0.001$

Iteration	$a_1$	$a_2$	$a_3$
0	1.000	1.000	1.000
1	2.387	2.436	2.550
2	5.567	3.877	4.548
3	0.362	3.877	5.510
4	10.343	3.714	5.618
5	10.361	3.710	5.620

Using the data from the first experiment, the results in Tables B-8, B-9, and B-10 were obtained.



TABLE B-8

1-Butene Problem

Data Set One  $\sigma = 0.1$

Iteration	$a_1$	$a_2$	$a_3$
0	1.000	1.000	1.000
1	4.670	0.198	34.811
2	12.749	-1.617	23.507
3	5.855	7.626	-2.158
4	9.454	5.182	3.252
5	8.796	5.725	1.782
6	9.744	4.806	3.515
7	9.361	5.173	2.815
8	9.673	4.887	3.337
9	9.519	5.028	3.074
10	9.615	4.941	3.235

complete convergence not obtained

TABLE B-9

1-Butene Problem

Data Set One  $\sigma = 0.01$

Iteration	$a_1$	$a_2$	$a_3$
0	1.000	1.000	1.000
1	4.321	5.667	30.005
2	12.267	-1.394	24.771
3	0.281	4.514	2.203
4	10.275	3.873	5.511
5	10.177	3.923	5.203
6	10.167	3.932	5.188
7	10.167	3.932	4.189

TABLE B-10

1-Butene Problem

Data Set One  $\sigma = 0.001$

Iteration	$a_1$	$a_2$	$a_3$
0	1.000	1.000	1.000
1	4.287	0.604	29.525
2	12.224	-1.376	24.913
3	9.784	4.061	3.017
4	10.453	3.659	5.894
5	10.325	3.745	5.570
6	10.324	3.746	5.569

For data from the second experiment the results in Tables B-11, B-12, and B-13 were obtained.

TABLE B-11

1-Butene Problem

Data Set Two  $\sigma = 0.01$

Iteration	$a_1$	$a_2$	$a_3$
0	1.000	1.000	1.000
1	4.403	31.596	1.686
2	15.161	31.968	1.825
3	7.605	8.436	6.205
4	11.859	10.018	5.230
5	14.661	14.493	4.516
6	18.369	21.451	3.464
7	28.487	38.500	0.678
8	775.187	1092.55	-193.895

The integration of fundamental matrix became unstable and a solution was not obtained.

TABLE B-12

1-Butene Problem

Data Set Two  $\sigma = 0.001$

Iteration	$a_1$	$a_2$	$a_3$
0	1.000	1.000	1.000
1	4.614	32.859	1.622
2	11.088	23.740	3.063
3	0.733	-0.267	5.722
4	10.404	4.016	5.600
5	10.355	3.758	5.614
6	10.355	3.758	5.614

Attempts were also made to identify the parameters from experiment three, from experiment five, and from experiment six. All three of these attempts were complete failures. The results diverged and were out of bound within a few iterations.

To test the sensitivity of the method to error in the initial conditions, perturbations were introduced into the initial conditions for experiments one, two and three. Attempts were then made to determine the parameters using the first three data sets with standard deviations of 0.001 and 0.1.

First with the exact initial conditions of

$$a_1(0) = \begin{bmatrix} 1.0 \\ 0.0 \end{bmatrix}; \quad x_2(0) = \begin{bmatrix} 0.0 \\ 1.0 \end{bmatrix}; \quad x_3(0) = \begin{bmatrix} 0.0 \\ 0.0 \end{bmatrix} \quad (\text{B-5})$$

the solutions

$$\underline{a} = \begin{bmatrix} 10.346 \\ 3.727 \\ 5.631 \end{bmatrix} \quad (\text{B-6})$$

and

$$\underline{a} = \begin{bmatrix} 10.638 \\ 3.930 \\ 5.471 \end{bmatrix} \quad (\text{B-7})$$

were found for standard deviations of 0.001 and 0.1 respectively.

Perturbating the initial condition to

$$\underline{x}_1(0) = \begin{bmatrix} 0.99 \\ 0.01 \end{bmatrix}; \quad \underline{x}_2(0) = \begin{bmatrix} 0.01 \\ 0.99 \end{bmatrix}; \quad \underline{x}_3(0) = \begin{bmatrix} 0.01 \\ 0.01 \end{bmatrix}$$

(B-8)

produced the results

$$\underline{a} = \begin{bmatrix} 10.177 \\ 3.724 \\ 5.545 \end{bmatrix} \quad (B-9)$$

and

$$\underline{a} = \begin{bmatrix} 10.479 \\ 3.921 \\ 5.389 \end{bmatrix} \quad (B-10)$$

respectively for the two standard deviations of 0.001 and 0.1.

With the initial conditions perturbed to

$$\underline{x}_1(0) = \begin{bmatrix} 0.9 \\ 1.0 \end{bmatrix}; \quad \underline{x}_2(0) = \begin{bmatrix} 0.1 \\ 0.9 \end{bmatrix}; \quad \underline{x}_3(0) = \begin{bmatrix} 0.1 \\ 0.1 \end{bmatrix} \quad (B-11)$$

the results for the standard deviation of 0.001 were

$$\underline{a} = \begin{bmatrix} 8.487 \\ 3.968 \\ 4.876 \end{bmatrix} \quad (B-12)$$

and for the standard deviation of 0.1 they were

$$\underline{a} = \begin{bmatrix} 8.866 \\ 4.143 \\ 4.759 \end{bmatrix} \quad (\text{B-13})$$

The input data which was used to produce the results in Tables B-2, B-3, and B-4 is presented immediately following the Fortran IV listing of the SLOPE subroutine required for this problem. The input data used for the other results can be formed by deleting the data sets for the appropriate experiments.

```

SUBROUTINE SLCPE(R,T,IJACK)
C      SLOPE SUBROUTINE FOR THE 1-BUTENE PROBLEM
REAL X(10,10),JX(10,10),JK(10,10),G(10),T,C(11,10),XD(3
10,10)
INTEGER R,NE,NK,NO,II,NDS,IJACK
COMMON /AB3/C,NE,NK,NO/AB5/JX,JK,X,G/AB8/XD,II,NDS
REAL X1,X2,K1,K2,K3,KE1,KE2,KE3
INTEGER I,J
DO 16 I=1,NE
IF(ABS(X(R,I)).LE.10.0) GOTO 16
WRITE(6,17)
STOP
16 CONTINUE
17 FORMAT('O STATE VARIABLE BOUND EXCEEDED')
X1=X(R,1)
X2=X(R,2)
K1=C(R,1)
K2=C(R,2)
K3=C(R,3)
GOTO(11,12),NO
11 DO 13 I=1,NE
G(I)=0.0
DO 14 J=1,NE
14 JX(I,J)=C.0
DO 13 J=1,NK
13 JK(I,J)=C.0
NO=2
KE1=0.4469
KE2=0.2685
KE3=0.6002
12 G(1)=-K1*(X1-KE1*X2)-K2*(X1-KE2*(1.0-X2-X1))
G(2)=K1*(X1-KE1*X2)-K3*(X2-KE3*(1.0-X2-X1))
IF(IJACK.LT.0) GOTO 15
JX(1,1)=-K1-K2-KE2*K2
JX(1,2)=K1*KE1-K2*KE2
JX(2,1)=K1-K3*KE3
JX(2,2)=-K1*KE1-K3-K3*KE3
JK(1,1)=-X1+KE1*X2
JK(1,2)=-X1+KE2*(1.0-X2-X1)
JK(2,1)=X1-KE1*X2
JK(2,3)=-X2+KE3*(1.0-X2-X1)
15 RETURN
END

```

THE SEVEN DATA SETS FOR THE 1-BUTENE PROBLEM WITH A STANDARD  
 DEVIATION OF 0.100 ARE LISTED BELOW.

2	3	3	7	1	2	-1			
0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 02	0.100000E 02			
0.500000E-04	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 02	0.500000E-01				
1.000000	0.000000								
10									
2	2	2	2	2	2	2	2	2	2
0.050000	0.100000	0.150000	0.200000	0.250000	0.300000	0.350000	0.400000		
0.450000	0.500000								
5	5	5	5	5	5	5	5	5	5
1	2								
0.507118	0.260621								
1	2								
0.313926	0.351547								
1	2								
0.228383	0.387955								
1	2								
0.173996	0.420883								
1	2								
0.181994	0.417436								
1	2								
0.188465	0.341238								
1	2								
0.160618	0.305402								
1	2								
0.165400	0.328010								
1	2								
0.186677	0.330466								
1	2								
0.133576	0.274951								
0.000000	1.000000								
10									
2	2	2	2	2	2	2	2	2	2
0.050000	0.100000	0.150000	0.200000	0.250000	0.300000	0.350000	0.400000		
0.450000	0.500000								



5	5	5	5	5	5	5	5	5	5	5
1	2									
0.155366	0.627946									
1	2									
0.137741	0.559183									
1	2									
0.173343	0.339282									
1	2									
0.159357	0.369584									
1	2									
0.137372	0.329324									
1	2									
0.156581	0.311299									
1	2									
0.123356	0.384320									
1	2									
0.148975	0.363200									
1	2									
0.138390	0.348492									
1	2									
0.144595	0.313914									
0.000000	0.000000									
10										
2	2	2	2	2	2	2	2	2	2	2
0.050000	0.100000	0.150000	0.200000	0.250000	0.300000	0.350000	0.400000			
0.450000	0.500000									
5	5	5	5	5	5	5	5	5	5	5
1	2									
0.054789	0.138555									
1	2									
0.081386	0.204061									
1	2									
0.089425	0.257753									
1	2									
0.133569	0.234877									
1	2									







Leaf B 19 omitted in page numbering.

0.119677 0.257658  
1 2  
0.143333 0.325099  
1 2  
0.144715 0.307242  
1 2  
0.169965 0.343454

THE SEVEN DATA SETS FOR THE 1-BUTENE PROBLEM WITH A STANDARD  
 DEVIATION OF 0.010 ARE LISTED BELOW.

2	3	7	1	2	-1				
0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01
0.500000E-04	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.500000E-01
1.000000	C.600000								
10									
2	2	2	2	2	2	2	2	2	2
0.050000	0.100000	0.150000	0.200000	0.250000	0.300000	0.350000	0.400000	0.450000	0.400000
5	5	5	5	5	5	5	5	5	5
1	2								
0.528761	0.256866								
1	2								
0.328549	C.378734								
1	2								
0.238214	0.383155								
1	2								
0.193450	0.374873								
1	2								
0.174100	C.361719								
1	2								
0.163808	0.343946								
1	2								
0.154798	0.333179								
1	2								
0.151608	0.330619								
1	2								
0.151522	0.327716								
1	2								
0.144854	C.320140								
2	3	1	2	-1					
0.000000	1.000000								
10									
2	2	2	2	2	2	2	2	2	2
0.050000	0.100000	0.150000	0.200000	0.250000	0.300000	0.350000	0.400000	0.450000	0.400000

0.450000	C.500000	5	5	5	5	5	5	5	5
1	2								
0.134690	C.650664	1	2						
0.168332	0.492452	1	2						
0.171044	0.413835	1	2						
0.165218	0.374649	1	2						
0.158704	0.352653	1	2						
0.153907	C.340116	1	2						
0.150044	0.333537	1	2						
0.147931	C.328902	1	2						
0.146278	C.326038	1	2						
0.145345	0.324008	1	2						
0.000000	0.000000	10							
2	2	2	2	2	2	2	2	2	2
0.050000	0.100000	0.150000	0.200000	0.250000	0.300000	0.350000	0.400000	0.400000	0.400000
C.450000	C.500000	5	5	5	5	5	5	5	5
1	2								
0.046055	0.129808	1	2						
0.078804	0.203874	1	2						
0.100269	C.249667	1	2						
0.118340	0.272038	1	2						



1	2	0.126891	0.294485						
1	2	0.133454	0.302918						
1	2	0.136215	0.307111						
1	2	0.138888	0.311714						
1	2	0.141110	0.315076						
1	2	0.141325	0.319954						
1	2	0.240000	0.760000						
10									
2	2	2	2	2	2	2	2	2	2
0.050000	0.100000	0.150000	0.200000	0.250000	0.300000	0.350000	0.400000		
0.450000	0.500000	0.550000	0.600000	0.650000	0.700000	0.750000	0.800000	0.850000	0.900000
5	5	5	5	5	5	5	5	5	5
1	2	0.201585	0.589314						
1	2	0.203735	0.433844						
1	2	0.227104	0.422627						
1	2	0.184963	0.419012						
1	2	0.167976	0.329534						
1	2	0.170179	0.331136						
1	2	0.162638	0.306683						
1	2	0.164281	0.338909						
1	2	0.137677	0.315165						

1  
1  
2  
3  
1

1 2  
0.145448 0.324803  
0.349200 0.650800

10  
2 2 2 2 2 2 2 2 2 2  
0.050000 0.100000 0.150000 0.200000 0.250000 0.300000 0.350000 0.400000  
0.450000 0.500000

5 5 5  
1 2  
0.269375 0.522002

1 2  
0.229303 0.451744

1 2  
0.194940 0.404843

1 2  
0.177802 0.377099

1 2  
0.163164 0.357359

1 2  
0.157170 0.337104

1 2  
0.149375 0.338790

1 2  
0.146837 0.322228

1 2  
0.148403 0.323143

1 2  
0.145999 0.323441

1 2  
0.000000 0.493700

10

2 2  
0.050000 0.100000

5 5  
0.450000 0.500000

1 2  
0.500000 0.500000

1 2  
0.500000 0.500000

1 2  
0.500000 0.500000

1 2  
0.500000 0.500000

1 2  
0.500000 0.500000

1	2	0.123840	0.346843
1	2	0.135977	0.330149
1	2	0.142934	0.323471
1	2	0.142431	0.315500
1	2	0.142169	0.322580
1	2	0.144147	0.320436
1	2	0.146512	0.327451
1	2	0.143114	0.319613
1	2	0.145238	0.321160
0.413000	0.000000		
10			
2	2	0.050000	0.100000
2	2	0.150000	0.200000
2	2	0.250000	0.300000
2	2	0.350000	0.400000
5	5	0.450000	0.500000
1	2	0.246082	0.201325
1	2	0.179085	0.281652
1	2	0.159378	0.258330
1	2	0.148985	0.313317
1	2	0.145705	0.319601
1	2	0.145199	0.324409

1	2	0.141515	0.314622
1	2	0.143703	0.321551
1	2	0.143771	C.319831
1	2	0.146268	0.323475

THE SEVEN DATA SETS FOR THE 1-BUTENE PROBLEM WITH A STANDARD  
 DEVIATION OF 0.001 ARE LISTED BELOW.

2	3	7	1	2	-1				
	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01
	0.500000E-04	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.100000E 01	0.500000E-01
	1.000000	0.000000							
10									
2	2	2	2	2	2	2	2	2	2
	0.050000	0.100000	0.150000	0.200000	0.250000	0.300000	0.350000	0.400000	0.400000
	0.450000	0.500000							
5	5	5	5	5	5	5	5	5	5
1	2								
	0.530926	0.300490							
1	2								
	0.330011	0.377452							
1	2								
	0.239197	0.382676							
1	2								
	0.195396	0.370272							
1	2								
	0.173311	0.356148							
1	2								
	0.161342	0.344217							
1	2								
	0.154216	0.335957							
1	2								
	0.150229	0.330879							
1	2								
	0.148006	0.327441							
1	2								
	0.145982	0.324659							
0	000000	1.000000							
10									
2	2	2	2	2	2	2	2	2	2
	0.050000	0.100000	0.150000	0.200000	0.250000	0.300000	0.350000	0.400000	0.400000
	0.450000	0.500000							

5	5	5	5	5	5	5	5	5	5
1	2								
0.136570	0.648599								
1	2								
0.165551	0.498519								
1	2								
0.171253	0.407058								
1	2								
0.164686	0.374189								
1	2								
0.156765	0.350532								
1	2								
0.154150	0.337496								
1	2								
0.147618	0.338154								
1	2								
0.148026	0.332020								
1	2								
0.145561	0.328080								
1	2								
0.145277	0.323090								
0.000000	0.000000								
10									
2	2	2	2	2	2	2	2	2	2
0.050000	0.100000	0.150000	0.200000	0.250000	0.300000	0.350000	0.400000		
0.450000	0.500000								
5	5	5	5	5	5	5	5	5	5
1	2								
0.045182	0.128933								
1	2								
0.078546	0.203856								
1	2								
0.101354	0.248859								
1	2								
0.116818	0.275754								
1	2								



0.145573	0.324366						
0.349200	0.650800						
10							
2	2	2	2	2	2	2	2
0.050000	0.100000	0.150000	0.200000	0.250000	0.300000	0.350000	0.400000
0.450000	0.500000						
5	5	5	5	5	5	5	5
1	2						
C.272641	0.528006						
1	2						
0.225473	0.451800						
1	2						
C.194873	0.403567						
1	2						
0.176063	0.373388						
1	2						
C.163839	0.354165						
1	2						
0.156468	0.341283						
1	2						
0.151426	0.334619						
1	2						
C.148489	C.329662						
1	2						
0.146957	0.326047						
1	2						
0.145654	0.324373						
0.000000	0.493700						
10							
2	2	2	2	2	2	2	2
0.050000	0.100000	0.150000	0.200000	0.250000	0.300000	0.350000	0.400000
0.450000	0.500000						
5	5	5	5	5	5	5	5
1	2						
0.089222	0.386509						
1	2						

1  
B-30  
1





0.143699	0.320318
1	2
0.143740	0.321196
1	2
0.143676	0.321090
1	2
0.143898	0.321477

APPENDIX C

Non-Isothermal Pyrolysis of Propane

To model the non-isothermal pyrolysis of propane in a tubular reactor, the following equation is sufficient.

$$\frac{df}{dL} = \frac{s}{F \times 10^4} \exp \left[ A - \frac{E}{R'T(L)} \right] \left[ \frac{P(L)}{RT(L)} \right]^\alpha \left[ \frac{1-f}{L + \frac{N_0}{F} + f} \right]^\alpha \quad (C-1)$$

To determine the parameters A, E, and  $\alpha$ , data from sixteen different experiments was available.

The conversion at the outlet of the reactor  $f(L_m)$  was measured for each experiment. The temperature was measured at twenty-seven equally spaced points, so that intermediate points could be accurately established by linear interpolation. The pressure was measured at both the inlet and outlet of the reactor. Intermediate values were determined by assuming that pressure was a linear function of L. The inlet feed rate of propane F and of inlet feed rate of inerts  $N_0$  were also observed. All of this information is presented in Table C-1.

In addition to this information, the physical dimensions of the reactor must be specified. The cross

sectional area  $s$  is  $0.0742242 \text{ cm}^2$ . The length  $L_m$  is  $69.0118 \text{ cm}$ .

The constants  $R$  and  $R'$  in equation (C-1) are the ideal gas constants with the appropriate units.

TABLE C-1\*

Data for Propane Pyrolysis

Data Set No.	1	2	3	4	5	6	7	8
$F \times 10^4 \left( \frac{\text{g-mole}}{\text{sec}} \right)$	8.80	5.30	4.26	1.93	1.85	2.69	3.57	1.72
$N \times 10^4 \left( \frac{\text{g-mole}}{\text{sec}} \right)$	41.5	28.1	17.5	46.4	31.6	30.9	29.9	19.9
Pi (mmHg)	974	896	834	986	915	915	900	839
Pe (mmHg)	742	742	742	740	744	734	734	739
Z (L <sub>m</sub> )	0.6660	0.5890	0.6685	0.6173	0.6090	0.6318	0.6992	0.6952
Temp. at Equally Spaced Points (°F)	340	290	280	364	462	486	443	510
	631	545	584	646	761	792	746	842
	928	820	875	962	1055	1087	1029	1116
	1082	1057	1123	1182	1242	1273	1224	1288
	1166	1190	1264	1300	1359	1382	1335	1397
	1218	1286	1364	1374	1447	1460	1417	1474
	1279	1363	1444	1444	1518	1523	1486	1530
	1376	1442	1507	1520	1575	1578	1549	1567
	1430	1504	1552	1581	1612	1617	1593	1584
	1437	1551	1581	1617	1634	1637	1618	1589
	1456	1574	1593	1636	1637	1641	1628	1589
	1499	1598	1593	1656	1637	1641	1629	1577
	1583	1617	1591	1682	1633	1640	1629	1559
	1621	1635	1588	1693	1622	1631	1622	1533
	1638	1634	1578	1690	1602	1611	1608	1497
	1647	1637	1558	1678	1578	1587	1585	1454
	1650	1627	1534	1651	1543	1551	1551	1402
	1647	1610	1499	1619	1503	1512	1512	1350
	1623	1582	1462	1577	1449	1461	1463	1288
	1589	1548	1409	1525	1387	1403	1407	1221
	1542	1501	1351	1454	1308	1324	1329	1133
	1474	1438	1272	1367	1213	1228	1235	1020
	1412	1349	1169	1277	1123	1129	1141	920
	1238	1262	1082	1152	964	964	986	725
	1070	1033	841	939	744	747	779	517
	873	810	604	738	526	543	573	336
	670	595	405	560	360	390	415	205

\* This data has been taken from Kershenbaum's Ph.D. dissertation (University of Michigan 1964)

TABLE C-1 (Continued)

Data for Propane Pyrolysis

Data Set No.	9	10	11	12	13	14	15	16
$F \times 10^4 \left( \frac{\text{g-mole}}{\text{sec}} \right)$	1.69	2.33	0.93	0.80	0.82	1.01	1.31	1.42
$N_o \times 10^4$	19.1	27.4	53.3	55.3	37.0	50.7	40.3	25.2
Pi (mmHg)	839	890	1013	994	1014	1001	927	854
Pe (mmHg)	739	728	727	727	740	740	740	740
Z (L <sub>m</sub> )	0.7909	.4771	.6391	.3740	.3876	.5592	.7197	.8022
Temp. at Equally Spaced Points (°F)	233	321	182	342	396	522	516	545
	543	713	449	706	718	805	792	836
	858	1063	798	1057	972	1039	1028	1074
	1117	1316	1107	1300	1117	1151	1154	1217
	1273	1459	1268	1431	1188	1217	1234	1312
	1365	1550	1364	1504	1226	1292	1302	1384
	1433	1618	1433	1569	1408	1509	1473	1476
	1479	1671	1507	1642	1609	1619	1579	1537
	1506	1710	1588	1720	1684	1677	1629	1558
	1514	1720	1637	1749	1726	1708	1654	1558
	1514	1719	1663	1767	1751	1727	1668	1553
	1511	1716	1687	1798	1772	1741	1669	1543
	1499	1710	1711	1832	1789	1751	1667	1526
	1477	1696	1739	1843	1797	1751	1659	1502
	1449	1683	1741	1840	1797	1751	1642	1472
	1411	1654	1740	1824	1793	1739	1620	1437
	1373	1624	1723	1801	1783	1719	1592	1397
	1325	1583	1692	1771	1766	1691	1554	1349
	1276	1541	1656	1728	1737	1696	1507	1297
	1216	1479	1602	1677	1697	1609	1454	1235
	1149	1406	1539	1605	1638	1542	1381	1159
	1063	1312	1461	1517	1564	1468	1303	1073
	953	1187	1358	1415	1483	1363	1207	971
	862	1081	1281	1296	1273	1101	963	742
	676	829	1073	1050	929	786	642	454
	489	596	879	845	682	583	455	293
	323	405	686	655	530	420	334	205

Two problems were considered. In the first,  $\alpha$  was fixed at one and the other two parameters were determined such that the least square error was minimized. Secondly, all three parameters were determined simultaneously.

The maximum step size  $S_{\max}$ , the maximum allowable relative change in the parameters for one iteration  $C_{\max}$ , and the minimum allowable relative change in the parameters for one step  $C_{\min}$  which were used with the different initial guesses for A and E/R are specified in Table C-2. The 360/67 machine time is also given in this table.

TABLE C-2

Control Data for First Propane Problem

Initial A	Guess E/R	$S_{\max}$	$C_{\max}$	$C_{\min}$	IBM 360/67 Time (min)
35.0	26.0	$2 \times 10^{-3}$	2.0	0.5	3.90
10.0	10.0	$1 \times 10^{-4}$	5.0	0.5	4.56
30.0	30.0	$1 \times 10^{-4}$	5.0	0.5	4.34
40.0	40.0	$1 \times 10^{-4}$	5.0	0.5	4.44
0.0	0.0	$1 \times 10^{-4}$	5.0	0.5	7.73
50.0	50.0	$1 \times 10^{-4}$	5.0	0.5	4.03
35.4	26.22	$1 \times 10^{-4}$	5.0	0.5	3.98

The convergent sequences of parameters which evolved from each of the initial guesses in Table C-2 are shown in Tables C-3, C-4, C-5, C-6, C-7, C-8, and C-9.

TABLE C-3

First Propane Problem First Initial Guess

Step No.	A	E/R	Sum of Errors Squared	Comment
0	35.00	26.00	.4456	Begin Phase I
1	34.92	25.90	.4390	
2	34.77	25.71	.4260	
3	34.81	25.33	.4005	
4	33.94	24.63	.3525	
5	32.99	23.41	.2679	
6	31.54	21.52	.1424	
7	29.80	19.20	.0382	Begin Phase II
8	29.46	18.73	.0335	Solution



TABLE C-4

	First Propane Problem	Second Initial Guess		
Step No.	A	E/R	Sum of Errors Squared	Comment
0	10.00	10.00	2.535	Begin Phase I
1	15.41	14.98	2.535	
2	16.24	15.40	2.535	
3	17.08	15.73	2.535	
4	17.88	15.94	2.534	
5	18.63	16.06	2.534	
6	19.37	16.13	2.532	
7	20.08	16.17	2.530	
8	20.79	16.19	2.525	
9	21.49	16.20	2.515	
10	22.19	16.21	2.494	
11	22.90	16.23	2.454	
12	23.62	16.25	2.375	
13	24.36	16.31	2.219	
14	25.17	16.41	1.925	
15	26.10	16.65	1.399	
16	27.33	17.20	0.6114	Begin Phase II
17	29.45	18.72	0.0345	Solution

TABLE C-5

Step No.	First Propane Problem		Third Initial Guess	
	A	E/R	Sum of Errors Squared	Comment
0	30.00	30.00	2.534	Begin Phase I
1	29.14	28.86	2.534	
2	27.79	26.06	2.534	
3	26.02	24.66	2.533	
4	24.19	22.06	2.533	
5	22.78	10.83	2.532	
6	22.00	18.26	2.529	
7	21.81	17.30	2.524	
8	22.02	16.78	2.514	
9	22.46	16.50	2.494	
10	23.03	16.37	2.453	
11	23.68	16.32	2.374	
12	24.40	16.34	2.219	
13	25.18	16.43	1.924	
14	26.10	16.65	1.398	
15	27.33	17.20	0.6109	Begin Phase II
16	29.45	18.72	0.0336	Solution

TABLE C-6

	First Propane Problem	Fourth Initial Guess		
Step No.	A	E/R	Sum of Errors Squared	Comment
0	40.00	40.00	2.530	Begin Phase I
1	39.73	39.65	2.530	
2	39.20	38.98	2.529	
3	38.23	37.73	2.529	
4	36.56	35.58	2.529	
5	34.03	32.30	2.527	
6	30.88	28.16	2.525	
7	27.86	24.07	2.520	
8	25.67	20.86	2.510	
9	24.48	18.76	2.489	
10	24.10	17.56	2.449	
11	24.22	16.93	2.370	
12	24.66	16.64	2.214	
13	25.31	16.57	1.920	
14	26.16	16.72	1.394	
15	27.36	17.23	0.6081	Begin Phase II
16	29.45	18.72	0.0336	Solution

TABLE C-7

First Propane Problem      Fifth Initial Guess

Step No.	A	E/R	Sum of Errors Squared	Comment
0	0.00	0.00	2,535	Begin Phase I
1	0.00	0.00	2.535	$s_{max} \rightarrow s_{max}/2$
2	0.00	0.00	2.535	$s_{max} \rightarrow s_{max}/2$
3	0.00	0.00	2.535	$s_{max} \rightarrow s_{max}/2$
4	0.00	0.00	2.535	$s_{max} \rightarrow s_{max}/2$
5	0.00	0.00	2.535	$s_{max} \rightarrow s_{max}/2$
6	0.00	0.00	2.535	$s_{max} \rightarrow s_{max}/2$
7	0.00	0.00	2.535	$s_{max} \rightarrow s_{max}/2$
8	0.26	0.19	2.535	$s_{max} \rightarrow s_{max}/2$
9	0.80	0.62	2.535	
10	1.48	1.20	2.535	
11	2.06	1.71	2.535	
12	2.67	2.27	2.535	
13	3.20	2.76	2.535	
14	4.08	3.60	2.535	
15	4.86	4.36	2.535	
16	6.08	5.55	2.535	
17	7.00	6.46	2.535	
18	8.48	7.91	2.535	
19	10.43	9.79	2.535	
20	12.56	11.78	2.535	
21	14.52	13.46	2.535	
22	16.11	14.63	2.535	
23	17.36	15.35	2.534	
24	18.36	15.75	2.534	
25	19.23	15.97	2.532	
26	20.01	16.09	2.530	
27	20.75	16.15	2.525	
28	21.47	16.18	2.515	
29	22.18	16.20	2.494	
30	22.89	16.22	2.454	
31	23.62	16.25	2.375	
32	24.36	16.30	2.219	
33	25.17	16.41	1.925	
34	26.10	16.65	1.399	
35	27.33	17.20	0.6114	Begin Phase II
36	29.45	18.72	0.0336	Solution

TABLE C-8

First Propane Problem      Sixth Initial Guess

Step No.	A	E/R	Sum of Errors Squared	Comment
0	50.00	50.00	2.502	Begin Phase I
1	49.94	49.92	2.501	
2	49.82	49.77	2.501	
3	49.59	49.48	2.501	
4	49.14	48.90	2.501	
5	48.27	47.79	2.499	
6	46.66	45.74	2.497	
7	43.92	42.24	2.492	
8	39.88	37.06	2.483	
9	35.15	30.93	2.463	
10	30.97	25.37	2.433	
11	28.17	21.39	2.343	
12	26.75	18.99	2.187	
13	26.35	17.73	1.892	
14	26.64	17.24	1.367	
15	27.54	17.43	0.488	Begin Phase II
16	29.45	18.72	0.0336	Solution

TABLE C-9

First Propane Problem      Seventh Initial Guess

Step No.	A	E/R	Sum of Errors Squared	Comment
0	35.40	26.22	0.2728	Begin Phase I
1	35.40	26.22	0.2728	
2	35.40	26.22	0.2728	
3	35.40	26.22	0.2727	
4	35.39	26.21	0.2726	
5	35.59	26.21	0.2722	
6	35.38	26.19	0.2715	
7	35.34	26.16	0.2701	
8	35.02	26.10	0.2673	
9	35.20	26.97	0.2617	
10	35.01	25.73	0.2507	
11	34.63	25.26	0.2297	
12	33.93	24.38	0.1913	
13	32.71	22.85	0.1289	
14	30.89	20.54	0.0564	Begin Phase II
15	29.45	18.72	0.0336	Solution

For the second case, with  $\alpha$  being unknown, the computer time required was considerably larger, as shown in Table C-10. Also given in Table C-10 are the three initial guesses which were used and the corresponding initial control variables.

TABLE C-10

Control Data for Second Propane Problem

A	Initial Guess		$S_{\max}$	$C_{\max}$	$C_{\min}$	IBM 360/67 Time (Min)
	E/R	$\alpha$				
18	15	1.0	$2 \times 10^{-3}$	2.0	0.5	6.94
18	15	0.5	$1 \times 10^{-4}$	2.0	0.5	8.35
18	15	1.5	$1 \times 10^{-7}$	2.0	0.5	> 15

The convergent sequence of parameters for each of the initial guesses given in Table C-10 are listed in Tables C-11, C-12, and C-13. The third initial guess was not carried all the way to solution because of the large amount of computing time required.

TABLE C-11

Second Propane Problem    First Initial Guess

Step No.	A	E/R	$\alpha$	Sum of Errors Squared	Comment
1	18.00	15.00	1.000	2.533	Begin Phase I
2	25.87	20.14	0.749	0.9034	
3	26.00	20.06	0.7599	0.8717	
4	26.17	19.97	0.7740	0.8304	
5	26.49	19.82	0.800	0.7513	
6	27.12	19.62	0.844	0.6068	
7	28.34	19.55	0.916	0.3711	
8	30.90	20.24	1.025	0.944	Begin Phase II
9	33.43	21.48	1.109	0.0303	Solution



TABLE C-12

Second Propane Problem Second Initial Guess

Step No.	A	E/R	$\alpha$	Sum of Errors Squared	Comment
0	18.00	15.00	0.500	0.7150	Begin Phase I
1	18.01	15.00	0.500	0.7146	
2	18.02	15.01	0.501	0.7138	
3	18.05	15.02	0.502	0.7122	
4	18.12	15.04	0.505	0.7090	
5	18.24	15.89	0.510	0.7025	
6	18.47	15.18	0.520	0.6897	
7	18.93	15.34	0.540	0.6644	
8	10.78	15.66	0.576	0.6155	
9	21.30	16.20	0.641	0.5241	
10	23.80	17.12	0.748	0.3671	
11	27.76	18.70	0.908	0.1496	Begin Phase II
12	33.43	21.48	1.109	0.0303	Solution

TABLE C-13

Second Propane Problem Third Initial Guess

Step No.	A	E/R	$\alpha$	Sum of Errors Squared	Comment
0	18.00	15.00	1.500	2.535	Begin Phase I
1	12.49	13.12	1.180	2.535	
2	11.22	12.37	1.111	2.535	
3	10.93	12.68	1.042	2.535	
4	11.91	13.59	1.022	2.535	
5	11.95	13.61	0.987	2.535	
6	12.69	14.05	0.972	2.535	
7	13.80	14.64	0.969	2.535	
8	14.84	15.07	0.971	2.535	
9	15.66	15.26	0.970	2.535	
10	16.45	15.38	0.970	2.535	
11	17.19	15.45	0.970	2.534	
12	17.92	15.49	0.970	2.533	
13	18.63	15.52	0.970	2.532	
14	19.34	15.53	0.970	2.528	
15	20.04	15.54	0.970	2.522	
16	20.75	15.55	0.970	2.509	
17	21.47	15.57	0.971	2.483	
18	22.21	15.61	0.972	2.432	
19	22.99	15.68	0.973	2.331	
20	23.87	15.82	0.977	2.135	Stopped after
21	24.45	16.13	0.984	1.769	
22	26.52	16.82	1.000	1.141	15 minutes

The required SLOPE subroutines for the two problems are listed on the following pages.

```

SUBROUTINE SLOPE(R,T,IJACK)
C   SLOPE SUBROUTINE FOR THE PRGPANE PRGBLEM WITH THE
C   ORDER OF REACTION FIXED AT UNITY.
REAL X(10,10),JX(10,10),JK(10,10),G(10),T,C(11,10),XD(3
10,10)
INTEGER R,NE,NK,NA,II,NDS,IJACK
COMMON /AB3/C,NE,NK,NA/AB5/JX,JK,X,G/AB8/XC,II,NDS
REAL NC(10),F(16),PI(16),PE(16),TL(16,27),DL(27),D,S,L,
1RR,Q,Z,A,E,
1TEMP,SUMA
DO 16 I=1,NE
IF(ABS(X(R,I)).LE.10.0) GOTO 16
WRITE(6,17)
STOP
16 CONTINUE
17 FORMAT('O STATE VARIABLE BOUND EXCEEDED')
Z=X(R,1)
A=C(R,1)
E=C(R,2)
GOTO(11,12),NA
11 DO 13 I=1,NE
G(I)=0.0
DO 14 J=1,NK
14 JX(I,J)=0.0
DO 13 J=1,NK
13 JK(I,J)=0.0
NA=2
DO 15 I=1,NDS
READ(5,1) F(I),NC(I),PI(I),PE(I)
WRITE(6,1) F(I),NC(I),PI(I),PE(I)
READ(5,1) (TL(I,J),J=1,27)
15 WRITE(6,1) (TL(I,J),J=1,27)
1 FORMAT(8X,9F8.2)
S=7.42242
L=0.69C118
RR=62361000.0
D=0.026543
DL(1)=0.0
DO 16 J=1,27
DO 17 I=1,NDS
17 TL(I,J)=(TL(I,J)+460.0)/1800.0
IF(J.EQ.1) GOTO 16
DL(J)=DL(J-1)+D
16 CONTINUE
12 J=1.0+T/D
TEMP=(TL(II,J)*(DL(J+1)-T)+TL(II,J+1)*(T-DL(J)))/D
P=PI(II)-T*(PI(II)-PE(II))/L
SUMA=S*EXP(A-E/TEMP)*P/(RR*TEMP*F(II))
G(1)=SUMA*(1.0-Z)/(1.0+NC(II)/F(II)+Z)
IF(IJACK.LT.0) GOTO 15

```

```
JX(1,1)=-SUMA*(2.0+NO(II)/F(II))/(1.0+NO(II)/F(II)+Z)**  
12 JK(1,1)=G(1)  
JK(1,2)=-G(1)/TEMP  
15 RETURN  
END
```

```

SUBROUTINE SLOPE(R,T,IJACK)
C      SLOPE SUBROUTINE FOR THE PROPANE PROBLEM WITH THE
C      ORDER OF REACTION UNSPECIFIED.
REAL X(10,10),JX(10,10),JK(10,10),G(10),T,C(11,10),XO(3
10,10)
INTEGER R,NE,NK,NA,II,NDS,IJACK
COMMON /AB3/C,NE,NK,NA/AB5/JX,JK,X,G/AB8/XO,II,NDS
REAL NO(16),F(16),PI(16),PE(16),TL(16,27),DL(27),D,S,L,
1RR,Q,Z,A,E,
1TEMP,SUMA
DO 16 I=1,NE
IF(ABS(X(R,I)).LE.10.0) GOTO 16
WRITE(6,17)
STOP
16 CONTINUE
17 FORMAT('OSTATE VARIABLE BOUND EXCEEDED')
Z=X(R,1)
A=C(R,1)
E=C(R,2)
Q=C(R,3)
GOTO(11,12),NA
11 DO 13 I=1,NE
G(I)=0.0
DO 14 J=1,NE
14 JX(I,J)=0.0
DO 13 J=1,NK
13 JK(I,J)=0.0
NA=2
DO 15 I=1,NDS
READ(5,1) F(I),NO(I),PI(I),PE(I)
WRITE(6,1) F(I),NO(I),PI(I),PE(I)
READ(5,1) (TL(I,J),J=1,27)
15 WRITE(6,1)(TL(I,J),J=1,27)
1 FORMAT(8X,9F8.2)
S=7.42242
L=0.690118
RR=62361000.0
D=0.026543
DL(1)=0.0
DO 16 J=1,27
DO 17 I=1,NDS
17 TL(I,J)=(TL(I,J)+460.0)/1800.0
IF(J.EQ.1) GOTO 16
DL(J)=DL(J-1)+D
16 CONTINUE
12 J=1.0+T/D
TEMP=(TL(II,J)*(DL(J+1)-T)+TL(II,J+1)*(T-DL(J)))/D
P=PI(II)-T*(PI(II)-PE(II))/L
SUMA=S*EXP(A-E/TEMP)/F(II)
G(1)=SUMA*(P*(1.0-Z)/(RR*TEMP*(1.0+NO(II)/F(II)+Z)))**Q

```

```
IF(IJACK.LT.0) GOTO 15
JX(1,1)=-SUMA*Q*(2.0+NO(II)/F(II))*(1.0-Z)**(Q-1.0)*(P/
1(RR*TEMP))*
1*Q/(1.0+NO(II)/F(II)+Z)**(1.0+Q)
JK(1,1)=G(1)
JK(1,2)=-G(1)/TEMP
JK(1,3)=G(1)*ALOG(P*(1.0-Z)/(RR*TEMP*(1.0+NO(II)/F(II)+
1Z)))
15 RETURN
END
```

APPENDIX D

Catalytic Hydrogen Chloride Oxidation\*

The data obtained for the oxidation of hydrogen chloride was taken from a system which was essentially a batch reactor. Once the charge entered the reactor, the system was free from external interference except for the agitation produced by a circulating pump and the removal of the samples for analysis.

An adequate mathematical model of this system is given in the following equations.

$$\frac{dP_{O_2}}{dt} = \frac{W'P_i}{N_B} \frac{a_1 \left( P_{O_2}^{\frac{1}{2}} - \frac{P_{H_2O} P_{Cl_2}}{K_e P_{HCl}^2} \right)}{1 + a_2 P_{HCl} + a_3 P_{H_2O} + a_4 \frac{P_{H_2O} P_{Cl_2}}{K_e P_{HCl}^2}} \quad (D-1)$$

$$P_{HCl} = \left[ N_{HCl} - 4 \left( N_{O_2} - \frac{N_B}{P_i} P_{O_2} \right) \right] \frac{P_i}{N_B} B(t) \quad (D-2)$$

$$P_{Cl_2} = \left[ N_{Cl_2} + 2 \left( N_{O_2} - \frac{N_B}{P_i} P_{O_2} \right) \right] \frac{P_i}{N_B} B(t) \quad (D-3)$$

\* All the raw data for this example was supplied by Harding Bliss of Yale University.

$$P_{H_2O} = \left[ N_{H_2O} + 2 \left( N_{O_2} - \frac{N_B}{P_i} P_{O_2} \right) \right] \cdot \frac{P_i}{N_B} B(t) \quad (D-4)$$

$$B(t) = \frac{P(t)}{\frac{P_i}{N_B} \left[ N_B - \left( N_{O_2} - \frac{N_B}{P_i} P_{O_2} \right) \right]} \quad (D-5)$$

- $K_e$  = known equilibrium constant  
 $P_{H_2O}$  = partial pressure of water  
 $P_{O_2}$  = partial pressure of oxygen  
 $P_{Cl_2}$  = partial pressure of chlorine  
 $P_{HCl}$  = partial pressure of hydrogen chloride  
 $N_B$  = total number of gm-moles initially present in the reactor  
 $N_{O_2}$  = number of moles of oxygen initially in the reactor  
 $N_{HCl}$  = number of moles of HCl  
 $N_{Cl_2}$  = number of moles of chlorine  
 $N_{H_2O}$  = number of moles of water initially in the reactor  
 $W'$  = weight of catalyst present in the reactor.  
 $P_i$  = the initial pressure of the reactor  
 $P(t)$  = the total pressure of the reactor at time t  
 $N_I$  = number of moles of inerts



The correction factor  $B(t)$  was correlated from the actual pressure data using polynomials of the form:

$$B(t) = b_1 + b_2t + b_3t^2 + b_3t^3 \quad (D-6)$$

The maximum amount of correction was about fifteen per cent and the correction factors are all correct to within one and a half percent.

All the data used to identify the parameters at  $355^{\circ}\text{C}$  are shown in the tables below starting with Table D-1. The data used to identify the parameters at  $340^{\circ}\text{C}$  are shown in the tables beginning with Table D-11. The data used to attempt the identification of the parameters at  $325^{\circ}\text{C}$  are shown starting with Table D-23.

TABLE D-4

Data for Hydrogen Chloride Problem at 355°C

Data Set No.	1	2	3	4	5	6	7	8	9
$P_i$ (atm)	1.31	1.304	1.303	1.335	1.322	1.330	1.311	1.330	1.317
$K_e$ (atm <sup>-<math>\frac{1}{2}</math>)</sup>	20.3	20.3	20.3	20.3	20.3	20.3	20.3	20.3	20.3
$W$ (gm)	15.55	15.55	15.55	15.55	15.55	15.55	15.55	15.55	15.55
$N_{HCl}$ (g-mole)	0.04396	0.04374	0.04374	0.04529	0.05932	0.02002	0.02083	0.07203	0.04174
$NO_2$ (g-mole)	0.01109	.01105	0.01104	0.01123	0.01153	0.01641	0.01596	0.00550	0.01038
$N_{Cl_2}$ (g-mole)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$NH_2O$ (g-mole)	0.04174	0.04159	0.04152	0.04226	0.02674	0.06184	0.06006	0.02069	0.03908
$b_1$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$b_2$	-0.16090	-0.1100	-0.10940	-0.15820	-0.16260	-0.08528	0.07152	-0.05412	-0.11320
$b_3$	0.05841	0.02245	0.0	0.05452	0.09505	0.03386	-0.33020	0.0	0.01996
$b_4$	0.0	0.0	0.0	0.0	-0.02928	0.0	0.0	0.0	0.0

TABLE D-2

Hydrogen Chloride Problem Data Set One at 355°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P (t) (atm)
0	0.1501	1.310
1	0.410	1.272
4	0.118	1.195
7	0.0958	0.155
10	0.0853	1.122
13	0.0772	1.097

TABLE D-3

Hydrogen Chloride Problem Data Set Two at 355°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P (t) (atm)
0	0.1496	1.304
1	1.1404	1.282
4	0.1150	1.209
7	0.1002	1.170
10	0.0890	1.136
13	0.0795	1.110
21	0.0633	1.055

TABLE D-4

Hydrogen Chloride Problem Data Set Three at 355°C

t(min)	P <sub>O<sub>2</sub></sub> (atm)	P(t) (atm)
0	0.1495	1.303
1	0.1380	1.281
4	0.1155	1.206
7	0.0998	1.161

TABLE D-5

Hydrogen Chloride Problem Data Set Four at 355°C

t(min)	P <sub>O<sub>2</sub></sub> (atm)	P(t) (atm)
0	0.1520	1.335
1	0.1445	1.313
4	0.1147	1.220
7	0.0988	1.177
10	0.0890	1.142
13	0.0808	1.119

TABLE D-6

Hydrogen Chloride Problem Data Set Five at 335°C

t (min)	$P_{O_2}$ (atm)	P (t) (atm)
0	0.1560	1.322
1	0.4196	1.298
4	0.1252	1.221
7	0.1115	1.183
10	0.1006	1.152
13	0.0907	1.124
19	0.0785	1.080

TABLE D-7

Hydrogen Chloride Problem Data Set Six at 355°C

t (min)	$P_{O_2}$ (atm)	P (t) (atm)
0	0.2221	1.330
1	0.2095	1.310
4	0.1831	1.250
7	0.1720	1.226
10	0.1660	1.210
13	0.1622	1.201

TABLE D-8

Hydrogen Chloride Problem Data Set Seven At 355°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P (t) (atm)
0	0.2160	1.311
1	0.2050	1.305
4	0.1809	1.245

TABLE D-9

Hydrogen Chloride Problem Data Set Eight at 355°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P (t) (atm)
0	0.0745	1.330
10	0.0491	1.234

TABLE D-10

Hydrogen Chloride Problem Data Set Nine at 355°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P (t) (atm)
0	0.1405	1.317
2	0.1225	1.270
5	0.1060	1.211
8	0.0949	1.170
11	0.0882	1.140
14	0.0788	1.110
21	0.0654	1.054

TABLE D-11

Data for Hydrogen Chloride Problem at 340°C

Data Set No.	1	2	3	4	5	6
$P_i$ (atm)	1.3070	1.3190	1.334	1.340	1.312	1.322
$K_e$ (atm <sup>-1/2</sup> )	26.7	26.7	26.7	26.7	26.7	26.7
$W$ (gm)	15.55	15.55	15.55	15.55	15.55	15.55
$N_{HCl}$ (g-moles)	0.03491	0.07544	0.007562	0.07165	0.10125	0.10070
$N_{O_2}$ (g-moles)	0.00883	0.01904	0.01909	0.01903	0.01964	0.01954
$N_{Cl_2}$ (g-moles)	0.0	0.0	0.0	0.0	0.0	0.0
$N_{H_2O}$ (g-moles)	0.0	0.0	0.0	0.0	0.0	0.0
$N_I$ (g-moles)	0.00332	0.07166	0.07176	0.07537	0.04555	0.04534
$b_1$	1.0	1.0	1.0	1.0	1.0	1.0
$b_2$	-0.08296	-0.10040	-0.07202	-0.09691	-0.08223	-0.06723
$b_3$	0.0	0.0	0.0	0.0	0.01660	0.0
$b_4$	0.0	0.0	0.0	0.0	0.0	0.0

TABLE D-11 (continued)

Data for Hydrogen Chloride Problem at 340°C

Data Set No.	7	8	9	10	11
$P_i$ (atm)	1.301	1.320	1.319	1.316	1.339
$K_e$ ( $\text{atm}^{-\frac{1}{2}}$ )	26.7	26.7	26.7	26.7	26.7
W (gm)	15.55	15.55	15.55	15.55	15.55
$N_{\text{HCl}}$ (g-moles)	0.10713	0.03369	0.03369	0.11550	0.07551
$N_{\text{O}_2}$ (g-moles)	0.02260	0.02778	0.02778	0.01064	0.01906
$N_{\text{Cl}_2}$ (g-moles)	0.0	0.0	0.0	0.0	0.0
$N_{\text{H}_2\text{O}}$ (g-moles)	0.0	0.0	0.0	0.0	0.0
$N_{\text{I}}$ (g-moles)	0.03639	0.10446	0.1446	0.04001	0.07166
$b_1$	1.0	1.0	1.0	1.0	1.0
$b_2$	-0.09462	-0.04438	-0.04903	-0.05849	-0.10800
$b_3$	0.02058	0.0	0.0	0.0	0.0
$b_4$	0.0	0.0	0.0	0.0	0.0



TABLE D-12

Hydrogen Chloride Problem Data Set One at 340°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P (t) (atm)
0	0.1500	1.307
1	0.1416	1.284
4	0.1260	1.217
7	0.1123	1.182
13	0.0967	1.133

TABLE D-13

Hydrogen Chloride Problem Data Set Two at 340°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P (t) (atm)
0	0.1512	1.319
1	0.1418	1.297
4	0.1228	1.234
7	0.1147	1.195

TABLE D-14

Hydrogen Chloride Problem Data Set Three at 340°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P (t) (atm)
0	0.1530	1.334
1	0.1426	1.321
4	0.1269	1.266
7	0.1126	1.266
13	0.0988	1.102

TABLE D-15

Hydrogen Chloride Problem Data Set Four at 340°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P (t) (atm)
0	0.1535	1.340
1	0.1475	1.322
4	0.1241	1.253
7	0.1140	1.216

TABLE D-16

Hydrogen Chloride Problem Data Set Five at 340°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P (t) (atm)
0	0.1548	1.312
1	0.1482	1.291
4	0.1329	1.241
13	0.1078	1.172
22	0.0925	1.122

TABLE D-17

Hydrogen Chloride Problem Data Set Six at 340°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P (t) (atm)
0	0.1560	1.322
1	0.1450	1.310
4	0.1290	1.245
13	0.1062	1.165

TABLE D-18

Hydrogen Chloride Problem Data Set Seven at 340°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P (t) (atm)
0	0.1770	1.301
1	0.1705	1.281
4	0.1506	1.228
7	0.1365	1.192
16	0.1123	1.114

TABLE D-19

Hydrogen Chloride Problem Data Set Eight at 340°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P (t) (atm)
0	0.2210	1.320
1	0.2155	1.310
7	0.1825	0.232
13	0.1691	1.200

TABLE D-20

Hydrogen Chloride Problem Data Set Nine at 340°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P (t) (atm)
0	0.2205	1.319
1	0.2085	1.295
7	0.1762	1.215
13	0.1662	1.193

TABLE D-21

Hydrogen Chloride Problem Data Set Ten at 340°C

t(min)	P <sub>O<sub>2</sub></sub> (atm)	P(t) (atm)
0	0.0843	1.316
10	0.0694	1.225

TABLE D-22

Hydrogen Chloride Problem Data Set Eleven at 340°C

t(min)	P <sub>O<sub>2</sub></sub> (atm)	P(t) (atm)
0	0.1535	1.339
1	0.1475	1.322
4	0.1241	1.253

TABLE D-23

Data for Hydrogen Chloride at 325°C

Data Set No.	1	2	3	4	5	6	7	8	9
$P_i$ (atm)	1.333	1.327	1.344	1.320	1.333	1.328	1.320	1.326	1.319
$K_e$ (atm <sup>-½</sup> )	35.7	35.7	35.7	35.7	35.7	35.7	35.7	35.7	35.7
W(gm)	15.55	15.55	15.55	15.55	15.55	15.55	15.55	15.55	15.55
$N_{HCl}$ (g-mole)	0.03406	0.10077	0.03566	0.03536	0.12145	0.07112	0.08119	0.08125	0.08131
$N_{O_2}$ (g-mole)	0.00900	0.01960	0.02739	0.02737	0.00930	0.01768	0.01774	0.01775	0.01772
$N_{Cl_2}$ (g-mole)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$N_{H_2O}$ (g-mole)	0.0	0.0	0.0	0.0	0.0	0.01043	0.0	0.0	0.0
$N_I$ (g-mole)	0.03382	0.04544	0.010277	0.10143	0.03493	0.06650	0.06659	0.06675	0.06673
$b_1$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$b_2$	-0.12210	-0.14940	-0.07527	-0.05682	-0.02901	-0.08687	-0.10800	-0.09403	-0.08853
$b_3$	0.03372	0.12530	0.04979	0.01552	0.0	0.01127	0.02611	0.02166	0.03295
$b_4$	0.0	-0.03658	-0.01172	0.0	0.0	0.0	0.0	0.0	0.0

TABLE D-24

Hydrogen Chloride Problem Data Set One at 325°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P(t) (atm)
0	0.1560	1.333
1	0.1497	1.311
4	0.1392	1.255
7	0.1335	1.222
10	0.1271	1.191
13	0.1238	1.167

TABLE D-25

Hydrogen Chloride Problem Data Set Two at 325°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P(t) (atm)
0	0.1566	1.327
1	0.1503	1.295
4	0.1380	1.252
7	0.1338	1.236
10	0.1277	1.220
13	0.1238	1.210
18	0.1181	1.191

TABLE D-26

Hydrogen Chloride Problem Data Set Three at 325°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P(t) (atm)
0	0.2220	1.344
2	0.2020	1.317
5	0.1840	1.263
10	0.1746	1.251
15	0.1674	1.237
20	0.1631	1.227

TABLE D-27

Hydrogen Chloride Problem Data Set Four at 325°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P(t) (atm)
0	0.2180	1.320
5	0.1850	1.250
10	0.1719	1.222
15	0.1654	1.208
20	0.1604	1.195

TABLE D-28

Hydrogen Chloride Problem Data Set Five at 325°C

t(min)	P <sub>O<sub>2</sub></sub> (atm)	P(t) (atm)
0	0.0748	1.333
1	0.0741	1.327
4	0.0706	1.306
7	0.0710	1.298
10	0.0701	1.293
13	0.0694	1.280
20	0.0648	1.246

TABLE D-29

Hydrogen Chloride Problem Data Set Six at 325°C

t(min)	P <sub>O<sub>2</sub></sub> (atm)	P(t) (atm)
0	0.1417	1.328
2	0.1362	1.298
5	0.1268	1.255
8	0.1193	1.227
11	0.1160	1.197
14	0.1130	1.170
23	0.1005	1.106



TABLE D-30

Hydrogen Chloride Problem Data Set Seven at 325°C

t (min)	$P_{O_2}$ (atm)	P (t) (atm)
0	0.1415	1.320
1	0.1378	1.297
4	0.1228	1.240
7	0.1165	1.210
10	0.1101	1.189
13	0.1061	1.167
19	0.0989	1.132

TABLE D-31

Hydrogen Chloride Problem Data Set Eight at 325°C

t (min)	$P_{O_2}$ (atm)	P (t) (atm)
0	0.1420	1.326
1	0.1380	1.304
4	0.1243	1.255
7	0.1177	1.228
10	0.1112	1.204
13	0.1056	1.186
19	0.0981	1.150

TABLE D-32

Hydrogen Chloride Problem Data Set Nine at 325°C

t (min)	P <sub>O<sub>2</sub></sub> (atm)	P (t) (atm)
0	0.1410	1.319
1	0.1390	1.304
4	0.1235	1.256
7	0.1122	1.235
10	0.1120	1.221
13	0.1064	1.206

An attempt was made to determine the unknown parameters in equation (D-1) at each of the three temperatures. The results of each of these attempts is presented below. At 355°C the solution covered directly with quasilinearization as shown in Table D-33.

TABLE D-33

Solution of Hydrogen Chloride Problem at 355°C

Iteration Number	$a_1 \times 10^4$	$a_2$	$a_3$	$a_4$	Sum of Errors Squared
0	2.80	3.10	25.0	230	0.00315
1	5.44	6.91	36.1	401	
2	9.00	12.2	50.0	661	
3	9.47	12.6	47.3	704	
4	9.55	12.8	47.0	732	
5	9.76	13.1	47.8	755	
6	9.78	13.1	47.8	759	
7	9.80	13.2	47.9	762	
8	9.80	13.2	47.9	762	0.000747

At 340°C a solution could also be obtained using quasilinearization directly as shown in Table D-34.

TABLE D-34

Solution to Hydrogen Chloride Problem at 340°C

Iteration Number	$a_1 \times 10^4$	$a_2$	$a_3$	$a_4$	Sum of Errors Squared
0	0.920	0.220	21.0	142	0.00708
1	2.79	0.651	90.3	-65.1	
2	5.28	0.732	128.8	-50.3	
3	5.57	0.793	120.6	-34.8	
4	5.58	0.793	121.6	-34.9	
5	5.57	0.790	121.3	-34.8	
6	5.57	0.791	121.3	-34.8	0.00144

At 325°C no solution was found. An attempt to find the solution directly using quasilinearization failed because the maximum allowable relative change in the parameter  $C_{\max}$  was exceeded. The initial values of  $S_{\max}$  and  $C_{\max}$  were 0.05 and 50 respectively. The results are summarized in Table D-35. The SLOPE subroutine used for this problem is listed at the end of this section.

TABLE D-35  
An Attempt to Solve the Hydrogen Chloride Problem at 325°C

Step No.	$a_1 \times 10^4$	$a_2$	$a_3$	$a_4$	Sum of Errors Squared	Comment
0	0.26	0.01	11.0	18.0	0.01829	Begin Phase II
1	0.26	0.01	11.0	18.0	0.01829	Begin Phase I*
2	0.26	0.01	11.0	18.0	0.01829	Begin Phase I
3	0.26	0.01	11.0	18.0	0.01829	Begin Phase I
4	0.682	1.71	24.5	671	0.01349	
5	3.11	10.7	101	2259	0.009686	Begin Phase I
6	3.11	10.7	101	2759	0.009686	
7	34.1	124	1076	19864	0.008328	Begin Phase I

\* Each time Phase I is re-initiated the maximum step size  $S_{max}$  is halved.

```

SUBROUTINE SLCPE(R,T,IJACK)
C      SLOPE SUBROUTINE FOR THE HYDROGEN CHLORIDE PROBLEM.
REAL*4 X(10,10),JX(10,10),JK(10,10),G(10),T,C(11,10),XO
1(30,10)
INTEGER R,NE,NK,I,J,NO,II,NDS,IJACK
COMMON /AB3/C,NE,NK,NO/AB5/JX,JK,X,G/AB8/XC,II,NDS
REAL*4 F,K,B,GA,A,
1PI(30),KE(30),W(30),NHCL(30),NTOT(30),NO2(30),NCL2(30),
1NH2O(30),
2NN2(30),SUMA(30),SUMB(30),DPHCL(30),DPCL2(30),DPO2(30),
1PO2,PHCL,
3PH2O,PCL2,RA,SUMC,FG,GG,DRA,PTGT,NB(30),DPH2O(30),WW,XO
1(30,10)
4,A0(30),A1(30),A2(30),A3(30),TT(30),DHK,DSK,DHB,DSB,DHG
1A,DSGA,DHA,
5DSA,RR
INTEGER I,J
DO 16 I=1,NE
IF(ABS(X(R,I)).LE.10.0) GOTO 16
WRITE(6,17)
STOP
16 CONTINUE
17 FORMAT(' OSTATE VARIABLE BOUND EXCEEDED ')
PO2=X(R,1)
K=C(R,1)*0.001
B=C(R,2)
GA=C(R,3)*10.0
A=C(R,4)*100.0
GOTO(11,12),NO
11 DO 13 I=1,NE
G(I)=0.0
DO 14 J=1,NE
14 JX(I,J)=0.0
DO 13 J=1,NK
13 JK(I,J)=0.0
RR=1.987
NO=2
DO 15 I=1,NDS
READ(5,1) PI(I),KE(I),W(I),NHCL(I),NO2(I),NCL2(I),NH2O(
1I),NN2(I)
1,II(I)
WRITE(6,1)PI(I),KE(I),W(I),NHCL(I),NO2(I),NCL2(I),NH2O(
1I),NN2(I)
1,II(I)
READ(5,1) A0(I),A1(I),A2(I),A3(I)
WRITE(6,1)A0(I),A1(I),A2(I),A3(I)
1 FORMAT(8F10.5)
NB(I)=NO2(I)+NN2(I)+NHCL(I)+NH2O(I)+NCL2(I)
DPH2O(I)=PI(I)*(NH2O(I)+2.0*NO2(I))/NB(I)
DPCL2(I)=PI(I)*(NCL2(I)+2.0*NO2(I))/NB(I)

```

```
15 DPHCL(I)=PI(I)*(NHCL(I)-4.0*NO2(I))/NB(I)
12 CFT=A0(II)+T*(A1(II)+T*(A2(II)+A3(II)*T))
   PH2O=DPH2O(II)-2.0*PO2
   PCL2=DPCL2(II)-2.0*PO2
   PHCL=DPHCL(II)+4.0*PO2
   PH2O=PH2O*CFT
   PCL2=PCL2*CFT
   PHCL=PHCL*CFT
   SUMC=SQRT(ABS(PO2))
   IF(SUMC.LT.1.0E-6) SUMC=1.0E-6
   FG=SUMC*PHCL**2-PH2O*PCL2/KE(II)
   GG=PHCL**2+B*PHCL**3+GA*PH2O*PHCL**2+A*PH2O*PCL2/KE(II)
   DFG=0.5*PHCL**2/SUMC+(8.0*SUMC*PHCL+2.0*(PCL2+PH2O)/KE(
1 II))*CFT
   DGG=(8.0*PHCL+12.0*B*PHCL**2+GA*(8.0*PH2O*PHCL-2.0*PHCL
1 **2)
1 -2.0*A*(PCL2+PH2O)/KE(II))*CFT
   G(1)=-K*PI(II)*W(II)*FG/(NB(II)*GG)
   IF(IJACK.LT.0) GOTO 15
   JX(1,1)=-K*PI(II)*W(II)*(DFG*GG-DGG*FG)/(NB(II)*GG**2)
   JK(1,1)=G(1)/K*0.001
   SUMC=K*PI(II)*W(II)*FG/(NB(II)*GG**2)
   JK(1,2)=SUMC*PHCL**3
   JK(1,3)=SUMC*PH2O*PHCL**2*10.0
   JK(1,4)=SUMC*PH2O*PCL2/KE(II)*100.0
15 RETURN
   END
```

APPENDIX E

Chemcell Problem

Batch reactor data has been accumulated for a complex kinetic system. Six experiments were performed at 100°C, and five at 80°C. Three principal components  $x_1$ ,  $x_2$ , and  $x_3$  can be, and were directly measured. A fourth is given by a linear relation between  $x_1$ ,  $x_3$  and one or more intermediates which exist but cannot be measured.

Each of the experiments was performed in a dilute acidic solution. The concentration of water (W) and of hydrogen ion ( $H^+$ ) were constant throughout any one experiment. The initial conditions for each of the components except  $x_1$  were all zero. The initial condition for  $x_1$  was the constant  $c_0$ .

The first model that was proposed could be represented by the system of equations given below.

$$\frac{dx_1}{dt} = - a_1 H x_1 + a_5 x_4 \quad (E-1)$$

$$\frac{dx_2}{dt} = a_2 W x_4 + a_3 x_5 - a_6 x_2 x_5 - a_7 H x_6 x_2 \quad (E-2)$$



$$\frac{dx_3}{dt} = a_4 x_5 \quad (E-3)$$

$$x_5 = \frac{(a_7 H x_2^+ - a_2 W) a_1 H x_1^+ - a_7 H x_2^+ (c_0 - x_1 - x_3) (a_1 + a_2 W)}{(a_2 W - a_7 H x_2^+) a_6 x_6 - (a_6 x_2 + a_3 + a_4 + a_7 H x_2^+) (a_5 + a_2 W)} \quad (E-4)$$

$$x_4 + \frac{a_1 H x_1^+}{a_5 + a_2 W} + \frac{a_6 x_2}{a_5 + a_2 W} x_5 \quad (E-5)$$

$$x_6 = c_0 - (x_1 + x_3 + x_4 + x_5) \quad (E-6)$$

All attempts to fit the above model failed to converge.

A second and partially successful attempt was made to fit the data to the model given below.

$$\frac{dx_1}{dt} = - a_1 H^+ W x_1 \quad (E-7)$$

$$\frac{dx_2}{dt} = a_2 x_4 - a_5 H^+ x_2 x_6 + a_1 H^+ x_1 \quad (E-8)$$

$$\frac{dx_3}{dt} = a_3 x_4 \quad (E-9)$$

$$x_4 = \frac{a_1 x_1 H^+ W + a_5 x_2 (c_0 - x_1 - x_3)}{a_2 + a_3 + a_5 H^+ x_2} \quad (E-10)$$

A different solution was obtained for this problem for each initial guess employed. With the 80°C data, different solutions were found for each initial guess. The first solution was found starting with the initial guess:

$$\underline{a} = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_5 \end{bmatrix} = \begin{bmatrix} 0.10 \\ 1.00 \\ 0.10 \\ 1.00 \end{bmatrix} \quad (\text{E-11})$$

and with the initial maximum step size  $S_{\max}$  being 0.01. With this initial guess the results in Table E-1 were obtained.

TABLE E-1

First Solution for 80°C Data

Phase I Step No.	a <sub>1</sub>	a <sub>2</sub>	a <sub>3</sub>	a <sub>5</sub>	Sum of Errors Squared
0	0.10	1.00	0.10	1.00	0.3475
2	0.0848	0.976	0.131	0.508	0.3063
3	0.0715	0.956	0.157	0.245	0.2660
4	0.0701	0.940	0.179	0.0919	0.2266
5	0.0504	0.929	0.196	0.00127	0.1889
6	0.1421	0.923	0.209	-0.0474	0.1528
7	0.0351	0.920	0.217	-0.0626	0.1187
8	0.0291	0.923	0.220	-0.0453	0.08703
9	0.0161	0.963	0.191	0.335	0.01584
Phase II					
Iteration No.					
0	0.0161	0.903	0.191	0.335	
1	0.00963	1.100	0.154	0.822	
2	0.0106	1.019	0.136	1.249	
3	0.01064	1.017	0.1379	1.302	
4	0.01064	1.017	0.1379	1.301	0.00007009

With the second initial guess

$$\underline{a} = \begin{bmatrix} 0.040 \\ 1.90 \\ 0.58 \\ 1.58 \end{bmatrix} \quad (E-12)$$

and the same value for  $S_{\max}$  the results were as presented in Table E-2.

TABLE E-2

Second Solution for 80°C Data

Phase II Step No.	$a_1$	$a_2$	$a_3$	$a_4$	Sum of Errors Squared
0	0.040	1.90	0.580	1.580	0.1351
1	0.0329	1.896	0.600	1.120	0.1011
2	0.0175	2.007	0.516	0.786	0.02112
Phase II Iteration No.					
0	0.0175	2.007	0.516	0.786	
1	0.00908	2.149	0.381	0.745	
2	0.0107	2.244	0.284	1.189	
3	0.0107	2.227	0.302	1.298	
4	0.0106	2.227	0.302	1.293	0.00006993

With the third initial guess

$$\underline{a} = \begin{bmatrix} 0.1 \\ 0.1 \\ 0.1 \\ 0.1 \end{bmatrix} \quad (E-13)$$

and with the same initial value for  $S_{\max}$  the results in Table E-3 were obtained.

TABLE E-3

Third Solution for 80°C Data

Phase I Step No.	$a_1$	$a_2$	$a_3$	$a_4$	Sum of Errors Squared
0	0.1	0.1	0.1	0.1	0.2553
1	0.0766	0.102	0.0996	-0.0282	0.2154
2	0.0585	0.106	0.0978	-0.1098	0.1740
3	0.0448	0.1106	0.0944	-0.1547	0.1332
4	0.0345	0.1173	0.0891	-0.1678	0.09506
5	0.0154	0.01547	0.0535	0.1374	0.01070
Phase II					
Iteration No.	$a_1$	$a_2$	$a_3$	$a_4$	Sum of Errors Squared
0	0.0154	0.1547	0.0535	0.137	
1	0.00979	0.1780	0.0305	0.561	
2	0.0106	0.1840	0.0245	1.120	
3	0.0106	0.1835	0.0245	1.377	
4	0.0106	0.1835	0.0250	1.374	0.00007195

A similar phenomenon was encountered when attempts were made to determine the parameters characteristic of the 100°C data. Three attempts were made, all with different results. For each of the attempts the initial value of the maximum step size was retained at 0.01.

For the first, second, and third initial guesses, the results are given in Tables E-4, E-5, and E-6 respectively.

TABLE E-4  
First Solution for 100°C Data

Step No.	$a_1$	$a_2$	$a_3$	$a_4$	Sum of Errors Squared
0	0.1	1.0	0.1	1.0	0.2470
1	0.0124	1.03	0.0760	17.7	0.2048
2	0.0152	1.04	0.0619	33.6	0.1664
3	0.0185	1.05	0.0582	41.5	1.1318
4	0.0223	1.05	0.0644	38.0	0.1009
5	0.0423	1.00	0.121	13.9	0.03033
6	0.0692	0.975	0.151	7.61	0.001763
7	0.0815	0.979	0.150	7.14	0.0002298

TABLE E-5

Second Solution for 100°C Data

Step No.	a <sub>1</sub>	a <sub>2</sub>	a <sub>3</sub>	a <sub>4</sub>	Sum of Errors Squared
0	0.070	2.00	0.400	5.00	0.002076
1	0.0787	2.06	0.339	6.52	0.0003089
2	0.0815	2.10	0.321	7.11	0.0002301

TABLE E-6

Third Solution for 100°C Data

Step No.	a <sub>1</sub>	a <sub>2</sub>	a <sub>3</sub>	a <sub>4</sub>	Sum of Errors Squared
0	0.1	0.1	0.1	0.1	0.02516
1	0.0922	0.126	0.0738	1.30	0.009845
2	0.0854	0.154	0.0461	3.52	0.001711
3	0.0815	0.174	0.0270	7.47	0.0002271

The data used to produced the results in the previous six tables are listed in Tables E-7 through to E-17. The SLOPE subroutines used are listed immediately following the data.

TABLE E-7

Data Set One 80°C

$$(H^+) = 1.27 \times 10^{-2} \text{ g-mole/l}$$

$$c_o = 7.91 \times 10^{-2} \text{ g-mole/l}$$

t(min)	x <sub>1</sub>	x <sub>2</sub> (g-mole/l)x10 <sup>2</sup>	x <sub>3</sub>
0.0	7.91	0.00	0.00
5.3	7.61	0.52	0.07
9.8	7.39	0.97	0.07
19.9	6.87	1.93	0.14
29.8	6.40	2.87	0.14
43.7	5.79	4.04	0.20
59.6	5.08	5.31	0.34
80.1	4.41	6.59	0.41
100.5	3.78	7.78	0.48
150.3	2.68	9.85	0.62
204.9	1.76	11.46	0.83
14440.0*	0.00	13.07	2.75
28880.0*	0.00	11.81	4.01

\*These points were not used to find the parameters



TABLE E-8

Data Set Two 80°C

$$(H^+) = 2.30 \times 10^{-2} \text{ g-mole/l}$$

$$c_o = 7.95 \times 10^{-2} \text{ g-mole/l}$$

t (min)	x <sub>1</sub>	x <sub>2</sub> (g-mole/l)x10 <sup>2</sup>	x <sub>3</sub>
0.0	7.95	0.00	0.00
2.57	7.69	0.44	0.07
5.32	7.40	1.03	0.07
10.13	6.92	1.98	0.07
15.20	6.49	2.77	0.14
20.05	6.06	3.60	0.19
29.70	5.26	5.12	0.27
39.82	4.55	6.38	0.41
59.50	3.47	8.41	0.53
80.00	2.64	9.94	0.67
101.47	1.96	11.17	0.80
150.65	0.98	12.91	1.01
200.48	0.50	13.67	1.23
14440.0*	0.00	11.98	3.92
28880.0*	0.00	10.66	5.23

\* These points were not used to find the parameters

TABLE E-9

Data Set Three at 80°C

$$(H^+) = 3.68 \times 10^{-2} \text{ g-mole/l}$$

$$c_o = 8.22 \times 10^{-2} \text{ g-mole/l}$$

t(min)	x <sub>1</sub>	x <sub>2</sub> (g-mole/l)x10 <sup>2</sup>	x <sub>3</sub>
0.0	8.22	0.0	0.00
1.75	7.93	0.51	0.07
4.72	7.48	1.41	0.07
10.52	6.55	3.13	0.20
14.87	6.02	4.19	0.20
19.78	5.37	5.35	0.34
30.28	4.32	7.34	0.47
39.82	3.48	8.87	0.60
61.00	2.20	11.23	0.80
82.12	1.35	12.79	0.96
99.98	0.92	13.50	1.09
149.95	0.32	14.38	1.43
299.40	0.11	14.57	1.64
14440.00*	0.00	11.28	5.15
28880.00*	0.00	10.12	6.32

\* These points were not used to find the parameters

TABLE E-12

Data Set Four at 80°C

$$(H^+) = 3.45 \times 10^{-2} \text{ g-mole/l}$$

$$c_o = 8.25 \times 10^{-2} \text{ g-mole/l}$$

t (min)	$x_1$	$x_2$ (g-mole/l) $\times 10^2$	$x_3$
0.0	8.25	0.00	0.00
2.42	7.86	0.73	0.07
4.85	7.49	1.38	0.14
9.97	6.71	2.88	0.20
15.03	6.00	4.18	0.33
19.80	5.44	5.28	0.34
29.63	4.44	7.10	0.53
41.43	3.42	8.99	0.68
59.55	2.38	10.95	0.81
83.95	1.41	12.66	1.04
101.30	0.96	13.45	1.14
150.55	0.39	14.23	1.50
202.75	0.14	14.50	1.72
14440.00*	0.0	11.31	5.19
28880.00*	0.0	9.51	6.99

\* These points were not used to determine the parameter

TABLE E-11

Data Set Five at 80°C

$$(H^+) = 6.98 \times 10^{-2} \text{ g-mole/l}$$

$$c_o = 8.35 \times 10^{-2} \text{ g-mole/l}$$

t (min)	$x_1$	$x_2$ g-mole/l) x 10 <sup>2</sup>	$x_3$
0.00	8.35	0.00	0.00
7.40	7.60	1.35	0.14
9.80	5.64	5.08	0.34
15.2	4.45	7.32	0.49
19.8	3.71	8.69	0.60
24.9	3.01	4.99	0.70
29.9	2.41	11.08	0.80
40.0	1.63	12.49	0.95
50.1	1.05	13.41	1.18
60.2	0.67	14.06	1.79
87.5	0.22	14.71	1.55
104.7	0.10	14.63	1.86
156.7	0.04	14.36	2.27
211.8	0.00	13.95	2.76
14440.0	0.00	10.26	6.44
28880.0	0.00	9.73	6.97

TABLE E-12

Data Set One at 100°C

$$(H^+) = 6.14 \times 10^{-3} \text{ g-mole/l}$$

$$c_o = 8.28 \times 10^{-2} \text{ g-mole/l}$$

t (min)	x <sub>1</sub>	x <sub>2</sub> (g-mole/l) x 10 <sup>2</sup>	x <sub>3</sub>
0	8.28	0.00	0.00
5.9	7.08	2.26	0.14
10.6	6.17	3.95	0.27
40.1	2.59	10.49	0.89
59.9	1.44	12.66	1.03
100.2	0.44	14.30	1.37
149.9	0.11	14.68	1.66
206.0	0.03	14.44	2.06

TABLE E-13

Data Set Two at 100°C

$$(H^+) = 9.86 \times 10^{-3} \text{ g-mole/l}$$

$$c_o = 7.81 \times 10^{-2} \text{ g-mole/l}$$

t (min)	x <sub>1</sub>	x <sub>2</sub> (g-mole/l) x 10 <sup>2</sup>	x <sub>3</sub>
0.00	7.84	0.00	0.00
5.1	6.28	2.92	0.20
10.2	4.88	5.50	0.42
20.7	2.91	9.16	0.70
39.6	1.16	12.33	1.04
60.1	0.40	13.57	1.30
100.3	0.07	13.88	1.66
150.1	0.00	13.62	2.06
200.0	0.00	13.26	2.43

TABLE E-14

Data Set Three at 100°C

$$(H^+) = 1.25 \times 10^{-2} \text{ g-mole/l}$$

$$c_o = 7.49 \times 10^{-2} \text{ g-mole/l}$$

t (min)	$x_1$	$x_2$ (g-mole/l) x 10 <sup>2</sup>	$x_3$
0.0	7.49	0.00	0.00
5.1	5.80	3.16	0.21
20.2	2.36	4.57	0.69
39.8	0.75	12.38	1.09
60.0	0.21	13.28	1.30
99.8	0.04	13.21	1.73
152.8	0.00	12.80	2.18
201.7	0.00	12.42	2.56

TABLE E-15

Data Set Four at 100°C

$$(H^+) = 2.41 \times 10^{-3} \text{ g-mole/l}$$

$$c_o = 7.74 \times 10^{-2} \text{ g-mole/l}$$

t (min)	$x_1$	$x_2$ (g-mole/l) x 10 <sup>2</sup>	$x_3$
0.0	7.74	0.00	0.00
5.9	7.29	0.82	0.07
20.5	6.23	2.82	0.20
40.6	5.05	5.05	0.34
59.7	4.06	6.88	0.48
100.0	2.72	9.35	0.69
150.8	1.60	11.40	0.88
203.9	0.85	12.69	1.09

TABLE E-16

Data Set Four at 100°C

$$(H^+) = 1.03 \times 10^{-2} \text{ g-mole/l}$$

$$c_o = 1.563 \times 10^{-2} \text{ g-mole/l}$$

t (min)	$x_1$	$x_2$ (g-mole/l) x 10 <sup>2</sup>	$x_3$
0.0	1.563	0.000	0.000
3.1	1.374	0.353	0.026
6.0	1.187	0.699	0.053
15.5	0.748	1.514	0.117
24.7	0.476	2.014	0.161
41.3	0.206	0.474	0.241
62.3	0.077	2.642	0.330
88.0	0.020	2.670	0.415
108.1	0.013	2.628	0.468
157.3	0.003	2.528	0.595
210.0	0.000	2.431	0.695

TABLE E-17

Data Set Six at 100°C

$$(H^+) = 1.20 \times 10^{-2} \text{ g-mole/l}$$

$$c_o = 7.59 \times 10^{-2} \text{ g-mole/l}$$

t (min)	$x_1$	$x_2$ (g-mole/l) x 10 <sup>2</sup>	$x_3$
0.0	7.59	0.00	0.00
2.4	6.84	1.44	0.07
5.3	5.92	3.12	0.22
9.8	4.59	5.59	0.41
15.1	3.47	7.70	0.54
20.0	2.64	9.22	0.68
30.6	1.47	11.41	0.83
39.6	0.90	12.35	1.04
49.5	0.52	12.98	1.17
60.9	0.30	13.17	1.40
80.5	0.11	13.42	1.54
101.6	0.00	13.35	1.83
160.7	0.00	13.02	2.16



```

SUBROUTINE SLOPE(R,T,IJACK)
C   SLOPE SUBROUTINE FOR THE SEVEN CONSTANT CHEMCELL
C   PROBLEM AT 80 DEGREES.
REAL*4 X(10,10),JX(10,10),JK(10,10),G(10),T(11,10),XO
1(30,10)
INTEGER R,NE,NK,NO,II,NDS,IJACK
COMMON /AB3/C,NE,NK,NO/AB5/JX,JK,X,G/AB8/XC,II,NDS
REAL*4 X1,X2,X3,X4,X5,X6,K1,K2,K3,K4,K5,K6,K7,H(05),W(0
15),CC(05)
1,FF,GG,GG2,DX4X1,DX4X2,DX4X3,DX4K1,DX4K2,DX4K3,DX4K4,DX
14K5,DX4K6,
1DX4K7,DX5X1,DX5X2,DX5X3,DX5K1,DX5K2,DX5K3,DX5K4,DX5K5,D
1X5K6,DX5K7
INTEGER I,J
DO 16 I=1,NE
IF(ABS(X(R,I)).LE.10.0) GOTO 16
WRITE(6,17)
STOP
16 CONTINUE
17 FORMAT(' OSTATE VARIABLE BOUND EXCEEDED' )
X1=X(R,1)
X2=X(R,2)
X3=X(R,3)
K1=C(R,1)
K2=C(R,2)
K3=C(R,3)
K4=C(R,4)
K5=C(R,5)
K6=C(R,6)
K7=C(R,7)
GOTC(11,12),NO
11 DO 13 I=1,NE
G(I)=0.0
DO 14 J=1,NE
14 JX(I,J)=0.0
DO 13 J=1,NK
13 JK(I,J)=0.0
NO=2
DATA H(1),W(1),CO(1)/0.0127,55.6,0.0791/
DATA H(2),W(2),CO(2)/0.0230,55.6,0.0795/
DATA H(3),W(3),CO(3)/0.0368,55.6,0.0822/
DATA H(4),W(4),CO(4)/0.0345,55.6,0.0825/
DATA H(5),W(5),CO(5)/0.0698,55.6,0.0835/
12 FF=(K7*H(11)*X2-K2*W(11))*K1*H(11)*X1-K7*H(11)*X2*(CO(I
11)-(X1+X3))
1*(K5+K2*W(11))
GG=(K2*W(11)-K7*H(11)*X2)*K6*X2-(K6*X2+K3+K4+K7*H(11)*X
12)*(K5+K2*
1W(11))
X5=FF/GG.

```

```

X4=(K1*H(II)*X1+K6*X2*X5)/(K5+K2*W(II))
G(1)=-K1*H(II)*X1+K5*X4
G(2)=K2*W(II)*X4+K3*X5-K6*X2*X5-K7*H(II)*X2*(CO(II)-(X1
1+X3+X4+X5))
G(3)=K4*X5
IF(IJACK.LT.0) GOTO 15
DX5X1=((K7*H(II)*X2-K2*W(II))*K1*H(II)+K7*H(II)*X2*(K5+
1K2*W(II)))/
1GG
DX5X2=((K7*K1*X1*H(II)**2-K7*H(II)*(CO(II)-(X1+X3))*(K5
1+K2)*W(II))
1*GG-(K6*(K2*W(II)-K7*H(II)*X2)-K7*H(II)*K6*X2-(K5+K2*W(
1II))*(K6+K7
2*H(II)))*FF)/GG**2
DX5X3=K7*H(II)*X2*(K5+K2*W(II))/GG
DX5K1=(K7*H(II)-K2*W(II))*H(II)*X1/GG
DX5K2=((-W(II)*K1*H(II)*X1-W(II)*K7*H(II)*X2*(CO(II)-(X
11+X3)))*GG
1-(W(II)*K6*X2-W(II)*(K6*X2+K3+K4+K7*H(II)*X2))*FF)/GG**
12
DX5K3=FF*(K5+K2*W(II))/GG**2
DX5K4=DX5K3
DX5K5=(-K7*H(II)*X2*(CO(II)-(X1+X3))*GG+(K6*X2+K3+K4+K7
1*H(II)*X2)*
1FF)/GG**2
DX5K6=(X2*(K5+K2*W(II))-(K2*W(II)-K7*H(II)*X2)*X2)*FF/G
1G**2
DX5K7=((X2*X1*K1*H(II)**2-H(II)*X2*(CO(II)-(X1+X3))*(K5
1+K2*W(II)))
1*GG+(H(II)*K6*X2**2+H(II)*X2*(K5+K2*W(II)))*FF)/GG**2
GG=K5+K2*W(II)
DX4X1=(K1*H(II)+K6*X2*DX5X1)/GG
DX4X2=K6*X5/GG+K6*X2*DX5X2/GG
DX4X3=K6*X2*DX5X3/GG
DX4K1=(H(II)*X1+K6*X2*DX5K1)/GG
DX4K2=(K6*X2*DX5K2*(K5+K2*W(II))-W(II)*(K1*H(II)*X1+K6*
1X2*X5))/GG*
1*2
DX4K3=K6*X2*DX5K3/GG
DX4K4=K6*X2*DX5K4/GG
DX4K5=(K6*X2*DX5K5*(K5+K2*W(II))-(K1*H(II)*X1+K6*X2*X5)
1)/GG**2
DX4K6=X2*(X5+DX5K6)/GG
DX4K7=K6*X2*DX5K7/GG
JX(1,1)=-K1*H(II)+K5*DX4X1
JX(1,2)=K5*DX4X2
JX(1,3)=K5*DX4X3
JK(1,1)=-H(II)*X1+K5*DX4K1
JK(1,2)=K5*DX4K2
JK(1,3)=K5*DX4K3

```

$$x_4 = (K_1 * H(I_1) * X_1 + K_6 * X_2 * X_5) / (K_5 + K_2 * W(I_1))$$

$$G(1) = -K_1 * H(I_1) * X_1 + K_5 * X_4$$

$$G(2) = K_2 * W(I_1) * X_4 + K_3 * X_5 - K_6 * X_2 * X_5 - K_7 * H(I_1) * X_2 * (C_0(I_1) - (X_1 + X_3 + X_4 + X_5))$$

$$G(3) = K_4 * X_5$$

IF(1JACK.LT.C) GOTO 15

$$DX5X1 = ((K_7 * H(I_1) * X_2 - K_2 * W(I_1)) * K_1 * H(I_1) + K_7 * H(I_1) * X_2 * (K_5 + K_2 * W(I_1))) /$$

$$1GG$$

$$DX5X2 = ((K_7 * K_1 * X_1 * H(I_1)) * 2 - K_7 * H(I_1) * (C_0(I_1) - (X_1 + X_3))) * (K_5 + K_2 * W(I_1))$$

$$1 * GG - (K_6 * (K_2 * W(I_1) - K_7 * H(I_1) * X_2) - K_7 * H(I_1) * K_6 * X_2 - (K_5 + K_2 * W(I_1)) * (K_6 + K_7$$

$$2 * H(I_1))) * FF) / GG * 2$$

$$DX5X3 = K_7 * H(I_1) * X_2 * (K_5 + K_2 * W(I_1)) / GG$$

$$DX5K1 = (K_7 * H(I_1) - K_2 * W(I_1)) * H(I_1) * X_1 / GG$$

$$DX5K2 = ((-W(I_1) * K_1 * H(I_1) * X_1 - W(I_1) * K_7 * H(I_1) * X_2 * (C_0(I_1) - (X_1 + X_3))) * GG$$

$$1 - (W(I_1) * K_6 * X_2 - W(I_1) * (K_6 * X_2 + K_3 + K_4 + K_7 * H(I_1) * X_2)) * FF) / GG * 2$$

$$12$$

$$DX5K3 = FF * (K_5 + K_2 * W(I_1)) / GG * 2$$

$$DX5K4 = DX5K3$$

$$DX5K5 = (-K_7 * H(I_1) * X_2 * (C_0(I_1) - (X_1 + X_3)) * GG + (K_6 * X_2 + K_3 + K_4 + K_7$$

$$1 * H(I_1) * X_2) *$$

$$1FF) / GG * 2$$

$$DX5K6 = (X_2 * (K_5 + K_2 * W(I_1)) - (K_2 * W(I_1) - K_7 * H(I_1) * X_2) * X_2) * FF / G$$

$$1G * 2$$

$$DX5K7 = ((X_2 * X_1 * K_1 * H(I_1)) * 2 - H(I_1) * X_2 * (C_0(I_1) - (X_1 + X_3))) * (K_5 + K_2 * W(I_1))$$

$$1 * GG + (H(I_1) * K_6 * X_2 * 2 + H(I_1) * X_2 * (K_5 + K_2 * W(I_1))) * FF) / GG * 2$$

$$GG = K_5 + K_2 * W(I_1)$$

$$DX4X1 = (K_1 * H(I_1) + K_6 * X_2 * DX5X1) / GG$$

$$DX4X2 = K_6 * X_5 / GG + K_6 * X_2 * DX5X2 / GG$$

$$DX4X3 = K_6 * X_2 * DX5X3 / GG$$

$$DX4K1 = (H(I_1) * X_1 + K_6 * X_2 * DX5K1) / GG$$

$$DX4K2 = (K_6 * X_2 * DX5K2 * (K_5 + K_2 * W(I_1)) - W(I_1) * (K_1 * H(I_1) * X_1 + K_6 *$$

$$1 * X_2 * X_5)) / GG *$$

$$1 * 2$$

$$DX4K3 = K_6 * X_2 * DX5K3 / GG$$

$$DX4K4 = K_6 * X_2 * DX5K4 / GG$$

$$DX4K5 = (K_6 * X_2 * DX5K5 * (K_5 + K_2 * W(I_1)) - (K_1 * H(I_1) * X_1 + K_6 * X_2 * X_5)$$

$$1) / GG * 2$$

$$DX4K6 = X_2 * (X_5 + DX5K6) / GG$$

$$DX4K7 = K_6 * X_2 * DX5K7 / GG$$

$$JX(1,1) = -K_1 * F(I_1) + K_5 * DX4X1$$

$$JX(1,2) = K_5 * DX4X2$$

$$JX(1,3) = K_5 * DX4X3$$

$$JK(1,1) = -n(I_1) * X_1 + K_5 * DX4K1$$

$$JK(1,2) = K_5 * DX4K2$$

$$JK(1,3) = K_5 * DX4K3$$

```

JK(1,4)=K5*DX4K4
JK(1,5)=K5*DX4K5+X4
JK(1,6)=K5*DX4K6
JK(1,7)=K5*DX4K7
JX(2,1)=K2*W(11)*DX4X1+(K3-K6*X2)*DX5X1+K7*H(11)*X2*(1.

```

```

10+DX4X1+
1DX5X1)

```

```

JX(2,2)=K2*W(11)*DX4X2+(K3-K6*X2)*DX5X2-K6*X5-K7*H(11)*
1(CO(11)-
1(X1+X3+X4+X5))+K7*H(11)*X2*(DX4X2+DX5X2)

```

```

JX(2,3)=K2*W(11)*DX4X3+(K3-K6*X2)*DX5X3+K7*H(11)*X2*(1.
10+DX4X3+DX5
1X3)

```

```

JK(2,1)=K2*W(11)*DX4K1+(K3-K6*X2)*DX5K1+K7*H(11)*X2*(DX
14K1+DX5K1)

```

```

JK(2,2)=W(11)*X4+K2*W(11)*DX4K2+(K3-K6*X2)*DX5K2+K7*H(1
11)*X2*(DX4K
12+DX5K2)

```

```

JK(2,3)=X5+K2*W(11)*DX4K3+(K3-K6*X2)*DX5K3+K7*H(11)*X2*
1(DX4K3+DX5K
13)

```

```

JK(2,4)=K2*W(11)*DX4K4+(K3-K6*X2)*DX5K4+K7*H(11)*X2*(DX
14K4+DX5K4)

```

```

JK(2,5)=K2*W(11)*DX4K5+(K3-K6*X2)*DX5K5+K7*H(11)*X2*(DX
14K5+DX5K5)

```

```

JK(2,6)=X2*X5+K2*W(11)*DX4K6+(K3-K6*X2)*DX5K6+K7*H(11)*
1X2*(DX4K6+D
1X5K6)

```

```

JK(2,7)=H(11)*X2*(CO(11)-(X1+X3+X4+X5))+K2*W(11)*DX4K7+
1(K3-K6*X2)*
1DX5K7+K7*H(11)*X2*(DX4K7+DX5K7)

```

```

JX(3,1)=K4*DX5X1

```

```

JX(3,2)=K4*DX5X2

```

```

JX(3,3)=K4*DX5X3

```

```

JK(3,1)=K4*DX5K1

```

```

JK(3,2)=K4*DX5K2

```

```

JK(3,3)=K4*DX5K3

```

```

JK(3,4)=X5+K4*DX5K4

```

```

JK(3,5)=K4*DX5K5

```

```

JK(3,6)=K4*DX5K6

```

```

JK(3,7)=K4*DX5K7

```

```

15 RETURN
END

```

```

SUBROUTINE SLOPE(R,T,IJACK)
C      SLOPE SUBROUTINE FOR THE FOUR CONSTANT CHEMCELL
C      PROBLEM AT 80 DEGREES.
      REAL*8 X(10,05),JX(05,05),JK(05,05),G(05),T,C(11,05),XD
      1(30,05)
      INTEGER R,NE,NK,NO,II,NDS,IJACK
      COMMON /AB3/C,NE,NK,NO/AB5/JX,JK,X,G/AB8/XC,II,NDS
      REAL*8 X1,X2,X3,X4,X5,X6,K1,K2,K3,K4,K5,K6,K7,H(05),W(0
      15),CO(05)
      1,FF,GG,GG2,DX4X1,DX4X2,DX4X3,DX4K1,DX4K2,DX4K3,DX4K4,DX
      14K5
      INTEGER I,J
      DO 16 I=1,NE
      IF(DABS(X(R,I)).LE.10.0) GOTO 16
      WRITE(6,17)
      STOP
16 CONTINUE
17 FORMAT('OSTATE VARIABLE BOUND EXCEEDED')
      X1=X(R,1)
      X2=X(R,2)
      X3=X(R,3)
      K1=C(R,1)
      K2=C(R,2)
      K3=C(R,3)
      K5=C(R,4)
      GUTC(11,12),NO
11 DO 13 I=1,NE
      G(I)=0.0
      DO 14 J=1,NE
14 JX(I,J)=0.0
      DO 13 J=1,NK
13 JK(I,J)=0.0
      NG=2
      K4=C.0
      DATA H(1),W(1),CO(1)/0.0127,55.6,0.0791/
      DATA H(2),W(2),CO(2)/0.0230,55.6,0.0795/
      DATA H(3),W(3),CO(3)/0.0368,55.6,0.0822/
      DATA H(4),W(4),CO(4)/0.0345,55.6,0.0825/
      DATA H(5),W(5),CO(5)/0.0698,55.6,0.0835/
12 X5=CO(II)-X1-X3
      FF=K5*H(II)*X2*X5+K1*H(II)*W(II)*X1
      GG=K2+K3+K4*X2+K5*H(II)*X2
      X4=FF/GG
      X6=X5-X4
      G(1)=-K1*H(II)*W(II)*X1+K4*X2*X4
      G(2)=K2*X4+K1*H(II)*W(II)*X1-K4*X2*X4-K5*H(II)*X2*X6
      G(3)=K3*X4
      IF(IJACK.LT.0) GOTO 15
      GG2=GG**2
      DX4X1=(K1*H(II)*W(II)-K5*H(II)*X2)/GG

```

$$DX4X2=(K5*H(II)*X5*GG-(K4+K5*H(II))*FF)/GG2$$

$$DX4X3=-K5*H(II)*X2/GG$$

$$DX4K1=H(II)*W(II)*X1/GG$$

$$DX4K2=-1.0/GG2$$

$$DX4K3=DX4K2$$

$$DX4K4=X2*DX4K2$$

$$DX4K5=(H(II)*X2*X5*GG-H(II)*X2*FF)/GG2$$

$$JX(1,1)=-K1*H(II)*W(II)+K4*X2*DX4X1$$

$$JX(1,2)=K4*X4+K4*X2*DX4X2$$

$$JX(1,3)=K4*X2*DX4X3$$

$$JK(1,1)=-H(II)*W(II)*X1+K4*X2*DX4K1$$

$$JK(1,2)=K4*X2*DX4K2$$

$$JK(1,3)=K4*X2*DX4K3$$

$$JK(1,4)=K4*X2*DX4K5$$

$$FF=K2-K4*X2+K5*H(II)*X2$$

$$JX(2,1)=K1*H(II)*W(II)+K5*H(II)*X2+FF*DX4X1$$

$$JX(2,2)=-K4*X4-K5*H(II)*X6+FF*DX4X2$$

$$JX(2,3)=FF*DX4X3+K5*H(II)*X2$$

$$JK(2,1)=FF*DX4K1+H(II)*W(II)*X1$$

$$JK(2,2)=FF*DX4K2+X4$$

$$JK(2,3)=FF*DX4K3$$

$$JK(2,4)=FF*DX4K5-H(II)*X2*X6$$

$$JX(3,1)=K3*DX4X1$$

$$JX(3,2)=K3*DX4X2$$

$$JX(3,3)=K3*DX4X3$$

$$JK(3,1)=K3*DX4K1$$

$$JK(3,2)=K3*DX4K2$$

$$JK(3,3)=K3*DX4K3+X4$$

$$JK(3,4)=K3*DX4K5$$

15 RETURN

END

```

SUBROUTINE SLOPE(R,T,IJACK)
C      SLOPE SUBROUTINE FOR THE FOUR CONSTANT CHEMCELL
C      PROBLEM AT 100 DEGREES.
REAL*8 X(10,05),JX(05,05),JK(05,05),G(05),T,C(11,05),X0
1(30,05)
INTEGER R,NE,NK,NU,II,NDS,IJACK
COMMON /AB3/C,NE,NK,NU/AB5/JX,JK,X,G/AB8/XC,II,NDS
REAL*8 X1,X2,X3,X4,X5,X6,K1,K2,K3,K4,K5,K6,K7,H(06),W(0
16),CO(06)
1,FF,GG,GG2,DX4X1,DX4X2,DX4X3,DX4K1,DX4K2,DX4K3,DX4K4,DX
14K5
INTEGER I,J
DO 16 I=1,NE
IF(DABS(X(R,I)).LE.10.0) GOTO 16
WRITE(6,17)
STOP
16 CONTINUE
17 FORMAT('OSTATE VARIABLE BOUND EXCEEDED')
X1=X(R,1)
X2=X(R,2)
X3=X(R,3)
K1=C(R,1)
K2=C(R,2)
K3=C(R,3)
K5=C(R,4)
GOTO(11,12),NU
11 DO 13 I=1,NE
G(I)=0.0
DO 14 J=1,NE
14 JX(I,J)=0.0
DO 13 J=1,NK
13 JK(I,J)=0.0
NU=2
K4=0.0
DATA H(1),W(1),CO(1)/0.012,55.6,0.0759/
DATA H(2),W(2),CO(2)/0.00241,55.6,0.0774/
DATA H(3),W(3),CO(3)/0.00614,55.6,0.0828/
DATA H(4),W(4),CO(4)/0.00986,55.6,0.0784/
DATA H(5),W(5),CO(5)/0.0125,55.6,0.0749/
DATA H(6),W(6),CO(6)/0.0103,55.6,0.01563/
12 X5=CO(11)-X1-X3
FF=K5*H(11)*X2*X5+K1*H(11)*W(11)*X1
GG=K2+K3+K4*X2+K5*H(11)*X2
X4=FF/GG
X6=X5-X4
G(1)=-K1*H(11)*W(11)*X1+K4*X2*X4
G(2)=K2*X4+K1*H(11)*W(11)*X1-K4*X2*X4-K5*H(11)*X2*X6
G(3)=K3*X4
IF(IJACK.LT.0) GOTO 15
GG2=GG**2

```

```
DX4X1=(K1*H(II)*W(II)-K5*H(II)*X2)/GG
DX4X2=(K5*H(II)*X5*GG-(K4+K5*H(II))*FF)/GG2
DX4X3=-K5*H(II)*X2/GG
DX4K1=H(II)*W(II)*X1/GG
DX4K2=-1.0/GG2
DX4K3=DX4K2
DX4K4=X2*DX4K2
DX4K5=(H(II)*X2*X5*GG-H(II)*X2*FF)/GG2
JX(1,1)=-K1*H(II)*W(II)+K4*X2*DX4X1
JX(1,2)=K4*X4+K4*X2*DX4X2
JX(1,3)=K4*X2*DX4X3
JK(1,1)=-H(II)*W(II)*X1+K4*X2*DX4K1
JK(1,2)=K4*X2*DX4K2
JK(1,3)=K4*X2*DX4K3
JK(1,4)=K4*X2*DX4K5
FF=K2-K4*X2+K5*H(II)*X2
JX(2,1)=K1*H(II)*W(II)+K5*H(II)*X2+FF*DX4X1
JX(2,2)=-K4*X4-K5*H(II)*X6+FF*DX4X2
JX(2,3)=FF*DX4X3+K5*H(II)*X2
JK(2,1)=FF*DX4K1+H(II)*W(II)*X1
JK(2,2)=FF*DX4K2+X4
JK(2,3)=FF*DX4K3
JK(2,4)=FF*DX4K5-H(II)*X2*X6
JX(3,1)=K3*DX4X1
JX(3,2)=K3*DX4X2
JX(3,3)=K3*DX4X3
JK(3,1)=K3*DX4K1
JK(3,2)=K3*DX4K2
JK(3,3)=K3*DX4K3+X4
JK(3,4)=K3*DX4K5
15 RETURN
END
```



APPENDIX F

Tracer Problem

In order to correlated the behavior of the flow of a tracer through a packed bed, the following mathematical model was used.

$$\frac{dx_1}{dt} = x_2$$

$$\frac{dx_2}{dt} = - a_1 x_2 - a_2 [x_1 - f(t - t_D)] \quad (F-1)$$

The state variable  $x_1$  is the outlet concentration of the tracer. The inlet concentration at a time  $t$  is given by  $f(t)$ . The time delay  $t_D$  is not known but must be assumed in order to use the proposed method. The optimum time delay was determined by search.

To solve for the parameters  $a_1$  and  $a_2$  was not difficult once a time delay was specified.

Setting the maximum step size  $S_{\max}$  to 0.1 and the initial guess to

$$\underline{a} = \begin{bmatrix} 1.0 \\ 1.0 \end{bmatrix} \quad (F-2)$$

the solution converged rapidly, as shown in Table F-1, which gives the results for the optimum time delay ( $t_D = 0.187$ ).

TABLE F-1

Tracer Problem  $t_D = 0.187$

Phase I Step No.	$a_1$	$a_2$	Sum of Errors Squared
0	1.0	1.0	0.116
1	5.47	5.24	0.032
Phase II Iteration			
0	5.47	5.24	
1	9.42	11.43	
2	6.34	10.31	
3	6.54	10.62	0.00035

For the other values of the time delay considered, rapid convergence was also obtained.

The SLOPE subroutine required for this problem is listed on the following pages.

```

SUBROUTINE SLOPE(R,T,IJACK)
C ..... SLOPE SUBROUTINE FOR THE TRACER PROBLEM.
REAL X(10,10),JX(10,10),JK(10,10),G(10),T,C(11,10),X0(3
10,10)
INTEGER R,NE,NK,NO,I1,NDS,IJACK
COMMON /AB3/C,NE,NK,NO/AB5/JX,JK,X,G/AB8/X0,I1,NDS
REAL X1,X2,K1,K2,K3,K4,X3,X4
INTEGER I,J
DO 16 I=1,NE
IF(ABS(X(R,I)).LE.10.0) GOTO 16
WRITE(6,17)
STOP
16 CONTINUE
17 FORMAT('OSTATE VARIABLE BOUND EXCEEDED')
X1=X(R,1)
X2=X(R,2)
K1=C(R,1)
K2=C(R,2)
GOTO(11,12),NO
11 DO 13 I=1,NE
G(I)=0.0
DO 14 J=1,NE
14 JX(I,J)=0.0
DO 13 J=1,NK
13 JK(I,J)=0.0
NO=2
A=0.186
12 S11=S1(T-A,I1)
G(1)=X2
G(2)=-K1*X2-K2*(X1-S11)
IF(IJACK.LT.0) RETURN
JX(1,2)=1.0
JX(2,1)=-K2
JX(2,2)=-K1
JK(2,1)=-X2
JK(2,2)=-X1+S11
RETURN
END

```

```
REAL FUNCTION S1(T,I)
C      INPUT FUNCTION REQUIRED BY THE SLOPE SUBROUTINE FOR
C      THE TRACER PROBLEM
      S1=0.75
      IF(T.LT.0.0) -GOTO 10
      GOTC(11,12,13,14),I
11  S1=S1+C.25*SIN(10.0*T)
      GOTO 10
12  S1=S1+C.25*SIN(1.0*T)
      GOTO 10
13  S1=S1+C.25*SIN(0.1*T)
      GOTC 10
14  S1=S1+C.25*SIN(5.0*T)
10  RETURN
      END
```