SOME STUDIES OF SIMULATION AND ANALYSIS
OF INDICATOR REACTIONS FOR
CATALYTIC DETERMINATIONS

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BENNY EDWARD SIMPSON

Bachelor of Science

Oklahoma State University

Stillwater, Oklahoma

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SOME STUDIES OF SIMULATION AND ANALYSIS OF INDICATOR REACTIONS FOR CATALYTIC DETERMINATIONS

Thesis Approved:

Horacio A Mottola
Thesis Adviser

Tom E. Moore

H. Olin Spivey

N Durham
Dean of the Graduate College

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LIST OF ABBREVIATIONS

A = absorbance

C = catalyst

Cx = oxidized form of a catalyst

C_X = total analytical concentration of X

cat. = catalyzed

Dr = reduced form of a dye

Dx = oxidized form of a dye

ε = molar absorptivity of a dye solution

K_{eq} = equilibrium constant of first step in mechanism

K_f = formation constant

k = rate constant

Ox = oxidizing agent

Q = a reaction intermediate

R = reducing agent

T = transmittance

uncat. = uncatalyzed

$[X]$ = concentration of X in moles/liter

$[X]_o$ = total or initial concentration of X in moles/liter

CHAPTER I

INTRODUCTION

If a given sample is titrated with a species which has a catalytic effect on an independent reaction, the abrupt increase in rate of this independent reaction after the equivalence point in the titration has been reached may be used as an effective end-point detector. This method of end-point detection is referred to as catalytic end-point indication and the independent reaction is called the indicator reaction (1). This study is part of an effort to characterize these indicator reactions; particular attention has been given to a single selected chemical system.

Use of the digital computer to analyze the differential equations describing an indicator reaction allowed both the estimation of system parameters and the selection of a simplified mechanism which best described the system. Computer analysis consisted of two primary parts: (1) use of least-squares fitting to estimate rate constants assuming a particular simplified mechanism given absorbance versus time data and (2) simulation of absorbance versus time curves given system parameters and a mathematical model describing the system.

A review of existing simulators and modeling programs showed that considerable work had been done, especially in the area of bio-chemical enzyme systems. Methods of expressing and obtaining mathematical models vary, but almost all users of simulating techniques relied on one or more differential equations to show the dynamic qualities of their systems. Programs were of two general types: (1) those which simulated reactions given system parameters (2,3,4) and (2) those which analyzed data to obtain unknown parameters (5,6).

In the first class, extensive work had been done by Garfinkel who, in one particular simulation (2), used over 80 parameters in the model to simulate the concentration of all the species present in an enzyme system. This type of simulation (i.e.-curves given parameters) was fairly well cut and dried although no reference was found wherein a concentration gradient was introduced as is done in catalytic titrations.

In the second class of papers (determination of constants given absorbance versus time data), the work reported in reference (5) seems to represent the most general and readily adaptable program available. The authors used linear regression analysis to determine the parameters of a set of differential equations. A general outline for the analysis was given along with examples of both simple systems and output of the program. Output consisted of parameters and their standard errors. As in the papers mentioned above, no concentration ramp was included in the model.

A paper by Atkinson (6) was on a somewhat more basic level and dealt with a system quite similar to those used in catalytic titrations. He presented a straight forward outline of the elucidation of rate constants using a non-linear least squares method. In addition, some discussion of flow rates and statistical analysis was given.

A review of existing computer programs for the study of chemical systems, especially bio-chemical kinetics, has been prepared by Garfinkel, et al. (7), and includes discussions of theoretical aspects, applications, and programming languages and methodology. Childs and coauthors (8) have dealt more specifically with analytical applications of computers in their review and list at least ten references to programs dealing with reaction kinetics.

The programs which have been developed from this present study are original programs, based upon the same fundamental principals as those mentioned above. The advantages of this approach, that is development of original programs for specific problems as opposed to using an already developed "canned" program, lie chiefly in being better able to utilize computer time and storage space by omitting much of the programming necessary to make a program completely general. Thus, the work was not undertaken to offer a cure-all for all kinetic and mechanistic studies, but to develop a comparatively small and inexpensive set of programs for use only in the area of indicator reactions for catalytic end-point indication.

This study consists of two principle thrusts: (1) the use of a hypothetical chemical system for the development and testing of computer programs and (2) the application of these programs to a real system. The hypothetical system presented are not intended to approach generality, but are specific, totally hypothetical reactions used only for the purpose of developing computer programs and for showing the capabilities of those programs in the analysis of a given system. Chapter III in its entirety consists of the study of these hypothetical systems. Chapter IV, on the other hand, is devoted to showing the utility of the programs in deriving information about a real chemical system.

CHAPTER II

EXPERIMENTAL

Apparatus

Previous work in this lab involving catalytic end-point indication has been carried out using a Beckman DB spectrophotometer and a flow cell utilizing a peristaltic pump (9). However, the need for more reliable data and broader instrument response has prompted the introduction of the use of the Cary 14 spectrophotometer in the study of indicator reactions for catalytic end-point indication.

Using the Cary 14, titrations were done directly into the sample cell, thus eliminating any time lag between the introduction of the catalyst or other reactant and measurement of the resulting absorbance. Mixing of the reactants once in the cell called for a special stirring arrangement in the Cary 14 cell compartment. Such a cell holder has been designed and reported in the literature (10).

The holder, constructed mainly of phenolic resin due to its antimagnetic properties, features a brass, thermostatable cell compartment and an eight pound block of lead to act as ballast to help cut down vibration effects. The actual stirrer is first wrapped with approximately one hundred turns of fine enameled wire then coated with silicone rubber to both hold the coil in place and to provide additional insurance against vibration. The rate of rotation of the stirrer is monitored by measuring the current output of the coil surrounding the spinning magnet with an ordinary ammeter having a 100 micro-amp movement. Calibration of stirring speed versus current was accomplished by connecting the output leads of the stirrer to an event counter then recording the number of "events" for a given amount of time. Details of construction and performance are given in reference 10.

The constant speed, motor driven buret used in the catalytic titrations is also described in the reference mentioned above (10).

Reagents

All reagents used were prepared as outlined by Mottola and Harrison (11) with the exception of solutions of nitrilotriacetic acid (NTA). The free acid form of NTA is not soluble in water to the degree needed to prepare a useful stock solution of ~10^{-2} M. The NTA dissolved, however, when an excess of sodium acetate, a weak base, was added. The NTA was standardized potentiometrically by titrating the acetic acid liberated upon the dissolution of the pure NTA in sodium acetate with standard base (0.01 N NaOH).

Procedure

Preparation of Reaction Mixture

One ml of dye solution, periodate solution, and ligand solution (if any) were pipetted into a 10 ml volumetric flask. Five ml of buffer were then added and the mixture diluted to 10 ml with distilled water.

Obtaining Titration Curves

Three ml of the reaction mixture were pipetted into a one cm spectrophotometer cell which was then placed into the special cell holder in the Cary 14. The motor driven buret containing titrant was then moved into position above the cell compartment with the tip of the buret just below liquid level in the cell. Addition of catalyst was initiated by manually turning on the power to the motor driven buret. The time at which catalyst actually reached the solution in the cell, that is, $t=0$, was determined in the following manner. The amount of time required for the catalyst solution in the syringe to travel from a given index mark to the tip of the syringe was determined in separate experiments. After turning on the buret motor, a mark was placed on the chart paper after the delay time mentioned above had elapsed.

Standardization of NTA

The amount of NTA necessary to give the desired concentration was dissolved in a sodium acetate solution containing at least an equimolar amount of sodium acetate. It was found that a 50-100 per cent excess acetate gave good results and fairly fast dissolution of the NTA. Twenty-five ml of the resulting solution was pipetted into a beaker and diluted with another 25 ml of distilled water. The solution was then titrated with standard 0.01 M sodium hydroxide while recording the pH as a function of volume. The molarity of the NTA was calculated, realizing that at the observed pH of the original NTA solution (pH = 4.7), two moles of acetic acid were released for each mole of NTA present.

CHAPTER III

COMPUTER PROGRAMS

Simulation Program

The original plans for this study called for the use of CSMP, a Continuous System Modeling Program available from IBM. Initial efforts at using this language proved awkward, due primarily to fairly strict format limitations as to plot dimensions, data input and output, and sub-program structure. Due to these problems, in addition to debugging problems, CSMP was dropped and a FORTRAN IV program was written to do the simulation. For the particular application being studied here, FORTRAN IV offered several advantages over the more general CSMP program, namely: (1) greater output flexibility in both plots and numerical values, (2) execution of FORTRAN IV on the WATFIV terminal was about 60-70 per cent less expensive than the same job done with CSMP, (3) the programmer could know exactly what was going on in the execution of his program since he wrote the coding himself, and (4) FORTRAN IV or some other FORTRAN dialect is available on virtually every compiler whereas CSMP is usually limited to large computer installations.

Development of Simulation Program

The heart of any simulating program is the integration of the differential equations describing the system. The method used in the present study was trapezoidal integration. When compared to plots obtained using Runge-Kutta methods (12), the trapezoidal method gave the same results for a hypothetical system similar to the one which was chosen for study. The recursion relation for trapezoidal integration is as follows (13):

$$\text{Predictor:} \quad Y^{P}_{t + \Delta t} = Y_t + \Delta t \cdot X_t$$

$$\text{Estimator:} \quad Y_{t + \Delta t} = Y_t + \frac{\Delta t}{2} (X_t + X_{t + \Delta t})$$

$$\text{where:} \quad Y = f(t) \text{ and } X_t = \frac{dY}{dt} = f'(t)$$

A check of the integration technique is given in Appendix A.

A block diagram flow chart of the simulation program along with a complete print-out of the source program including definition of all FORTRAN variable names is given in Appendix B.

Application of Simulation Program to a Hypothetical System

It was felt that the best way to gain an insight into simulation applications was to use the program on a simplified hypothetical system before the study of a real experimental system. This also presented an opportunity to demonstrate the utility of the simulation program in predicting the shape of a titration curve as a function of various parameters. The following topics will be discussed in this section: (1) study of the pre-equilibrium and steady-state conditions without the presence of a complexing agent in the system, (2) study of several possibilities of three-body collisions in both the steady-state and pre-equilibrium conditions, and (3) study of steady-state and pre-equilibrium conditions in the presence of both inhibitory and rate increasing ligands.

The generalized equation of the reaction to be studied is the following:

$$Dr + Ox \overset{(C)}{=} Dx + R \tag{3-1}$$

where:

Dr = reduced form of a dye,

Ox = oxidizing agent,

Dx = oxidized form of dye,

R = reducing agent, and

C = catalyst.

<u>Pre-equilibrium Condition--No Complexing Agent</u>

In the pre-equilibrium approach, the catalyzed reaction is viewed as proceeding in the following manner:

$$C + Ox \underset{k_{-1}}{\overset{k_1}{=}} Cx + R \tag{3-2}$$

$$Cx + Dr \overset{k_2}{=} Dx + C \tag{3-3}$$

where, now, Cx = oxidized form of the catalyst and:

$$K_{eq} = \frac{[Cx]_{eq}[R]_{eq}}{[C]_{eq}[Ox]_{eq}} \tag{3-4}$$

If an equilibrium condition is assumed to exist in the first and faster step (Equation 3-2), then the second step (Equation 3-3) will be rate determining and the rate will be given by:

$$\text{rate} = -k_2[\text{Cx}][\text{Dr}] \qquad (3\text{-}5)$$

Using Equation 3-2 and the stoichiometry of the system, we may express the equilibrium concentrations of the various species as functions of their initial concentrations and the instantaneous concentration of the "activated" catalyst, Cx. That is:

$$[\text{Ox}]_{eq} = [\text{Ox}]_o - [\text{Cx}] \qquad (3\text{-}6)$$

$$[\text{C}]_{eq} = [\text{C}]_o - [\text{Cx}] \qquad (3\text{-}7)$$

$$[\text{R}]_{eq} = [\text{Cx}] \qquad (3\text{-}8)$$

We can then use these expressions along with Equation 3-4 to give:

$$[\text{Cx}] = \frac{([\text{C}]_o + [\text{Ox}]_o) \pm \sqrt{([\text{C}]_o - [\text{Ox}]_o)^2 + (4[\text{C}]_o[\text{Ox}]_o/K_{eq})}}{2(1 - 1/K_{eq})} \qquad (3\text{-}9)$$

Stoichiometry requires acceptance of the positive root and substitution into Equation 3-5 gives the final form of the catalyzed rate:

$$\text{rate} = \frac{-k_2[\text{Dr}]\{([\text{C}]_o+[\text{Ox}]_o) + \sqrt{([\text{C}]_o-[\text{Ox}]_o)^2+(4[\text{C}]_o[\text{Ox}]_o/K_{eq})^{\frac{1}{2}}}\}}{2(1 - 1/K_{eq})} \qquad (3\text{-}10)$$

It can be seen that if K_{eq} is large, $1/K_{eq}$ approaches zero and Equation 3-9 reduces to:

$$[\text{Cx}] = [\text{C}]_o \qquad (3\text{-}11)$$

which leads to the simpler rate expression:

$$\text{rate} = - k_2[\text{Dr}][\text{C}]_o \qquad (3\text{-}12)$$

For the special case when $K_{eq} = 1$, no second degree terms appear and the "activated" catalyst concentration is given by:

$$[\text{Cx}] = \frac{[\text{C}]_o[\text{Ox}]_o}{[\text{C}]_o + [\text{Ox}]_o} \qquad (3\text{-}13)$$

The validity of the assumption leading to Equation 3-11 was verified using computer simulation. Curves were generated using Equation 3-10 as the model letting Keq range from 10^8 to 10.0. No difference was observed in any of these curves.

In addition, a simulation using Equation 3-12 was identical to a curve generated from Equation 3-13 wherein there is no ambiguity in choice of root. This observation further verifies that for all K_{eq} greater than or equal to 1, the assumptions leading to Equation 3-11 are indeed valid.

Steady-State Condition--No Complex Added

In the steady-state approximation, we again look at Equations 3-1, 3-2, and 3-3. Instead of allowing an equilibrium condition to be established, however, we assume that the "activated" catalyst is consumed as rapidly as it is formed, that is:

$$\frac{d[\text{Cx}]}{dt} = 0 = k_1[\text{Ox}][\text{C}] - k_{-1}[\text{Cx}][\text{R}] - k_2[\text{Cx}][\text{Dr}] \qquad (3\text{-}14)$$

which leads to:

$$[\text{Cx}] = \frac{k_1[\text{Cx}][\text{C}]}{k_{-1}[\text{R}] + k_2[\text{Dr}]} \qquad (3\text{-}15)$$

Equation 3-2 is then rate determining and:

$$\text{rate} = k_1[\text{Ox}][\text{C}] - k_{-1}[\text{Cx}][\text{R}] \tag{3-16}$$

Substitution of Equation 3-15 into Equation 3-16 gives:

$$\text{rate} = \frac{-k_1k_2[\text{Dr}][\text{Ox}][\text{C}]}{k_{-1}[\text{R}] + k_2[\text{Dr}]} \tag{3-17}$$

Once again, stoichiometry leads to:

$$[\text{Dr}] = [\text{Dr}]_o - ([\text{Ox}]_o - [\text{Ox}]) \tag{3-18}$$

$$[\text{R}] = [\text{Dr}]_o - [\text{Dr}] \tag{3-19}$$

$$[\text{Ox}] = [\text{Dr}] - [\text{Dr}]_o + [\text{Ox}]_o \tag{3-20}$$

Substitution into Equation 3-17 yields the final, steady-state rate expression:

$$\text{rate} = \frac{-k_1k_2[\text{Dr}]([\text{Dr}] - [\text{Dr}]_o + [\text{Ox}]_o)[\text{C}]_o}{k_{-1}([\text{Dr}]_o - [\text{Dr}]) + k_2[\text{Dr}]} \tag{3-21}$$

If k_2 is much greater than k_{-1}, this expression simplifies to:

$$\text{rate} = -k_1([\text{Dr}] - [\text{Dr}]_o + [\text{Ox}]_o)[\text{C}]_o \tag{3-22}$$

Computer simulation showed that the results of using Equations 3-21 and 3-22 are identical for given values of k_1, the rate constant for the forward and rate determining reaction. It appears from these comparisons that the expression given in Equation 3-22 is a valid model for the steady state approximation under the specified conditions.

Consideration of a Three-Body Collision in the Mechanism of Reaction

The previous discussions concerned only two-body collisions in the mechanism of reaction. If three-body collisions are considered, several possible combinations occur. The most significant possibilities are discussed.

References are made to the generalized equations:

$$aC + bOx \underset{k_{-1}}{\overset{k_1}{=}} aCx + bR \qquad (3\text{-}23)$$

$$cCx + dDr \overset{k_2}{=} cC + dDx \qquad (3\text{-}24)$$

$$K_{eq} = [Cx]^a[R]^b/[C]^a[Ox]^b \qquad (3\text{-}25)$$

The procedure followed in all of the following derivations is the same as that used in the previous sections, therefore, only important results will be presented in this discussion. Complete derivations may be found in Appendix C.

Pre-equilibrium Condition-- a = 2, b = 1

In this situation, the expression for the activated catalyst concentration is a cubic equation which requires numerical solution. Using such a method, the concentration of the activated catalyst, [Cx], was found to be exactly the same as the initial catalyst concentration, $[C]_o$. This is the same result obtained when assuming a two-body collision. This means that only the stoichiometry of the second reaction (Equation 3-24) affects the rate expression for the reaction. That is, if c = 2:

$$\text{cat. rate} = -k_2[Cx]^2[Dr] \qquad (26)$$

and, if c = 1:

$$\text{cat. rate} = -k_2[Cx][Dr], \tag{3-27}$$

the same result obtained when assuming 1:1 stoichiometry for the first reaction (Equation 3-23).

Pre-equilibrium Condition-- a = 1, b = 2

As was the case above, a cubic equation arises giving again the same results as the 1:1 stoichiometry, $[Cx] = [C]_o$. The stoichiometry of Equation 3-24 would affect the rate in the same way as outlined above.

Steady-State Condition: a = 2, b = 1, c = 2, d = 1

Writing the differential rate equations, assuming no time rate of change of activated catalyst, and proper substitution yields the following expression for the catalyzed rate:

$$\text{cat. rate} = -k_2[Cx][Dr] \tag{3-28}$$

Solution of a quadratic equation in [Cx] and substitution of stoichiometric equalities finally gives:

$$[Cx] = \frac{-k_2[Dr] + \sqrt{(k_2[Dr])^2 + 4k_1k_{-1}[R][Ox][C]^2}}{2k_{-1}[R]} \tag{3-29}$$

where:

$[R] = [Dr]_o - [Dr]$ and

$[Ox] = [Dr] - [Dr]_o + [Ox]_o$.

It can be seen that if the second term under the square root is small, which it usually is due to the magnitude of [R] and $[C]^2$, that the expression goes to zero. This is expected since one of the basic assumptions of the steady-state approximation is that the activated species is used up as soon as it is formed.

Steady-State Condition: a = 1, b = 2, c = 1, d = 1

This stoichiometry yields a simpler expression for the rate due to the absence of any second degree terms in the expression giving the activated catalyst concentration, [Cx]. The rate equation is:

$$\text{cat. rate} = -2(k_2[Cx][Dr]) \tag{3-30}$$

where:

$$[Cx] = \frac{k_1[Ox]^2[C]}{k_{-1}[R]^2 + k_2[Dr]} . \tag{3-31}$$

Since k_2 is much greater than k_{-1}, the rate equation can be further simplified to:

$$\text{cat. rate} = -2k_1[Ox]^2[C] \tag{3-32}$$

where:

$$[Ox] = [Ox]_o - 2[Dr]_o + 2[Dr] .$$

The uncatalyzed reaction in this case is given by:

$$2Ox + Dr \overset{k_{uncat}}{=} Dx + 2R . \tag{3-33}$$

The uncatalyzed rate is then:

$$\text{uncat. rate} = k_{uncat} [Ox]^2[Dr] \tag{3-34}$$

3-Body Collision Involving Three Different Species

The reactions considered here are the following:

$$C + Dr + Ox \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Q \tag{3-35}$$

$$Q \xrightarrow{k_2} C + Dx + R \tag{3-36}$$

These are discussed in the light of both the pre-equilibrium and the steady-state conditions.

Pre-equilibrium Condition

The equilibrium constant for the reaction given by Equation 3-35 is:

$$K_{eq} = [Q]/[C][Dr][Ox] \tag{3-37}$$

Substitution of stoichiometric equalities for [C], [Dr], and [Ox] into the equilibrium expression gives the following cubic equation:

$$[Q]^3 - \{[Ox]_o + [C]_o + [Dr]_o\} [Q]^2 + \{[Ox]_o ([C]_o + [Dr]_o) + [C]_o[Dr]_o + \frac{1}{K_{eq}}\} [Q] - [C]_o[Dr]_o[Ox]_o = 0 \tag{3-38}$$

Computer analysis of the function reveals the following. As K_{eq} becomes smaller, the curve (i.e., f(Q) vs. Q) "shifts" upward along the ordinate axis until there is no intersection greater than zero. This means, of course, that there will be no positive root found for these cases. Secondly, solution of the cubic equation using a numerical method shows that if K_{eq} is quite large (say, K_{eq} greater than 10^{10}), then $[Q] = [C]_o$. If this is the case, the uncatalyzed reaction remains the same as that given for the two-body collision and the rate of the catalyzed reaction becomes:

$$\text{cat. rate} = -k_2[Q] \qquad (3\text{-}39)$$

and is therefore independent of the concentration of the species appearing in the expression for the uncatalyzed reaction.

Steady-State Condition

In this case, the rate is given by:

$$\text{cat. rate} = -k_2[Q] \qquad (3\text{-}40)$$

Making the steady-state approximation ($d[Q]/dt = 0$) and solving for [Q] gives

$$[Q] = \frac{k_1[C][Dr][Ox]}{k_2 + k_{-1}} . \qquad (3\text{-}41)$$

Since k_2 is much greater than k_{-1}, k_{-1} can be neglected to give finally:

$$\text{cat. rate} = -k_1[C][Dr][Ox] \qquad (3\text{-}42)$$

where:

$[C] = [C]_o$ and

$[Ox] = [Ox]_o - [Dr]_o + [Dr]$.

The uncatalyzed reaction rate is given by:

$$\text{uncat. rate} = -k_{\text{uncat}}[\text{Ox}][\text{Dr}]$$

Computer Simulation of Curves Assuming 3-Body Collisions

As would be expected due to higher order terms in the rate controlling step, the reactions were much slower than in the case of two-body collisions. These expressions would require constants of much greater magnitude than those used in the two-body problem to approach reality. In fact, using the constants from the two-body problem, the catalyzed reaction was not always faster than the uncatalyzed reaction.

When the steady-state condition was assumed, the curves obtained considering a 3-body collision in the rate determining step were all quite similar to those obtained for the 1:1 stoichiometry. In other words, constants of about the same order of magnitude as were used in the two-body problem gave curves similar to those already reported.

By far the most interesting of the 3-body collisions were those involving the collision of three different species. Simulation of the expression obtained assuming the pre-equilibrium model resulted in a curve quite similar to those obtained when assuming the steady-state mechanism in the two-body problem. Similarly, simulation of the 3-body curve obtained using the steady-state condition produced a curve almost identical to that which resulted when considering the pre-equilibrium condition in the two-body problem. By adjusting parameters, the curve obtained using Equation 3-42 can be superimposed upon the curve resulting from the pre-equilibrium condition (see Equation 3-12).

Addition of Rate Modifying Complexing Agents

The sections preceding this one have dealt mainly with the study of a hypothetical reaction of a dye and an oxidizing agent, catalyzed by some metal ion. This reaction was assumed to take place (in aqueous media) with only the dye, oxidizing agent, catalyst, and their intermediate and final products present. At this point, consideration is given to complicating the system with the addition of a complexing agent and is presented in two main parts: (1) addition of a ligand which ties up catalyst (or catalytic species) thus inhibiting the progress of the reaction and (2) addition of a ligand which, in addition to tying up the catalyst, forms a new species which itself exerts a rate increasing effect upon the reaction. For the sake of eliminating redundancy, the "normal catalytic cycle" is considered to occur by pre-equilibrium kinetics and is assumed to be a two-body collision (see page 9, this work).

Addition of Inhibitor: Derivation of Expressions

Consider the addition to the system of a ligand, L, which forms a complex with the catalyst, C, according to the following reaction:

$$C + L \rightleftarrows CL$$

with

$$K_f = \frac{[CL]}{[C][L]}$$

It follows, then, that if the initial catalyst concentration is represented by $[C]_o$, the amount of catalyst, C, available for participation in the dye reaction is given by:

$$[C] \rightleftarrows [C]_o - [CL] \qquad (3\text{-}46)$$

But, from the equilibrium expression, we have:

$$[CL] = K_f[C][L] \tag{3-47}$$

Substituting into Equation 3-46 and solving for [C] gives:

$$[C] = \frac{[C]_o}{1 + K_f[L]} \tag{3-48}$$

Further, we know that the ligand concentration, [L], can be expressed in terms of the total analytical ligand concentration, C_L, in the following manner similar to that used by Freiser and Fernando (14):

$$\alpha_L = \frac{[L]}{C_L} = \frac{1/K_f}{[C] + 1/K_f} \tag{3-49}$$

Solving for [L] gives:

$$[L] = \frac{C_L/K_f}{[C] + 1/K_f} \tag{3-50}$$

Substitution of Equation 3-50 into Equation 3-48 finally gives:

$$[C] = \frac{[C]_o}{1 + \dfrac{C_L}{[C] + 1/K_f}} \tag{3-51}$$

At this point, for simplification of the symbolism, we let:

$X = [C]$, $C = [C]_o$, Ꝁ $= 1/K_f$, and $L = C_L$

Equation 3-51 now becomes:

$$X = \frac{C}{1 + \frac{L}{X + K}} \qquad (3\text{-}52)$$

Proceeding with the solution for X, we have:

$$X + \frac{XL}{X + K} = C$$

$$X^2 + KX + XL = CX + CK$$

$$X^2 + (K + L - C)X - CK = 0$$

Applying the quadratic formula, we arrive at:

$$X = \frac{-(K + L - C) \pm \sqrt{(K + L - C)^2 + 4CK}}{2} \qquad (3\text{-}53)$$

or, in terms of the original symbols:

$$[C] = \tfrac{1}{2}\left[-(1/K_f + C_L - [C]_o) \pm \sqrt{(1/K_f + C_L - [C]_o)^2 + \frac{4[C]_o}{K_f}}\right] \qquad (3\text{-}54)$$

Analysis of this expression reveals that if K_f is large, $1/K_f$ approaches zero and we may represent Equation 3-54 as:

$$[C] = \tfrac{1}{2}\left[-(C_L - [C]_o) \pm \sqrt{(C_L - [C]_o)^2}\right] \quad \text{or:}$$

$$(3\text{-}55)$$

$$[C] = \tfrac{1}{2}\left[([C]_o - C_L) \pm (C_L - [C]_o)\right]$$

Consideration of experimental realities leads to three possible cases: (1) $[C]_o = C_L$, (2) $[C]_o < C_L$, or (3) $[C]_o > C_L$. Looking first at case

1, we see that if $[C]_o = C_L$, then:

$$[C] = \tfrac{1}{2}(0 \pm 0) = 0 \tag{5-56}$$

and there is no ambiguity in choice of positive or negative root. If $[C]_o < C_L$, however, we must choose the positive root, since the other choice leads to:

$$\begin{aligned} [C] &= \tfrac{1}{2}([C]_o - C_L - C_L + [C]_o) \quad \text{or:} \\ [C] &= [C]_o - C_L \end{aligned} \tag{5-57}$$

This, of course, is an impossibility in this case since [C] cannot be less than zero. This gives then, with choice of the positive root:

$$[C] = \tfrac{1}{2}([C]_o - C_L + C_L - [C]_o) = 0 \tag{5-58}$$

In the third case ($[C]_o > C_L$) either Equation 3-57 or 3-58 would fit theoretically. Equation 3-58 must be ruled out, however, since it is impossible for a given amount of ligand to tie up more than an equivalent amount of catalyst according to Equation 3-44. We then have from Equation 3-57 that:

$$[C] = [C]_o - C_L$$

These same results can be obtained numerically in the following manner: We first re-write Equation 3-55 taking only the positive root:

$$[C] = \tfrac{1}{2}\left[([C]_o - C_L) + \sqrt{(C_L - [C]_o)^2}\right] \quad \text{and say:} \tag{5-59}$$

$$\text{Term 1} = [C]_o - C_L \quad \text{and}$$

$$\text{Term 2} = (\sqrt{(C_L - [C]_o)^2})$$

It can be seen that Term 2 will always be positive and numerically equal to the absolute value of Term 1. When $[C]_o < C_L$, Term 1 will be less than zero which leads to:

$$[C] = \tfrac{1}{2}[-\text{Term 1} + \text{Term 2}] = 0 \tag{3-60}$$

On the other hand, if $[C]_o > C_L$, Term 1 is positive and:

$$[C] = \tfrac{1}{2}[\text{Term 1} + \text{Term 2}] \tag{3-61}$$

$$= \tfrac{1}{2}[2 \cdot \text{Term 1}] = \text{Term 1}$$

$$[C] = [C]_o - C_L$$

This numerical analysis is necessary to accurately apply the expressions developed above to computer simulation of the resulting catalytic titration curves.

Addition of Inhibitor: Computer Analysis

The system was simulated on the computer assuming various total ligand concentrations. Results of this simulation are shown in Figure 1, a composite graph of all the curves simulated from a total analytical concentration of $C_L = 1 \times 10^{-5}$ M (code = 1) to $C_L = 8 \times 10^{-5}$ (code = 8).

It is apparent from this set of curves that the distance from the inflection point to the baseline (represented by D in Figure 1) is a direct function of ligand concentration. Indeed, this fact is the basis

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THIS CHART IS A SUMMARY OF ALL THE CURVES SIMULATED IN THIS RUN 6/28/71

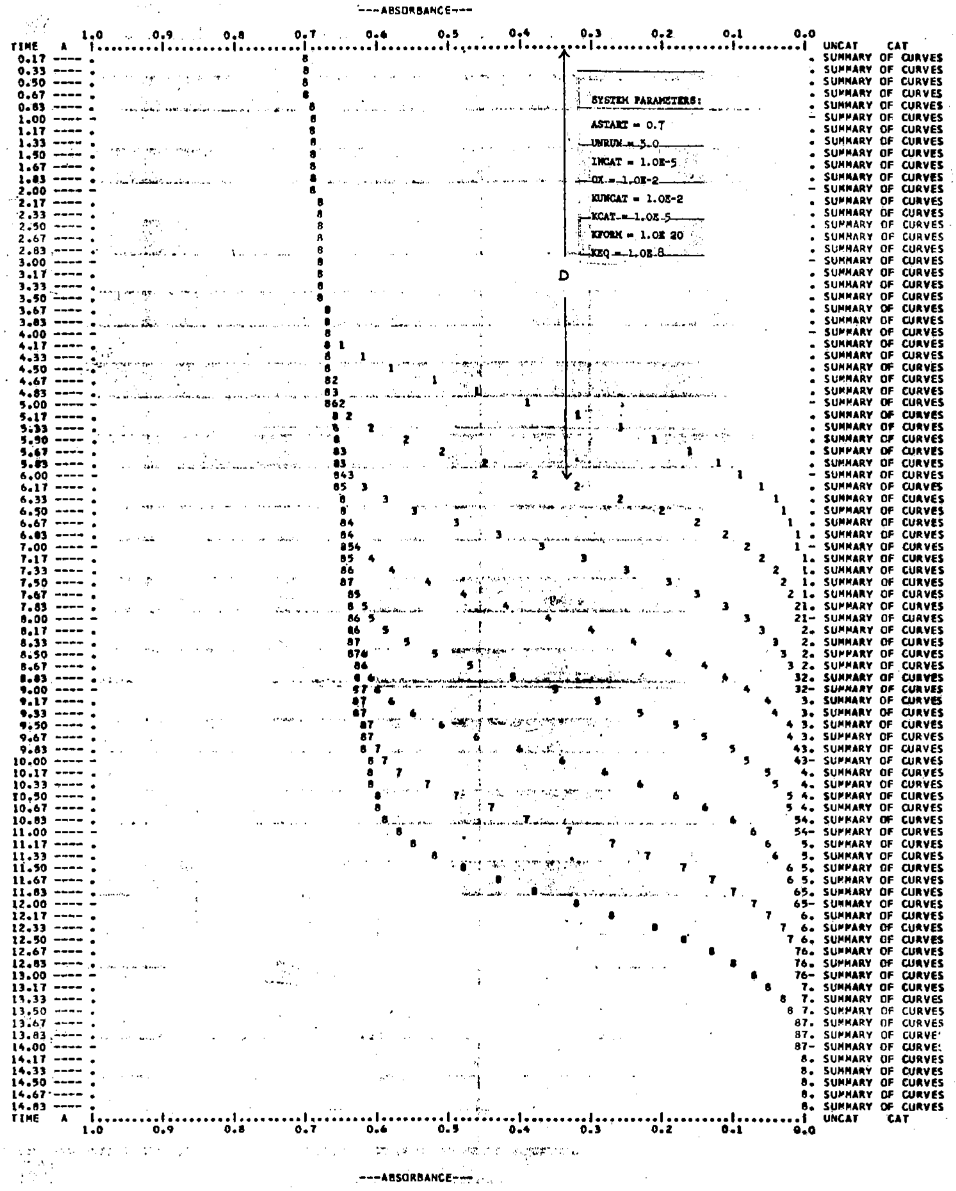


Figure 1. Computer Simulation of Hypothetical System; Effect of Rate Inhibiting Complexing Agent Concentration on Progress of Reaction

of catalytic end-point determination as discussed by Mottola (1).

Addition of Rate Increasing Ligand

In the hypothetical reaction between a dye and an oxidizing agent, catalyzed by a metal ion, the intermediate species in all approaches is the oxidized form of the catalyst (represented by Cx). If a rate-increasing ligand is introduced, it is assumed that it forms a complex with Cx which in some way results in an increase in the rate of the overall reaction, either by true catalysis or promotion. Catalysis is the speeding up of an already existing reaction, without destruction of the catalytic species. Promotion refers to the speeding up of a reaction in such a way as to destroy the rate-increasing species (15). The differences between these two aspects are covered later. In this section, two possible approaches to rate-increase are discussed: (1) a pre-equilibrium condition and (2) a steady-state condition.

Pre-Equilibrium Condition of Rate-Increase: Derivation of Expressions

Consider the addition of a ligand, L, to a system such as described above, and the formation of the following complex:

$$\mathrm{Cx} + \mathrm{L} \rightleftarrows \mathrm{CxL} \quad \text{where} \quad K_f = \frac{[\mathrm{CxL}]}{[\mathrm{Cx}][\mathrm{L}]} \tag{3-62}$$

One possible route of rate-increase is the following:

$$\mathrm{CxL} + \mathrm{Dr} \rightleftarrows \mathrm{Q} \quad \text{with} \quad K_{eq} = \frac{[\mathrm{Q}]}{[\mathrm{CxL}][\mathrm{Dr}]} \tag{3-63}$$

$$\mathrm{Q} \xrightarrow{k} \mathrm{Cx} + \mathrm{P} + \mathrm{Dx} \tag{3-64}$$

where:

P = some products of the decomposition of Q.

Here, we assume that the second step is the slow step and is irreversible. The rate of this reaction is therefore given by:

$$\text{rate}_L = k[Q] \qquad (3\text{-}65)$$

where:

$\text{rate}_L \equiv$ rate due to the ligand effect. But:

$$[Q] = K_{eq}[CxL][Dr], \quad \text{then:} \qquad (3\text{-}66)$$

$$\text{rate}_L = kK_{eq}[CxL][Dr] \qquad (3\text{-}67)$$

All quantities in this equation are either known or determinable, except [CxL]. An expression for [CxL] can be obtained in the following manner: From the mass balance relation for the total catalyst concentration we may write:

$$[C]_o = [Cx] + [CxL] + [Q] \qquad (3\text{-}68)$$

Then, solving for [CxL], we have:

$$[CxL] = [C]_o - [Cx] - [Q] \qquad (3\text{-}69)$$

but, $[Q] = K_{eq}[CxL][Dr]$. This leads to:

$$[CxL] = [C]_o - [Cx] - K_{eq}[CxL][Dr] \qquad (3\text{-}70)$$

or, solving for [CxL]:

$$[CxL] = \frac{[C]_o - [Cx]}{1 + K_{eq}[Dr]} \qquad (3\text{-}71)$$

This expression, substituted into Equation 3-67 gives:

$$\text{rate}_L = \frac{kK_{eq}[Dr]([C]_o - [Cx])}{1 + K_{eq}[Dr]} \qquad (3\text{-}72)$$

It now becomes necessary to obtain an expression for [Cx], hereafter called the "uncomplexed catalyst concentration", meaning the concentration of "activated" catalyst available for reaction by the normal catalytic cycle.

Solving Equation 3-70 for [Cx] gives:

$$\begin{aligned} [Cx] &= [C]_o - [CxL] - K_{eq}[CxL][Dr] \quad \text{or:} \\ [Cx] &= [C]_o - (1 + K_{eq}[Dr])\,[CxL] \end{aligned} \qquad (3\text{-}73)$$

From the ligand mass balance, we have:

$$C_L = [CxL] + [L] + [Q] \qquad (3\text{-}74)$$

But, from the appropriate equilibrium expressions we know:

$$[L] = \frac{[CxL]}{[Cx]K_f} \qquad (3\text{-}75)$$

and, as before, $[Q] = K_{eq}[CxL][Dr]$. Substituting these values into Equation 3-74 yields:

$$C_L = [CxL] + \frac{[CxL]}{[Cx]K_f} + K_{eq}[CxL][Dr] \qquad (3\text{-}76)$$

Proceeding with the algebra, we obtain:

$$[Cx]C_L = [Cx][CxL] + \frac{[CxL]}{K_f} + [Cx]K_{eq}[CxL][Dr]$$

$$= [CxL] \{[Cx] + \frac{1}{K_f} + K_{eq}[Dr][Cx]\}$$

$$= [CxL] \{\frac{1}{K_f} + (1 + K_{eq}[Dr]) [Cx]\}$$

Finally, solving for [CxL] yields:

$$[CxL] = \frac{[Cx]C_L}{1/K_f + [1 + K_{eq}[Dr]] [Cx]} \tag{3-77}$$

Substituting into Equation 3-73, we arrive at:

$$[Cx] = [C]_o - \{\frac{(1 + K_{eq}[Dr])[Cx]C_L}{1/K_f + (1 + K_{eq}[Dr])[Cx]}\} \tag{3-78}$$

Now, to simplify the algebra, let:

$X = [Cx]$, $C = [C]_o$, $D = K_{eq}[Dr]$, $L = C_L$, and $K = K_f$

Equation 3-78 is re-written as:

$$X = C - \frac{(1 + D)XL}{\frac{1}{K} + (1 + D)X} \tag{3-79}$$

Proceeding with the solution:

$$(D + 1)X^2 + \frac{X}{K} = \frac{C}{K} + (D + 1)CX - (D + 1)XL$$

$$(D + 1)X^2 + \frac{X}{K} - (D + 1)CX + (D + 1)LX - \frac{C}{K} = 0$$

$$(D + 1)X^2 + [\frac{1}{K} - (D + 1)C + (D + 1)L] X - \frac{C}{K} = 0$$

$$(D + 1)X^2 + [\frac{1}{K} - (D + 1)(C - L)] X - \frac{C}{K} = 0$$

Applying the quadratic formula:

$$X = \frac{-[1/K - (D + 1)(C - L)] + \sqrt{[1/K - (D + 1)(C - L)]^2 + 4(D + 1)C/K}}{-2(D + 1)}$$

or, converting back to the original terms:

$$[Cx] = \frac{1}{2(K_{eq}[Dr] + 1)} \{- [\frac{1}{K_f} - (K_{eq}[Dr] + 1)([C]_o - C_L)] +$$

$$. . . \sqrt{[\frac{1}{K_f} - (K_{eq}[Dr] + 1)([C]_o - C_L)]^2 + \frac{4(K_{eq}[Dr] + 1)[C]_o}{K_f}}\ \} \qquad (3\text{-}80)$$

It should be noted that all quantities in Equation 3-80 are known with the exception of C_L, the total ligand concentration. Since Equation 3-64 is assumed to be irreversible, C_L is not constant. Let C_L = L = total ligand concentration at time "t". Then:

$$\frac{dL}{dt} = \frac{-d[P]}{dt} = - \{- \frac{d[Q]}{dt}\} = \frac{kK_{eq}([C]_o - [Cx])}{1 + K_{eq}[Dr]} \qquad (3\text{-}81)$$

Or, to an approximation:

$$\Delta L = \frac{kK_{eq}([C]_o - [Cx])}{1 + K_{eq}[Dr]} \cdot \Delta t \quad \text{and:} \qquad (3\text{-}82)$$

$$C_{L(t + \Delta t)} = C_{L(t)} - \Delta L \qquad (3\text{-}83)$$

This expression, by no means intended to be rigorous, will yield an approximate value of the change in ligand concentration with time which can be used in computer simulation discussed in the following section.

Pre-equilibrium Condition of Rate-Increase: Computer Analysis

Using the expressions developed above to describe the system, it is both interesting and pertinent to study the effect of varying certain parameters on the behavior of the system.

The procedure for each parameter was the following: choose reasonable values for the parameters not being studied, hold these constant, vary the parameter of interest, and observe the effect on the shapes of the resulting simulated curves. A close study of these curves can lead to valuable conclusions concerning relative magnitude of parameters and possibly give an insight into when or if a given parameter may be assumed to have no effect on the system.

In the present system under study, the following parameters were varied with respect to the remaining parameters:

K_{eq} = equilibrium constant for the formation of the complex, Q (see Equation 3-63),

K_f = formation constant for the complex, CxL (see Equation 3-62),

k_p = rate constant for promotion path ($k_p = k$ in Equation 3-64), and

C_L = the concentration of total ligand in all forms at any time (see Equation 3-28).

The results of assigning different values to these parameters can be seen in Figures 2 through 8 and are summarized in the following sections.

Each graph in this series contains a legend. However, units have been omitted for sake of simplicity. Following is a list of the FORTRAN representations of the various parameters and a short explanation of the significance of each.

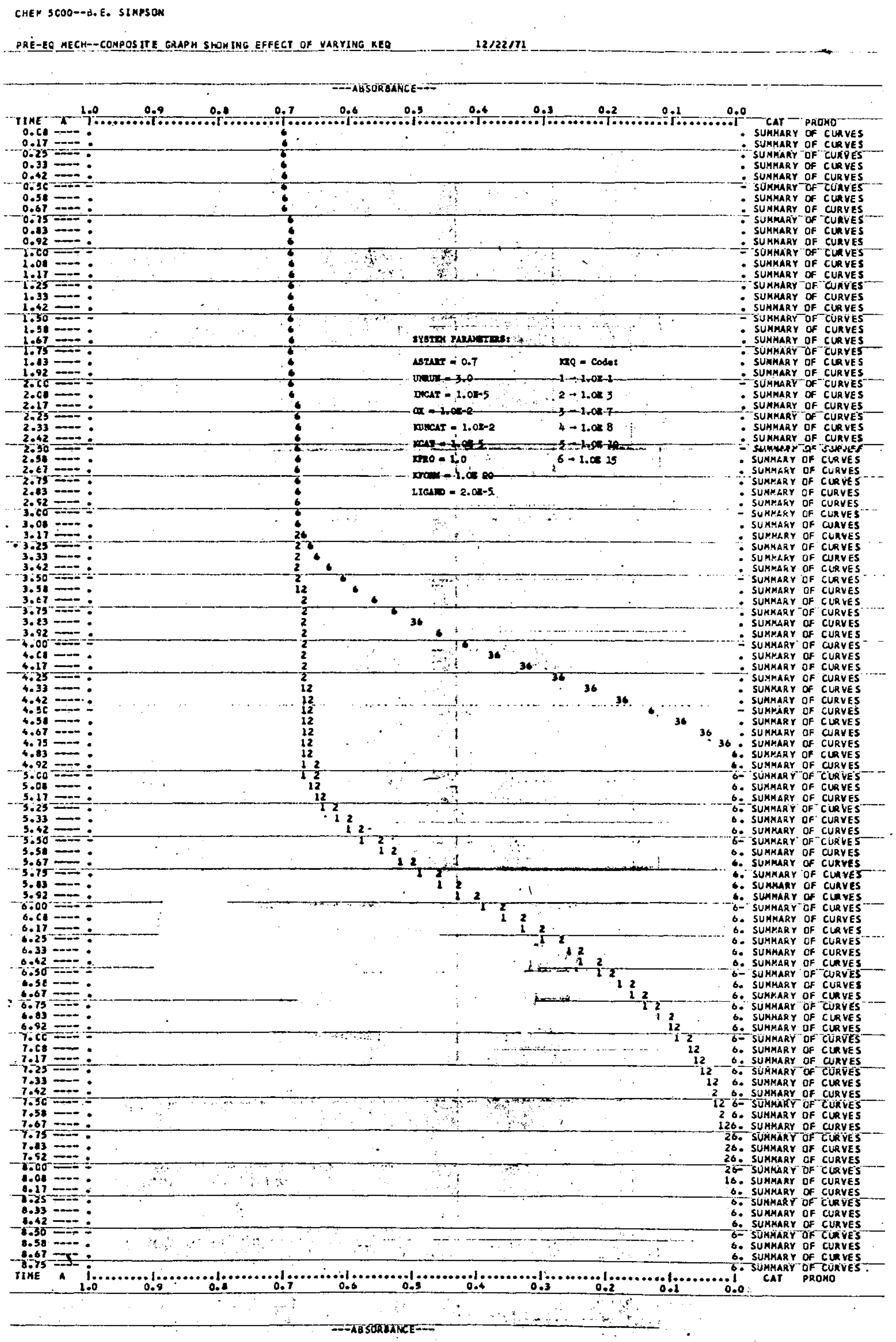
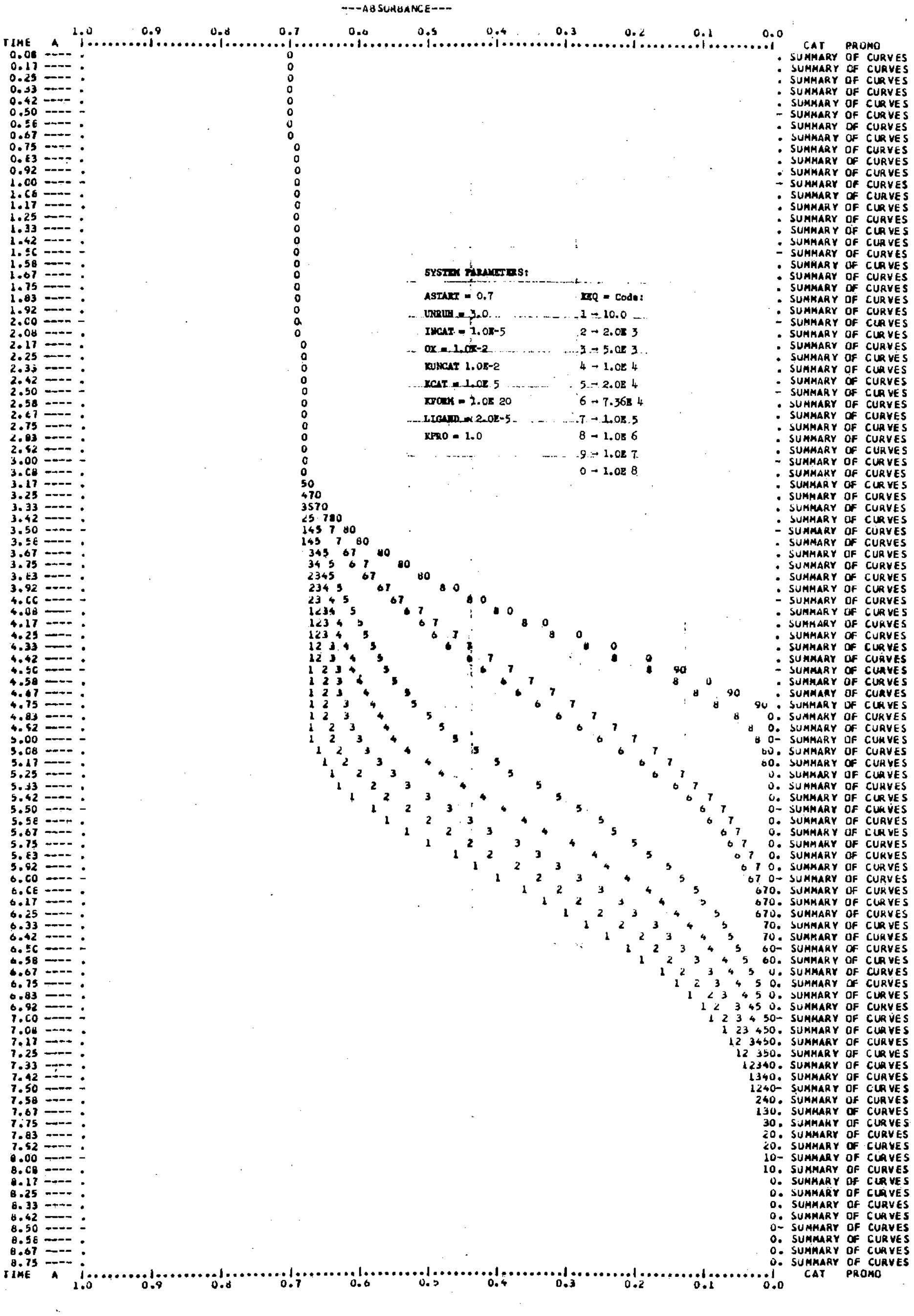


Figure 2. Computer Simulation of Hypothetical System; Addition of Rate-increasing Complexing Agent Assuming Pre-equilibrium Condition. Effect of varying K_{eq}

CHEM 5030--D.E. SIMPSON COPY 3 OF 3

PROMO--PRE-EQ MECH: EFFECT OF VARYING KEQ: 10 --> 1.0E 8 1/05/72



SYSTEM PARAMETERS:

ASTART = 0.7	KEQ = Code:
UNRUN = 3.0	1 → 10.0
INCAT = 1.0E-5	2 → 2.0E 3
OX = 1.0E-2	3 → 5.0E 3
KUNCAT 1.0E-2	4 → 1.0E 4
KCAT = 1.0E 5	5 → 2.0E 4
KFORM = 1.0E 20	6 → 7.36E 4
LIGAND = 2.0E-5	7 → 1.0E 5
KPRO = 1.0	8 → 1.0E 6
	9 → 1.0E 7
	0 → 1.0E 8

Figure 3. Computer Simulation of Hypothetical System; Addition of Rate-increasing Complexing Agent Assuming Pre-equilibrium Condition. Effect of varying K_{eq}

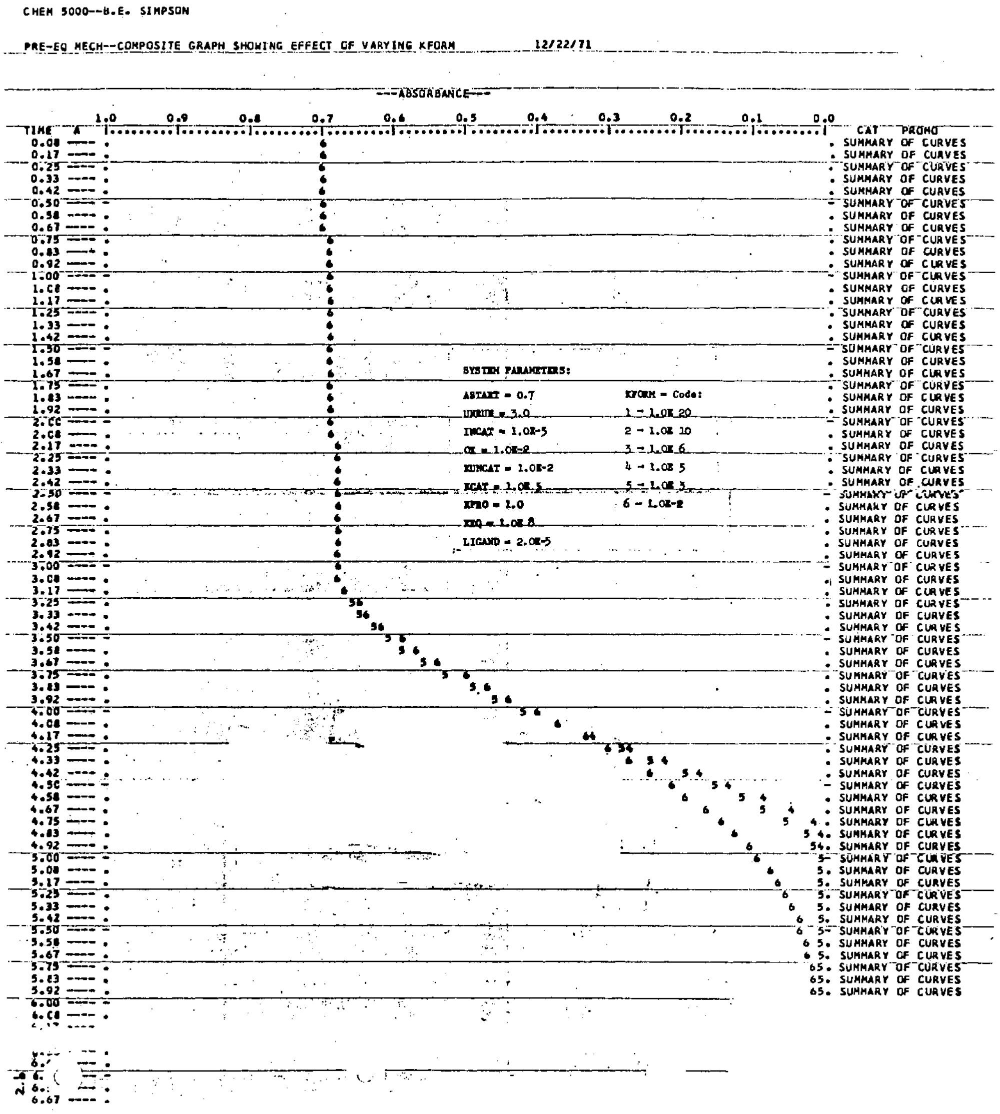


Figure 4. Computer Simulation of Hypothetical System; Addition of Rate-Increasing Complexing Agent Assuming Pre-equilibrium Condition. Effect of varying K_f

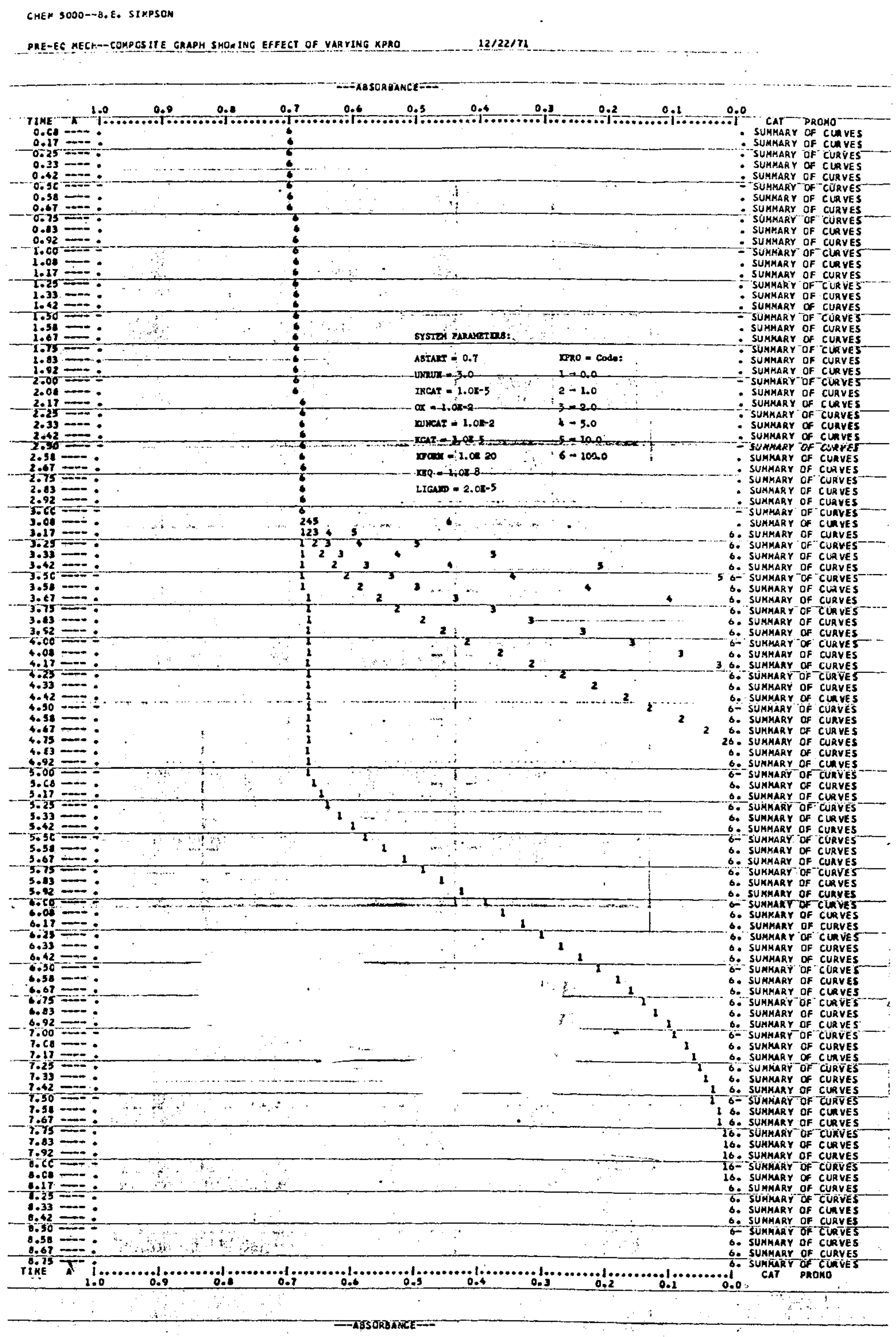
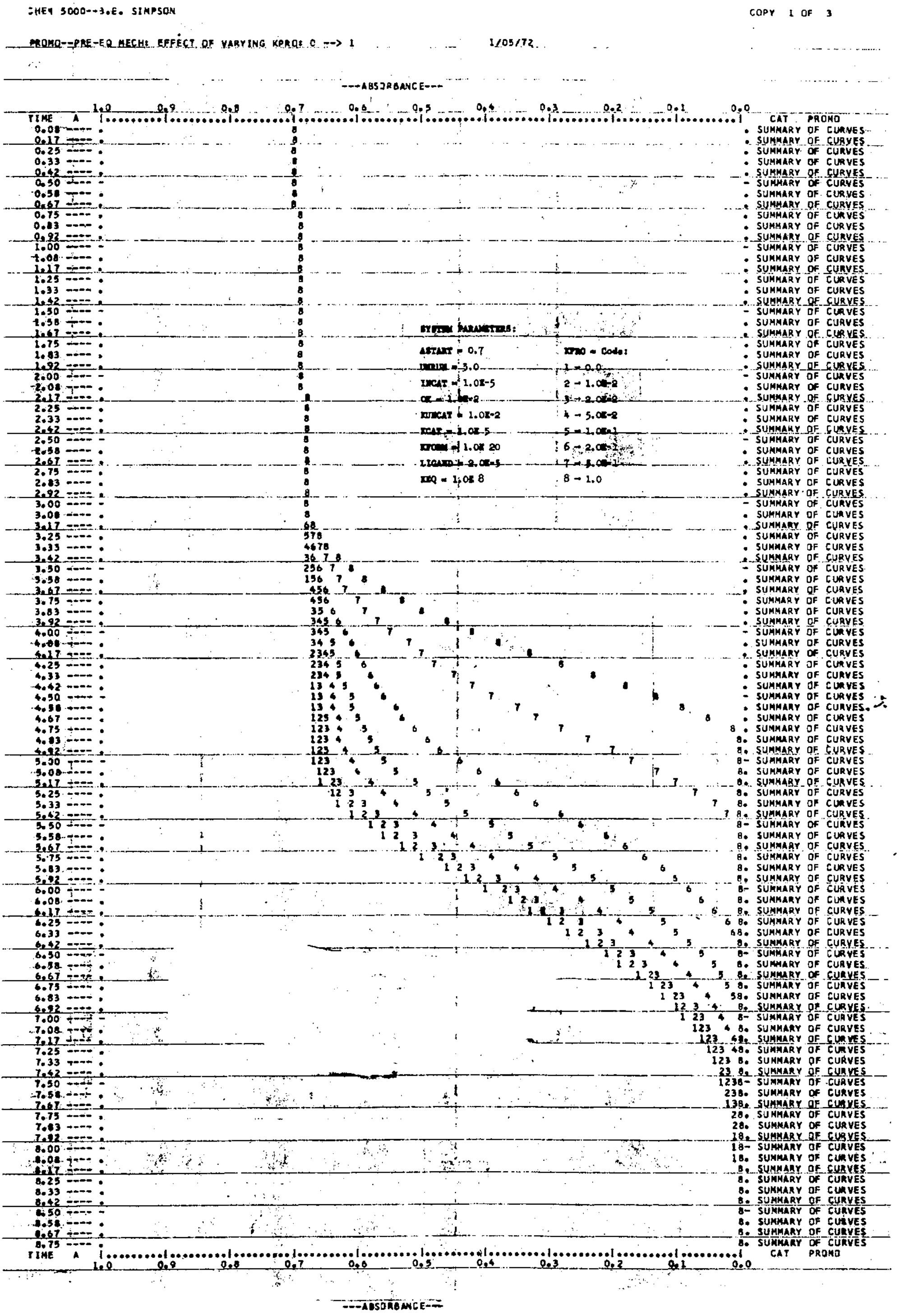


Figure 5. Computer Simulation of Hypothetical System; Addition of Rate-Increasing Complexing Agent Assuming Pre-equilibrium Condition. Effect of varying k_p


CHEM 5000--J.E. SIMPSON COPY 1 OF 3

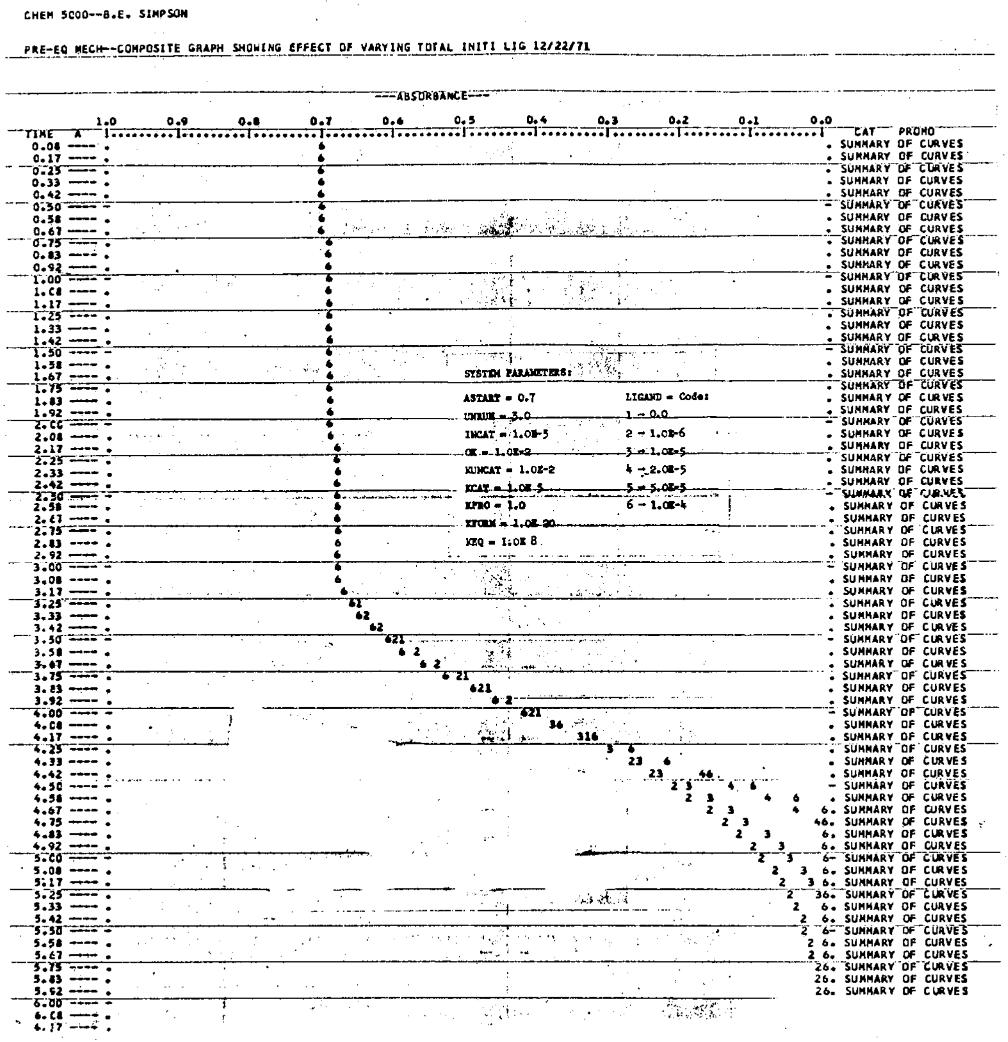
PROMO--PRE-EQ MECH: EFFECT OF VARYING KPRO: 0 --> 1 1/05/72

SYSTEM PARAMETERS:

ASTART = 0.7
IMRIN = 3.0
INCAT = 1.0E-5
OK = 1.0E-2
KUNCAT = 1.0E-2
KCAT = 1.0E 5
KFORM = 1.0E 20
LIGAND = 2.0E-5
KEQ = 1.0E 8

KPRO = Code:
1 → 0.0
2 → 1.0E-2
3 → 2.0E-2
4 → 5.0E-2
5 → 1.0E-1
6 → 2.0E-1
7 → 5.0E-1
8 → 1.0

Figure 6. Computer Simulation of Hypothetical System; Addition of Rate-Increasing Complexing Agent Assuming Pre-equilibrium Condition. Effect of varying k_p



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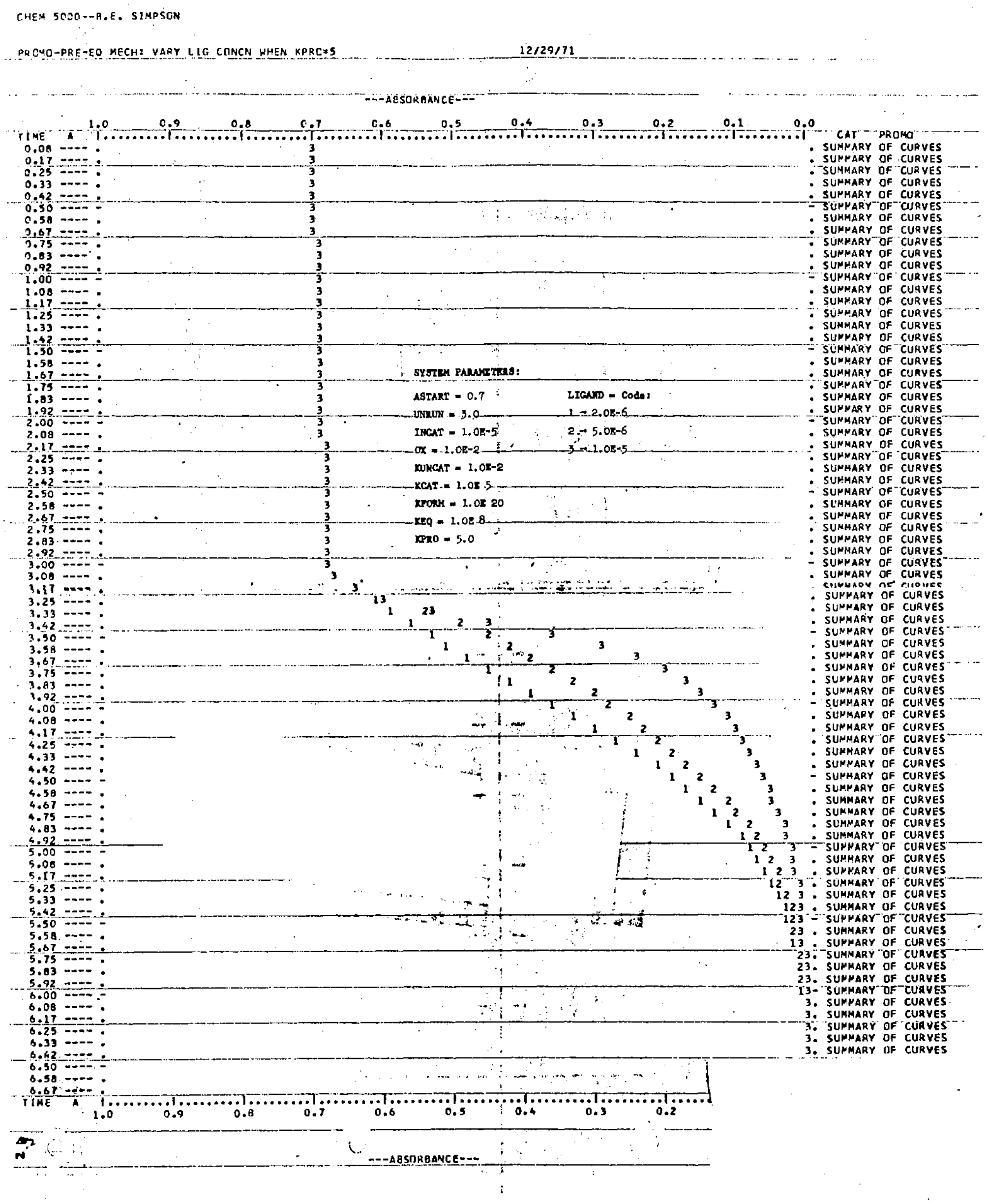
CHEM 5000--B.E. SIMPSON

PRE-EQ MECH--COMPOSITE GRAPH SHOWING EFFECT OF VARYING TOTAL INITI LIG 12/22/71

SYSTEM PARAMETERS:

ASTART = 0.7          LIGAND = Code:
UNRUN = 3.0           1 → 0.0
INCAT = 1.0E-5        2 → 1.0E-6
OK = 1.0E-2           3 → 1.0E-5
KUNCAT = 1.0E-2       4 → 2.0E-5
KCAT = 1.0E 5         5 → 5.0E-5
KPRO = 1.0            6 → 1.0E-4
KFORM = 1.0E 20
KEQ = 1:0E 8
```

Figure 7. Computer Simulation of Hypothetical System; Addition of Rate-Increasing Complexing Agent Assuming Pre-equilibrium Condition. Effect of Varying Initial Ligand Concentration



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PROMO-PRE-EQ MECH: VARY LIG CONCN WHEN KPRC=5 12/29/71

SYSTEM PARAMETERS:

ASTART = 0.7
UNRUN = 3.0
INCAT = 1.0E-5
OX = 1.0E-2
KUNCAT = 1.0E-2
KCAT = 1.0E 5
KFORM = 1.0E 20
KEQ = 1.0E 8
KPRO = 5.0

LIGAND = Code:
1 → 2.0E-6
2 → 5.0E-6
3 → 1.0E-5

Figure 8. Computer Simulation of Hypothetical System; Addition of Rate-Increasing Complexing Agent Assuming Pre-equilibrium Condition. Effect of Varying Initial Ligand Concentration

TABLE I

EXPLANATION OF VARIABLE NAMES AND UNITS OF CONSTANTS

Fortran Rep	Comment	Units
ASTART	Initial absorbance of the system at time = 0	unitless
UNRUN	Number of minutes of uncatalyzed reaction before catalyst is added	minutes
INCAT	Rate of catalyst addition	$M \cdot min^{-1}$
OX	Concentration of oxidizing agent	M
KUNCAT	Uncatalyzed rate constant	min^{-1}
KCAT	Catalyzed rate constant	$M^{-1}min^{-1}$
KPRO	Rate constant for ligand effect	min^{-1}
KFORM	Formation constant for the metal-ligand complex, CxL	M^{-1}
KEQ	Equilibrium constant for the formation of complex Q from CxL and dye	M^{-1}
LIGAND	Initial ligand concentration	M

Please note that in the following discussions, "reaction" refers to the portion of the curve after a time equal to UNRUN has elapsed; i.e., it does not refer to the uncatalyzed portion of the curve.

Variation of K_{eq}

A look at Figure 2 shows that codes 4 and 5 have been over-printed with a 6. This indicates that all values of KEQ greater than 10^8 have no effect on the system since $4 \rightarrow 10^8$. This observation is compatible with Equation 3-72. In the term $(1 + K_{eq}[Dr])$, we may neglect the value

1 if $K_{eq}[Dr]$ is large enough. If we accept a rejection criterion of 1%, then $K_{eq}[Dr] > 100$ in order to neglect the value 1. Since $[Dr] \approx 10^{-5}$, we have: $K_{eq} > 10^7$ in order to neglect 1. This agrees quite well with the simulation which shows that, under the assumed conditions, the point where K_{eq} need not be considered is somewhere between values of 10^7 and 10^8. Under these conditions, the rate expression becomes:

$$\text{rate} = \frac{k_p K_{eq}[Dr]([C]_o - [Cx])}{K_{eq}[Dr]}$$

which simplifies to:

$$\text{rate}_p = k_p([C]_o - [Cx]) \qquad (3\text{-}84)$$

It should be noted that this simplified expression is independent of dye concentration, except for the small contribution of [Dr] in the expression for [Cx] given by Equation 3-80.

Using the same reasoning, it can also be seen that if $K_{eq}[Dr] < 10^{-2}$ or $K_{eq} < 10^3$, then the value $K_{eq}[Dr]$ is negligible with respect to 1, and the rate expression becomes:

$$\text{rate}_p = k_p K_{eq}[Dr]([C]_o - [Cx]) \quad \text{or, letting } K^* = k_p K_{eq}\text{:} \qquad (3\text{-}85)$$

$$\text{rate}_p = K^*[Dr]([C]_o - [Cx]) \qquad (3\text{-}86)$$

Although in this case the value of K_{eq} still affects the behavior of the system, it would be impossible to separate the constants k_p and K_{eq} if an attempt were made to determine them given an absorbance versus time curve. It will be shown later that Equation 3-86 is in exactly the same form as the expression obtained assuming the steady-state condition. The curves represented by 1 and 2 in Figure 2 show curves resulting when values of $K_{eq} \leq 10^3$ are used.

The region between the extremes represented by Equations 3-84 and 3-86 has been studied in Figure 3. It can be seen that as the value of K_{eq} is increased, increments of equal magnitude affect the system less and less until the point at $K_{eq} > 10^7$, after which no additional effect is observed. Also, by noticing the change in curvature near the baseline going from curve 1 to curve 8 (increasing K_{eq}), it is apparent that the effect of the dye concentrations (proportional to A) is becoming less and less. That is, in the lower curves, a decrease in absorbance causes a corresponding decrease in rate causing gentle deterioration to zero absorbance. In the higher curves at corresponding A values, the rate is still relatively fast, resulting in a rapid decrease to zero.

The breaks in the curves which are most noticeable in curves 4 and 5 are a result of different periods of domination of promotion and catalytic paths. This is due to the term ($[C]_o - [Cx]$) in the rate expression. When the reaction is just under way, $[Cx] \approx 0$ since about all Cx is tied up by the complexing agent and, consequently, promotion predominates. As time passes, however, more catalyst is added as C_L is decreasing, until a point is reached where $[C]_o \geq C_L$ (Note: $[C]_o$ means "total catalyst added at time = t", not initial catalyst concentration) and $rate_c > rate_p$. From this point on, the catalytic path predominates.

In reality, it is usually the case that equilibrium constants of reactions we would be likely to study would be large enough to neglect, dependent upon reaction conditions, of course. Consequently, the equation which most favorably describes any given system, assuming a preequilibrium condition, would be Equation 3-84. In the section in which constants are determined, we will, in any case, assume that K_{eq} is either known or independently determinable.

Variation of K_f

The effect of varying K_f can be seen is Figure 4. It is quite easy to predict the outcome of changing K_f since this basically affects only the amount of catalyst available for reaction by the catalytic path. Figure 4 shows that values of $K_f > 10^5$ have no further effect on the system, under these conditions. A look at Equation 3-80 shows why. The predominant term is:

$$\text{Term} = \frac{1}{K_f} - (K_{eq}[Dr] + 1)([C]_o - C_L) \tag{3-87}$$

Assigning reasonable values, we have:

$$\text{Term} = \frac{1}{K_f} - (10^8 \cdot 10^{-5} + 1)(10^{-5} - 2 \times 10^{-5})$$

$$= \frac{1}{K_f} + 10^3 \cdot 10^{-5} = \frac{1}{K_f} + 10^{-2}$$

Again assuming a 1% rejection criterion, we have: $\frac{1}{K_f} < 10^{-4}$ or $K_f > 10^4$ in order to neglect $\frac{1}{K_f}$ in Equation 3-87. This agrees with results observed in Figure 4.

Variation of k_p

Figures 5 and 6 show the effect of varying k_p, the rate constant for promotion cycle. Figure 5 shows variation from the point where $\text{rate}_p \approx \text{rate}_c$ (curve 2) to where $\text{rate}_p \gg \text{rate}_c$. Figure 6 covers the region from $rate_p << rate_c$ to where $rate_p \approx rate_c$. The curves show that, in general, the system behaves as expected; i.e., an increase in k_p results in an increase in the reaction rate. Figure 6 shows that the break which was mentioned previously in the discussion of the equilibrium constant variation. As before, this is attributed to predominance of either $rate_p$ or $rate_c$ in different portions of the curve. Again, as is shown by curve 6, Figure 6, $rate_p$ predominates early because $[Cx] \approx 0$. It is interesting to note the sensitivity of the system to even small changes in k_p as is seen in Figure 6.

Variation of Total Initial Ligand Concentration

This is probably the most interesting aspect as far as chemical analysis is concerned. If the system is sensitive to changes in ligand concentration, we have a basis for a method to determine the ligand. Figures 7 and 8 show the effects of varying initial ligand concentration. Comparison of these two sets of curves shows the difference in sensitivity caused by an increase in the rate constant for promotion. Curves 2 and 3 in Figure 7 differ by approximately the same order of magnitude of curves 1 and 3 in Figure 8, yet the effect of the same change in ligand concentration is much greater in the second case.

It is obvious from studying the figures that in the early portions of the curves, the system is practically insensitive to ligand concentration. This can be attributed to the large formation constant of the metal-ligand complex, CxL. That is: in the early stages of reaction, not much catalyst has been added, and, if ligand is present, the metal will all be complexed if K_f is large (see previous section for definition of "large"). Under these conditions, two observations can be made:

(1) no catalyst will be available for reaction by the normal catalytic path and the rate of the reaction is therefore due only to promotion caused by the complex, CxL; and (2) as long as $C_L > C \cdot t$ where C = rate of catalyst addition and t = time, the catalyst will be the limiting factor in formation of the complex, CxL. Consequently, the resulting curve will be practically independent of C_L until enough time has passed to make $C \cdot t > C_L$. From this point on, the amount of complex formed will be negligible and catalyst will become available for reaction via the normal catalytic path. The rate will now be $\text{rate}_c + \text{rate}_p$ instead of only rate_p as it was at the beginning of the reaction. The main difference, then, between two curves with a difference only in initial ligand concentration, is the amount of time it takes for enough catalyst to be added to complex all of the ligand present. This effect is especially noticeable in Figure 8.

Although this reasoning does not explain all the differences in the curves, it does account for the similarity of the reactions in the early stages. Other differences arise from the relative magnitudes of rate_c and rate_p which, of course, depend upon the relative size of the rate constants and the amount of rate-increasing complex, CxL, formed in the first stages of the reactions.

It should be noted at this point that almost an infinite variety of shapes and rates can be obtained by varying the different parameters of the system. Only those systems which seem reasonable when compared to existing curves from previous experiments have generally been selected for simulation.

Steady-State Condition of Rate-Increase: Derivation of Expressions

We shall now look at another possible path of reaction rate increase making use of the steady-state approximation. As in the pre-equilibrium approach, we again consider the formation of the complex CxL according to the following reaction:

$$Cx + L \rightleftarrows CxL \qquad K_f = \frac{[CxL]}{[Cx][L]} \tag{3-62}$$

Again, as in the previous discussion, we choose the following reaction path:

$$CxL + Dr \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Q \tag{3-63}$$

$$Q \xrightarrow{k_2} Cx + P + Dx \tag{3-64}$$

In this case, however, the second step is fast and the first, Equation 3-63, becomes rate determining. This is used in the following derivation.

We can write the rate of the reaction as:

$$\text{rate}_L = -\frac{d[Dr]}{dt} = k_1[Dr][CxL] - k_{-1}[Q] \tag{3-88}$$

Making the steady-state approximation:

$$\frac{d[Q]}{dt} = k_1[CxL][Dr] - k_2[Q] - k_{-1}[Q] = 0 \tag{3-89}$$

we arrive at:

$$k_1[CxL][Dr] = k_{-1}[Q] + k_2[Q] \tag{3-90}$$

Substitution of Equation 3-90 into Equation 3-88 gives:

$$\text{rate}_L = k_{-1}[Q] + k_2[Q] - k_{-1}[Q] \quad \text{or:}$$

$$\text{rate}_L = k_2[Q] \tag{3-91}$$

Solving Equation 3-90 for [Q] gives:

$$[Q] = \frac{k_1}{k_{-1} + k_2}[CxL][Dr] \tag{3-92}$$

From the mass balance equation for total catalyst we have:

$$[C]_o = [CxL] + [Cx] + [Q], \text{ or:} \tag{3-93}$$

$$[CxL] = [C]_o - [Cx] - [Q] \tag{3-94}$$

Substitution of Equation 3-94 into Equation 3-92 gives:

$$[Q] = \frac{k_1}{k_{-1} + k_2}([C]_o - [Cx] - [Q])[Dr] \tag{3-95}$$

Letting $\frac{k_1}{k_{-1} + k_2} = K^{\ddagger}$, we solve for [Q]:

$$[Q] = K^{\ddagger}[C]_o[Dr] - K^{\ddagger}[Cx][Dr] - K^{\ddagger}[Q][Dr]$$

continuing:

$$[Q] + K^{\ddagger}[Q][Dr] = K^{\ddagger}[Dr]([C]_o - [Cx]), \text{ and finally:}$$

$$[Q] = \frac{K^{\ddagger}[Dr]([C]_o - [Cx])}{1 + K^{\ddagger}[Dr]} \tag{3-96}$$

In this instance, k_2 is greater than k_1 for the steady-state approximation and since $k_{-1} > 0$, it can be seen that $K^{\ddagger} < 1$. Since in actual laboratory practice $[Dr] \approx 10^{-5}$ M, we can neglect the term $K^{\ddagger}[Dr]$ in the expression $(1 + K^{\ddagger}[Dr])$ since the term $K^{\ddagger}[Dr] \leq [Dr] \approx 10^{-5}$. This gives a simplified expression for [Q]:

$$[Q] = \frac{k_1}{k_{-1} + k_2}[Dr]([C]_o - [Cx]) \tag{3-97}$$

Substitution of Equation 3-97 into Equation 3-91 gives the rate expression:

$$\text{rate}_L = \frac{k_2 k_1}{k_{-1} + k_2}[Dr]([C]_o - [Cx]) \tag{3-98}$$

An expression for [Cx] can be obtained in exactly the same way as it was for the pre-equilibrium condition if we note the similarity in Equation 3-66:

$$[Q] = K_{eq}[CxL][Dr] \quad \text{and Equation 3-92}$$

$$[Q] = \frac{k_1}{k_{-1} + k_2}[CxL][Dr].$$

In the expression for [Cx], Equation 3-80, we simply replace K_{eq} wherever it appears with $\frac{k_1}{k_{-1} + k_2}$. Since we have already shown that this constant is less than one and that $[Dr] \approx 10^{-5}$ M, we can again neglect $\frac{k_1}{k_{-1} + k_2}[Dr]$ when compared to 1 and Equation 3-80 simplifies to:

$$[Cx] = \frac{1}{2}\{-[\frac{1}{K_f} - ([C]_o - C_L)] + \sqrt{[\frac{1}{K_f} - ([C]_o - C_L)]^2 + \frac{4}{K_f}[C]_o}\} \tag{3-99}$$

where, as in Equation 3-83, $\Delta C_L = rate_L \cdot \Delta t$, since Equation 3-64 is not reversible.

A closer look at Equation 3-98 shows that if $k_2 >> k_{-1}$, we can neglect k_{-1} in the expression $(k_{-1} + k_2)$ and Equation 3-98 simplifies to:

$$rate_L = k_1[Dr]([C]_o - [Cx]) \tag{3-100}$$

As was mentioned previously, this equation is in the same form as Equation 3-86:

$$rate_L = K^*[Dr]([C]_o - [Cx]) \quad \text{where} \quad K^* = k_p K_{eq}. \tag{3-86}$$

It is interesting to note the similarity of these expressions. One, Equation 3-100, is obtained assuming steady-state conditions and the other, Equation 3-86 is derived assuming the pre-equilibrium condition.

Steady-State Condition of Rate Increase: Computer Analysis

As was done with the pre-equilibrium condition, we again look at the effect that varying different parameters has on the system. The same procedure was used and units are all the same as those given in Table I, with the exception of k_p. Here, due to the presence of [Dr] in Equation 3-100 k_p has units of $M^{-1}min^{-1}$. The results of varying certain parameters (k_p, K_f, and C_L) can be seen in Figures 9 through 11 and are summarized in the following paragraphs.

$$[Cx] = \frac{1}{2}\{-[\frac{1}{K_f} - ([C]_o - C_L)] + \sqrt{[\frac{1}{K_f} - ([C]_o - C_L)]^2 + \frac{4}{K_f}[C]_o}\} \qquad (3\text{-}99)$$

where, as in Equation 3-83, $\Delta C_L = rate_L \cdot \Delta t$, since Equation 3-64 is not reversible.

A closer look at Equation 3-98 shows that if $k_2 >> k_{-1}$, we can neglect k_{-1} in the expression $(k_{-1} + k_2)$ and Equation 3-98 simplifies to:

$$rate_L = k_1[Dr]([C]_o - [Cx]) \qquad (3\text{-}100)$$

As was mentioned previously, this equation is in the same form as Equation 3-86:

$$rate_L = K^*[Dr]([C]_o - [Cx]) \text{ where } K^* = k_p K_{eq}. \qquad (3\text{-}86)$$

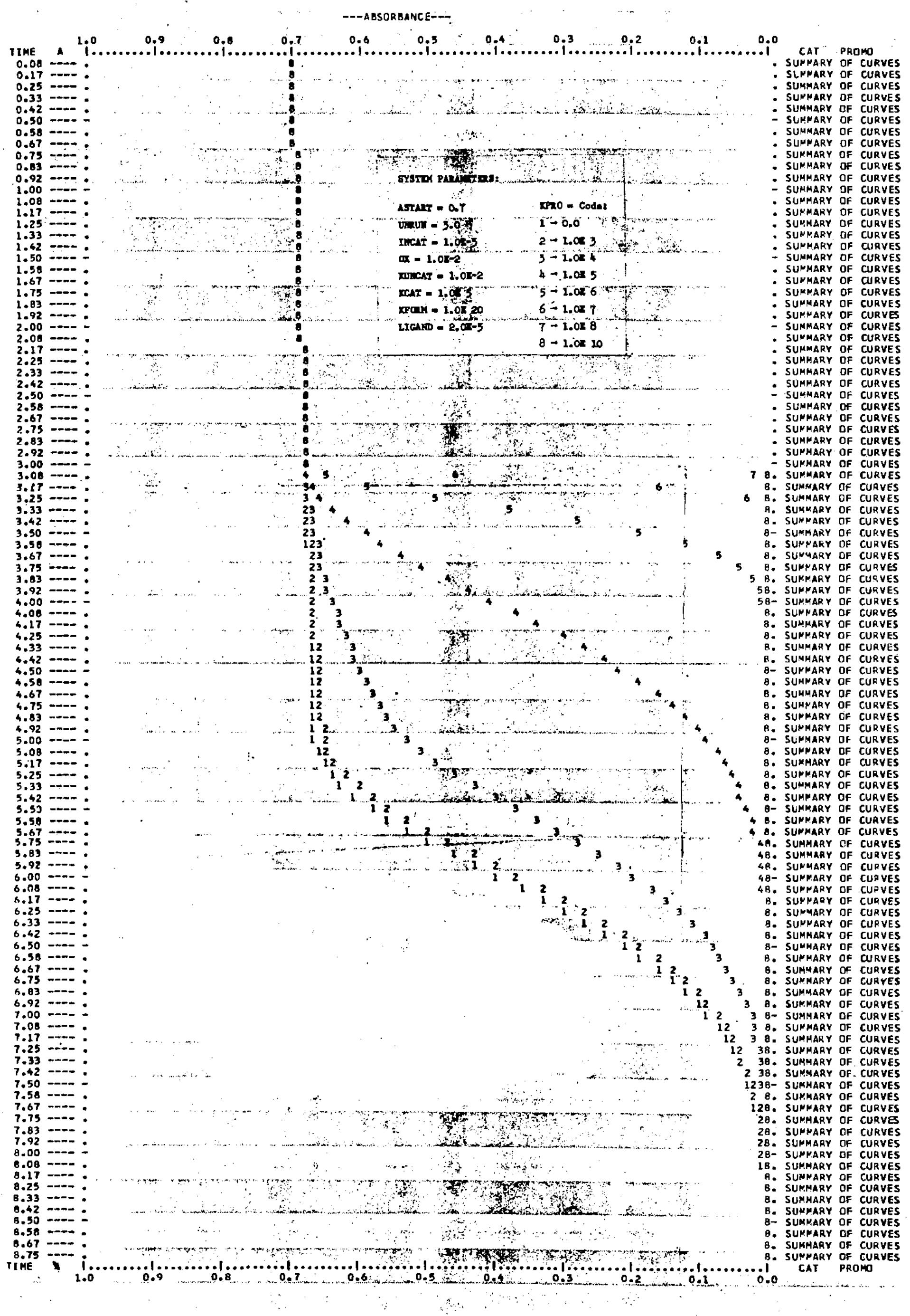
It is interesting to note the similarity of these expressions. One, Equation 3-100, is obtained assuming steady-state conditions and the other, Equation 3-86 is derived assuming the pre-equilibrium condition.

Steady-State Condition of Rate Increase: Computer Analysis

As was done with the pre-equilibrium condition, we again look at the effect that varying different parameters has on the system. The same procedure was used and units are all the same as those given in Table I, with the exception of k_p. Here, due to the presence of [Dr] in Equation 3-100 k_p has units of $M^{-1}min^{-1}$. The results of varying certain parameters (k_p, K_f, and C_L) can be seen in Figures 9 through 11 and are summarized in the following paragraphs.

CHEM 5000--[illegible].E. SIMPSON

COMPOSITE GRAPH SHOWING VARIATION OF CURVES WITH CHANGES IN KPRO 7/12/71



SYSTEM PARAMETERS:

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UNRUN = 5.0
INCAT = 1.0E-5
OX = 1.0E-2
KUNCAT = 1.0E-2
KCAT = 1.0E 5
KFORM = 1.0E 20
LIGAND = 2.0E-5

KPRO = Code:
1 → 0.0
2 → 1.0E 3
3 → 1.0E 4
4 → 1.0E 5
5 → 1.0E 6
6 → 1.0E 7
7 → 1.0E 8
8 → 1.0E 10

Figure 10. Computer Simulation of Hypothetical System; Addition of Rate-Increasing Complexing Agent Assuming Steady-State Condition. Effect of Varying k_p

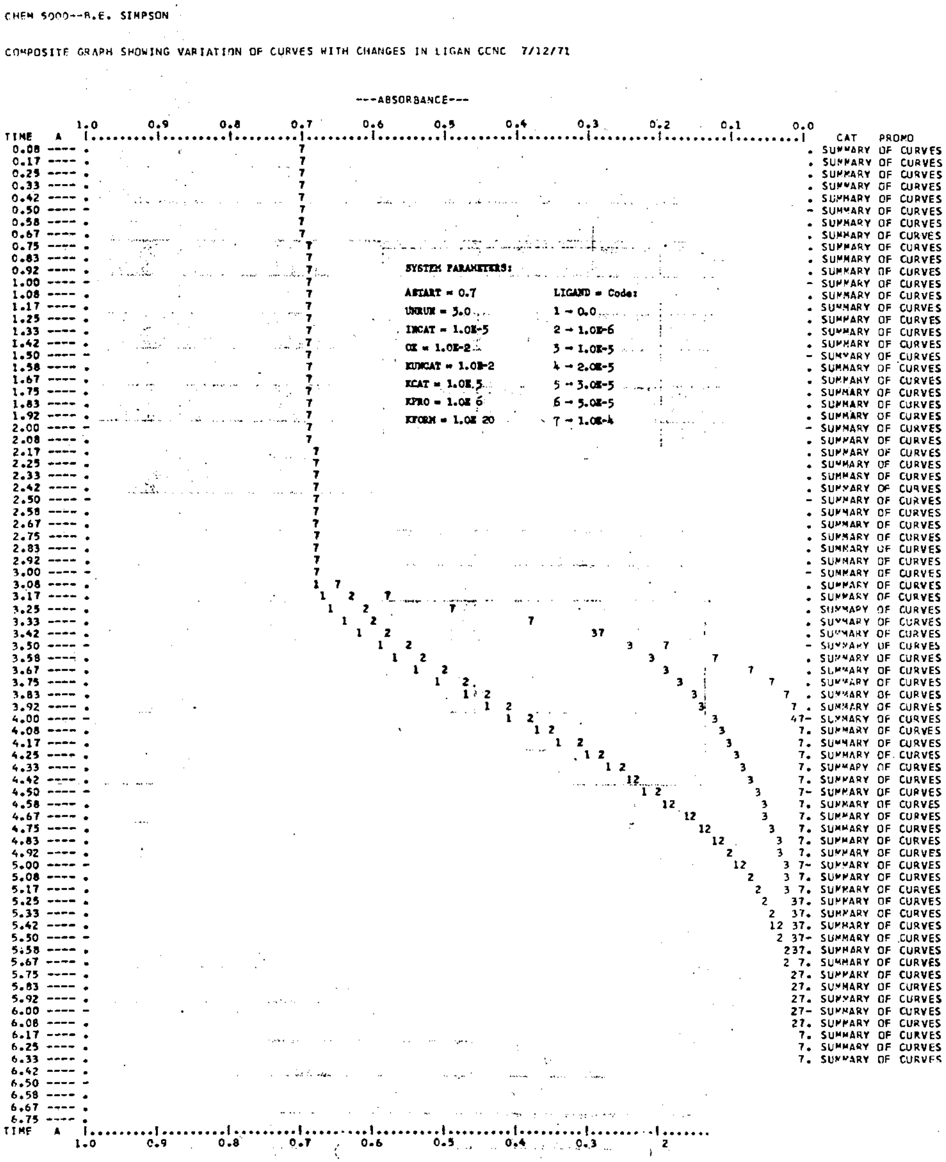

Figure 11. Computer Simulation of Hypothetical System; Addition of Rate-Increasing Complexing Agent Assuming Steady-State Condition. Effect Varying Initial Ligand Concentration

Variation of K_f

K_f is again the formation constant of the metal-ligand complex. Here again, its value affects most directly the amount of catalyst available for reaction by the normal catalytic cycle. That is, if K_f is large enough, practically all of the catalyst added is immediately complexed. How large must K_f be? If we look at Equation 3-99, the expression for [Cx], we can see that the predominant term is:

$$\text{Term} = \frac{1}{K_f} - ([C]_o - C_L) \qquad (3\text{-}101)$$

For example, if $C_L \sim 2 \times 10^{-5}$ and $[C]_o \sim 10^{-5}$, we have:

$$\text{Term} = \frac{1}{K_f} + 10^{-5}$$

Assuming a 1% rejection criterion, we have: $\frac{1}{K_f} < 10^{-5} \cdot 10^{-2}$ or $K_f > 10^7$ in order to neglect the term $\frac{1}{K_f}$ in Equation 3-101. This result agrees with the observation in Figure 9 in which values of $K_f \geq 10^7$ exhibit no further effect on the system.

Variation of k_p

Figure 10 shows the results of varying the rate constant for the promotion cycle. As in the pre-equilibrium condition, we again see a break in the curves where $k_p < k_c$ due to the predominance of rate_p and rate_c in different portions of the curve. Curve 3 especially shows the slower rate due only to promotion in the early portions of the curve where all catalyst is complexed and none is available for reaction by the normal catalytic path. At about t = 4.92 minutes, however, enough catalyst has been added to overcome the amount of complexing agent present and the reaction continues in such a way that rate = rate_c + rate_p instead of rate = rate_p only.

Curve 4 is noteworthy in that here $k_p = k_c$. The overall rate equation used in the simulation is:

$$\frac{dA}{dt} = -k_uA - k_cA[Cx] - k_pA([C]_o - [Cx]) \qquad (3\text{-}102)$$

After rearranging and grouping terms, this expression may be written as:

$$\frac{dA}{dt} = -k_uA - (k_c - k_p)A[Cx] - k_pA[C]_o$$

It can be seen that if $k_c = k_p$, the expression simplifies to:

$$\frac{dA}{dt} = -k_uA - k_pA[C]_o \quad \text{or, since } k_p = k_c\text{:} \qquad (3\text{-}104)$$

$$\frac{dA}{dt} = -k_uA - k_cA[C]_o$$

This is the exact expression obtained for the pre-equilibrium mechanism assuming no complexing agent present (see: Equation 3-12). Thus, if we assume this mechanism, it would be impossible to tell promotion from ordinary metal catalysis under these conditions.

Variation of Total Initial Ligand Concentration

Figure 11 shows the same effect observed in the pre-equilibrium condition. That is, if $[C]_o < C_L$, C_L has no further effect on the system as long as it is greater than a given value. Figure 11 shows that, under this particular set of conditions, the minimum value of C_L is

2×10^{-5} M. Any concentration greater than this has no further effect on the system.

Ligand Effect: True Catalysis or Promotion

The difference between true catalysis and promotion has been mentioned earler. The developments in the previous sections have considered only promotion. In other words, it has been assumed that $dC_L/dt \neq 0$.

If the system is truly catalyzed by the formation of a complex, we may write Equations 3-63 and 3-64 in the following manner:

$$CxL + Dr \rightleftarrows Q \qquad (3\text{-}106)$$

$$Q \rightarrow Dx + L + Cx \qquad (3\text{-}107)$$

The only difference in the expressions describing true catalysis and those for promotion is in the value of C_L. Before, since $\frac{dC_L}{dt} \neq 0$, it was necessary to numerically integrate the expression for $\frac{dC_L}{dt}$ to obtain a value for C_L. In the present case, however, we merely say: C_L = constant = the concentration of ligand initially added. The only modification to the simulating programs was the removal of the expressions giving the value of $\frac{\Delta C_L}{\Delta t}$. Results of computer simulation can be seen in Figures 12 through 17 (assuming the pre-equilibrium condition) and Figures 18 through 20 (assuming the steady-state condition). It can be seen that these curves are, in general, quite similar to their counterparts in Figures 2 through 11. There are a few subtle differences, however, and these contrasts are summarized in Table II.

```
CHEM 5000--B.E. SIMPSON                                                                COPY  1 OF  3

 PROMO--PRE-EQ:  VARIATION OF KEQ                   CLIG = CONSTANT          1/10/72
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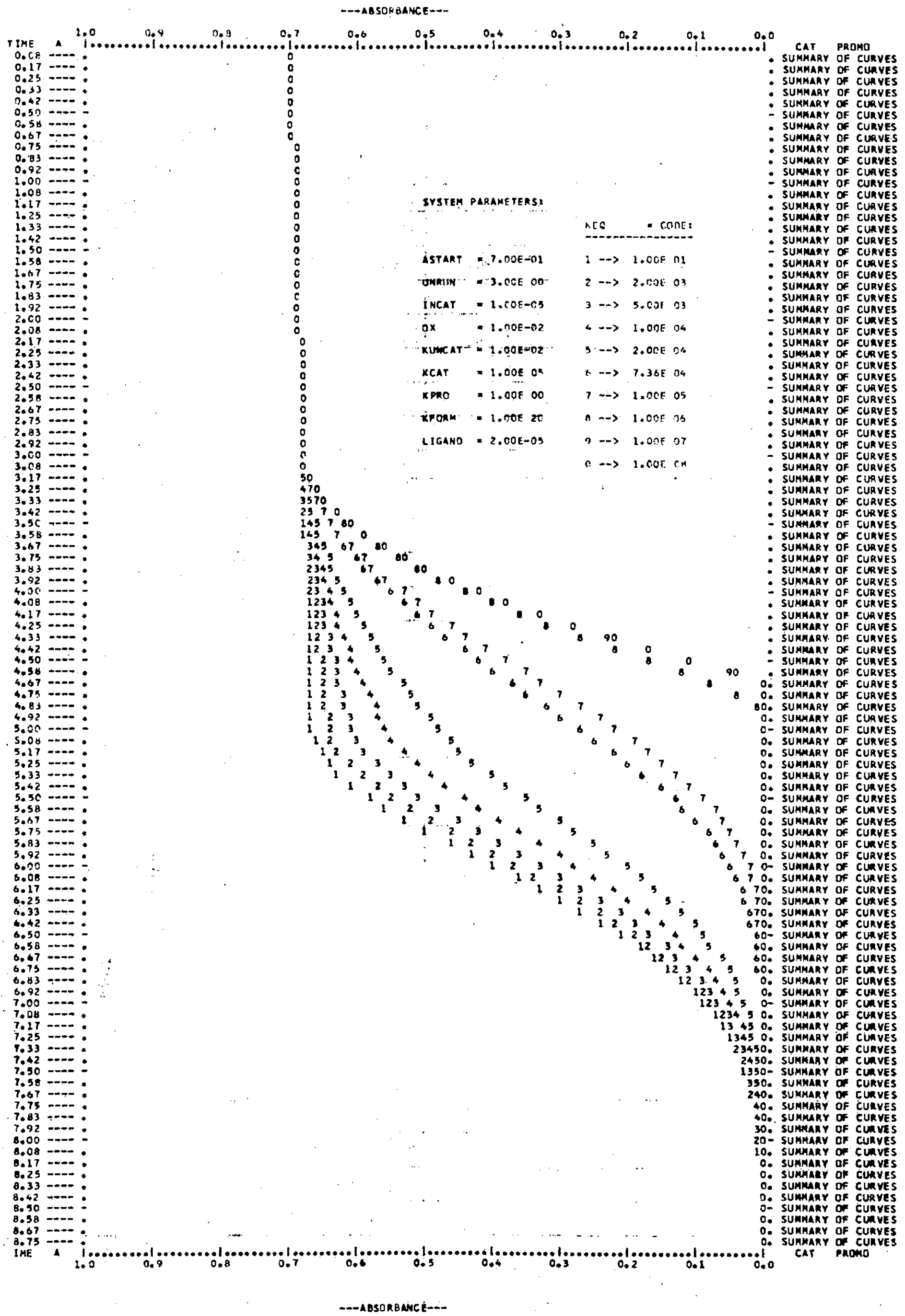

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                              ----------------
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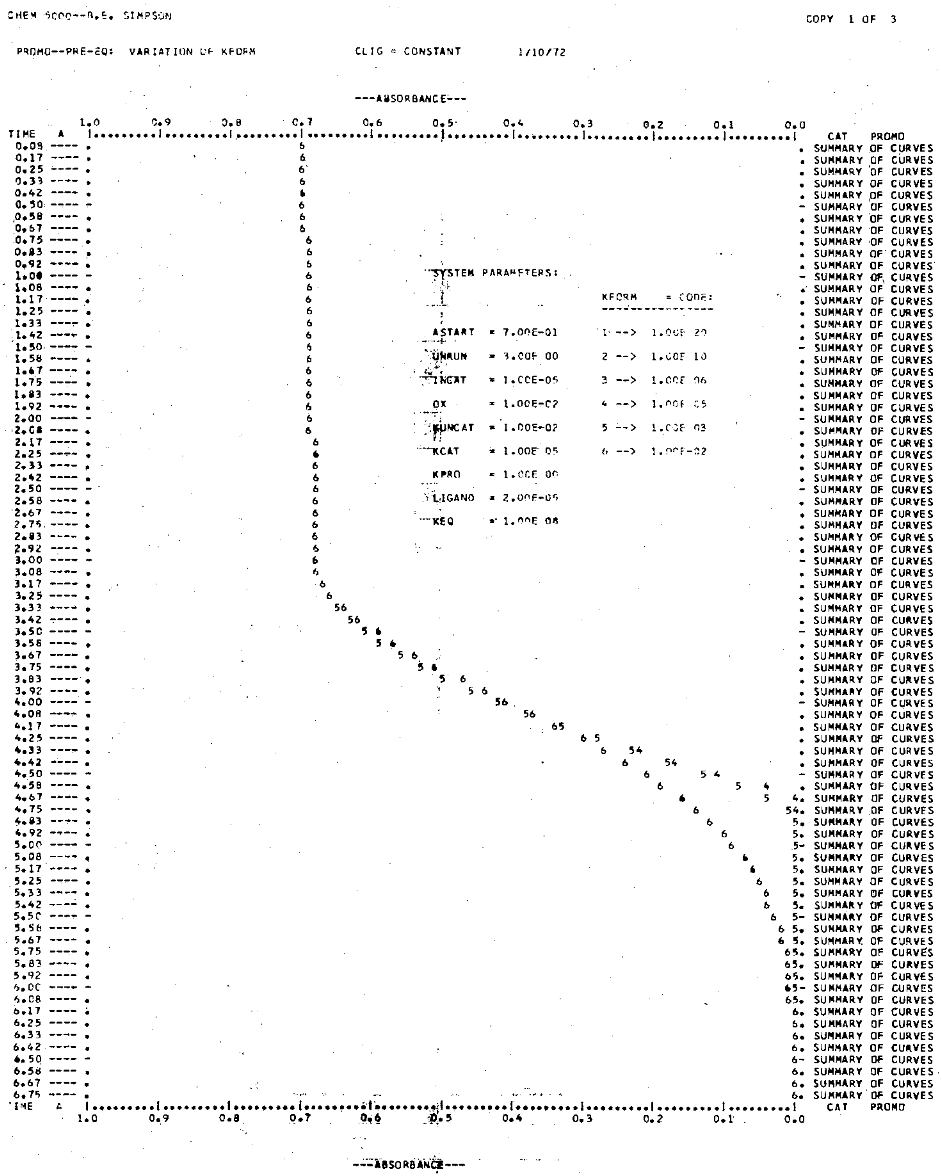
UNRUN   = 3.00E 00            2 -->  2.00E 03
INCAT   = 1.00E-05            3 -->  5.00E 03
OX      = 1.00E-02            4 -->  1.00E 04
KUNCAT  = 1.00E-02            5 -->  2.00E 04
KCAT    = 1.00E 05            6 -->  7.36E 04
KPRO    = 1.00E 00            7 -->  1.00E 05
KFORM   = 1.00E 20            8 -->  1.00E 06
LIGAND  = 2.00E-05            9 -->  1.00E 07
                              0 -->  1.00E 08
```

Figure 12. Computer Simulation of Hypothetical System; Addition of Rate-Increasing Complexing Agent Assuming Pre-equilibrium Condition and True Catalysis. Variation of K_{eq}



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CHEM 5000--R.E. SIMPSON                                          COPY  1 OF  3

 PROMO--PRE-EQ:  VARIATION OF KFORM          CLIG = CONSTANT       1/10/72

SYSTEM PARAMETERS:
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                                    ----------------
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UNRUN    = 3.00E 00                 2 -->  1.00E 10
INCAT    = 1.00E-05                 3 -->  1.00E 06
OX       = 1.00E-02                 4 -->  1.00E 05
KUNCAT   = 1.00E-02                 5 -->  1.00E 03
KCAT     = 1.00E 05                 6 -->  1.00E-02
KPRO     = 1.00E 00
LIGAND   = 2.00E-05
KEQ      = 1.00E 08
```

Figure 13. Computer Simulation of Hypothetical System; Addition of Rate-Increasing Complexing Agent Assuming Pre-equilibrium Condition and True Catalysis. Effect of Varying K_f

```
CHEM 5CCC--R.E. SIMPSON                                                              COPY  1 OF  3

PROMO--PRE-EQ:  VARIATION OF KPRC            CLIG = CONSTANT        1/10/72
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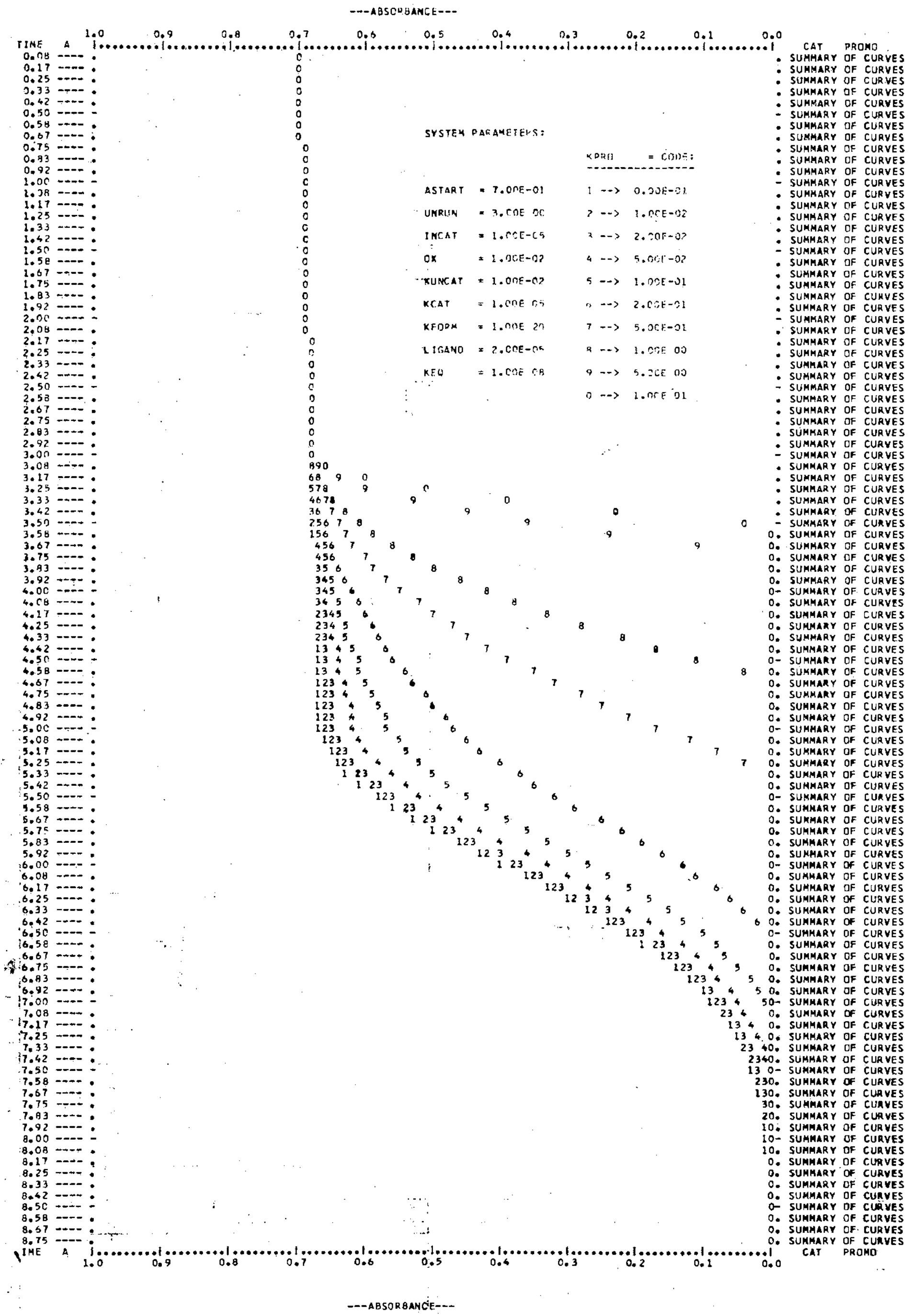

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SYSTEM PARAMETERS:

                              KPRO      = CODE:
                              ----------------

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UNRUN    = 3.00E 00           2 -->  1.00E-02
INCAT    = 1.00E-05           3 -->  2.00E-02
OX       = 1.00E-02           4 -->  5.00E-02
KUNCAT   = 1.00E-02           5 -->  1.00E-01
KCAT     = 1.00E 05           6 -->  2.00E-01
KFORM    = 1.00E 20           7 -->  5.00E-01
LIGAND   = 2.00E-05           8 -->  1.00E 00
KEQ      = 1.00E 08           9 -->  5.00E 00
                              0 -->  1.00E 01
```
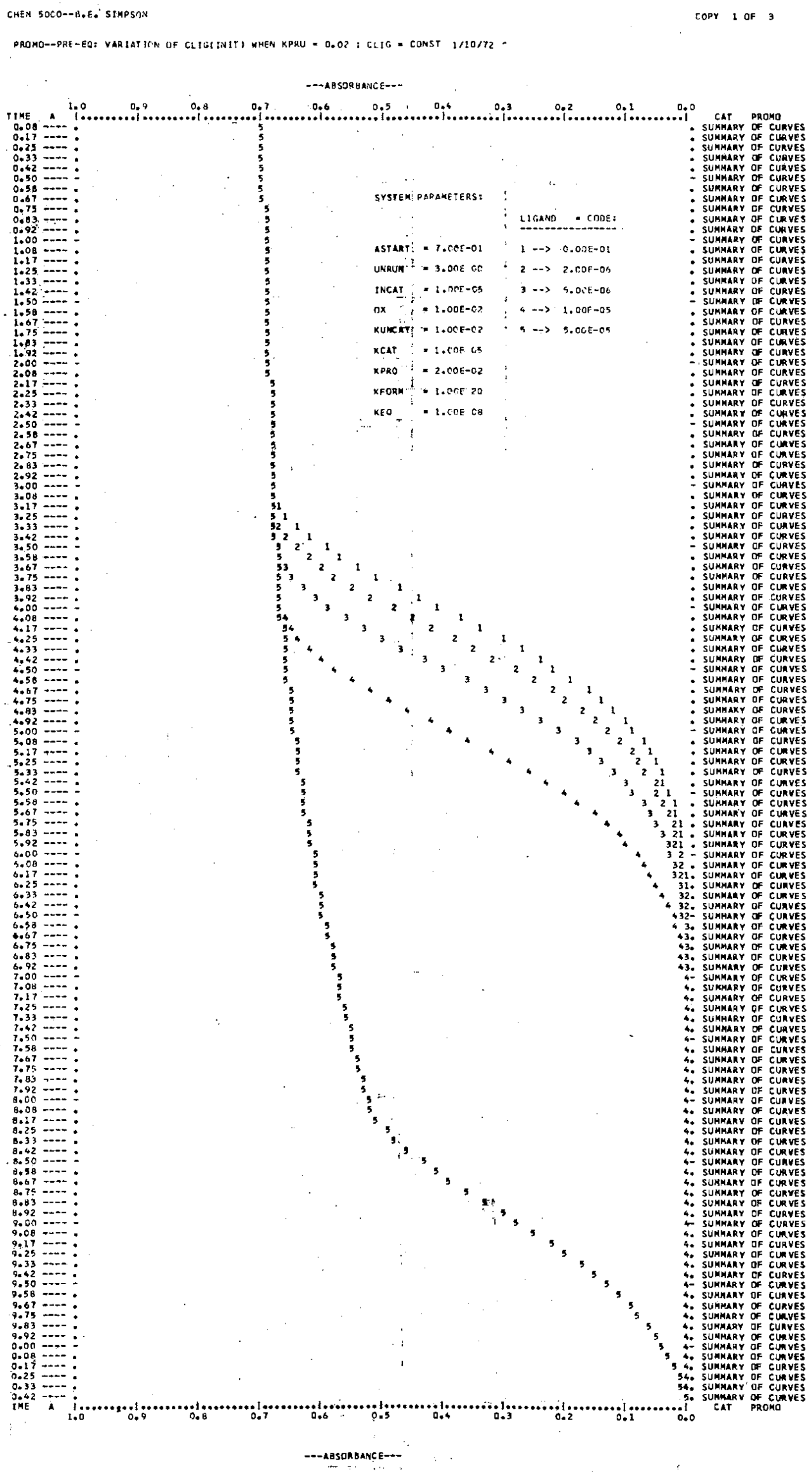

Figure 14. Computer Simulation of Hypothetical System; Addition of Rate-Increasing Complexing Agent Assuming Pre-equilibrium Condition and True Catalysis. Effect of Varying k_p.



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CHEN 5000--B.E. SIMPSON                                                    COPY  1 OF  3

 PROMO--PRE-EQ: VARIATION OF CLIG(INIT) WHEN KPRO = 0.02 : CLIG = CONST  1/10/72

           SYSTEM PARAMETERS:

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                                    ----------------
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           UNRUN   = 3.00E 00       2 -->  2.00E-06
           INCAT   = 1.00E-05       3 -->  5.00E-06
           OX      = 1.00E-02       4 -->  1.00E-05
           KUNCAT  = 1.00E-02       5 -->  5.00E-05
           KCAT    = 1.00E 05
           KPRO    = 2.00E-02
           KFORM   = 1.00E 20
           KEQ     = 1.00E 08
```

Figure 15. Computer Simulation of Hypothetical System; Addition of Rate-Increasing Complexing Agent Assuming Pre-equilibrium Condition and True Catalysis. Effect Varying Initial Ligand Concentration

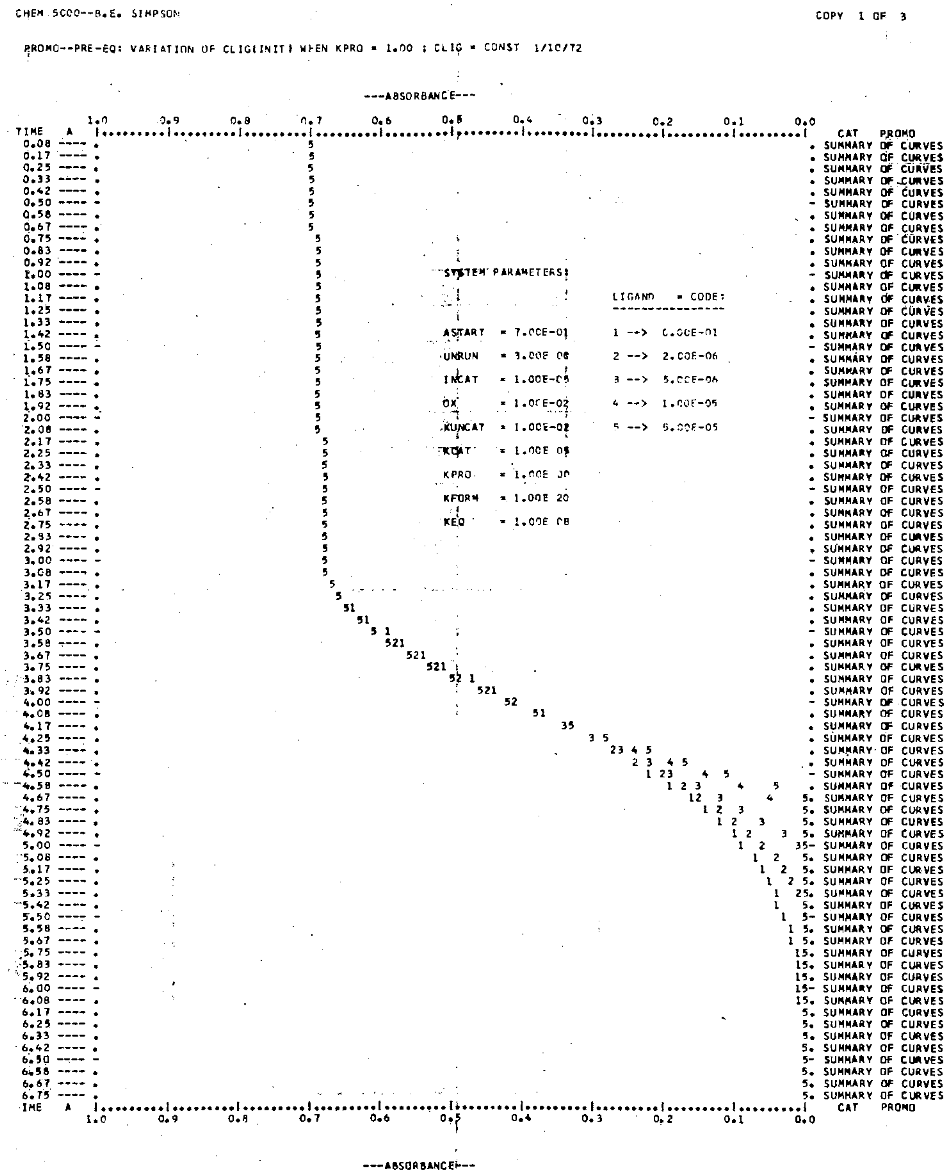

Figure 16. Computer Simulation of Hypothetical System; Addition of Rate-Increasing Complexing Agent Assuming Pre-equilibrium Condition and True Catalysis. Effect Varying Initial Ligand Concentration

```
CHEM 5000--B.E. SIMPSON                                                    COPY  1 OF  3

PROMO--PRE-EQ: VARIATION OF CLIG(INIT) WHEN KPRO = 5.00 ; CLIG = CONST  1/10/72
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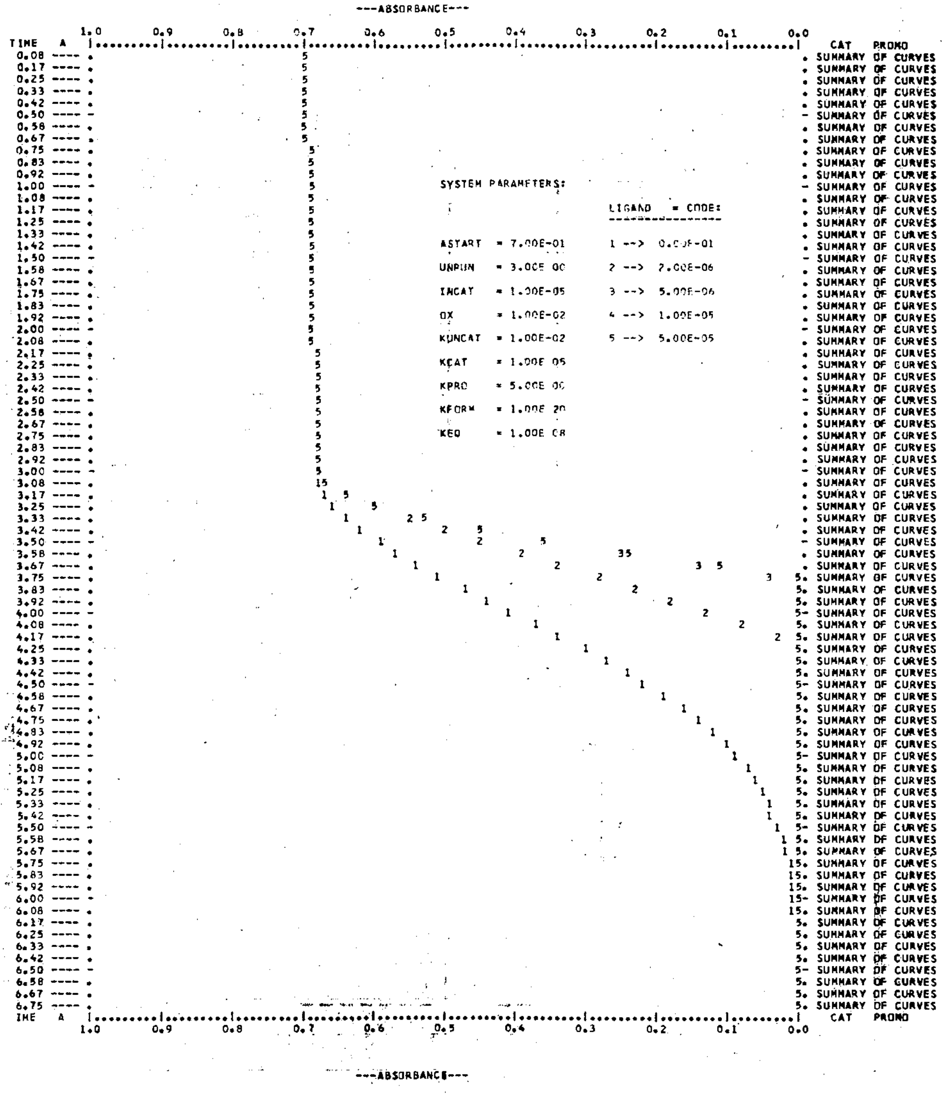

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SYSTEM PARAMETERS:

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INCAT    = 1.00E-05           3 -->  5.00E-06

OX       = 1.00E-02           4 -->  1.00E-05

KUNCAT   = 1.00E-02           5 -->  5.00E-05

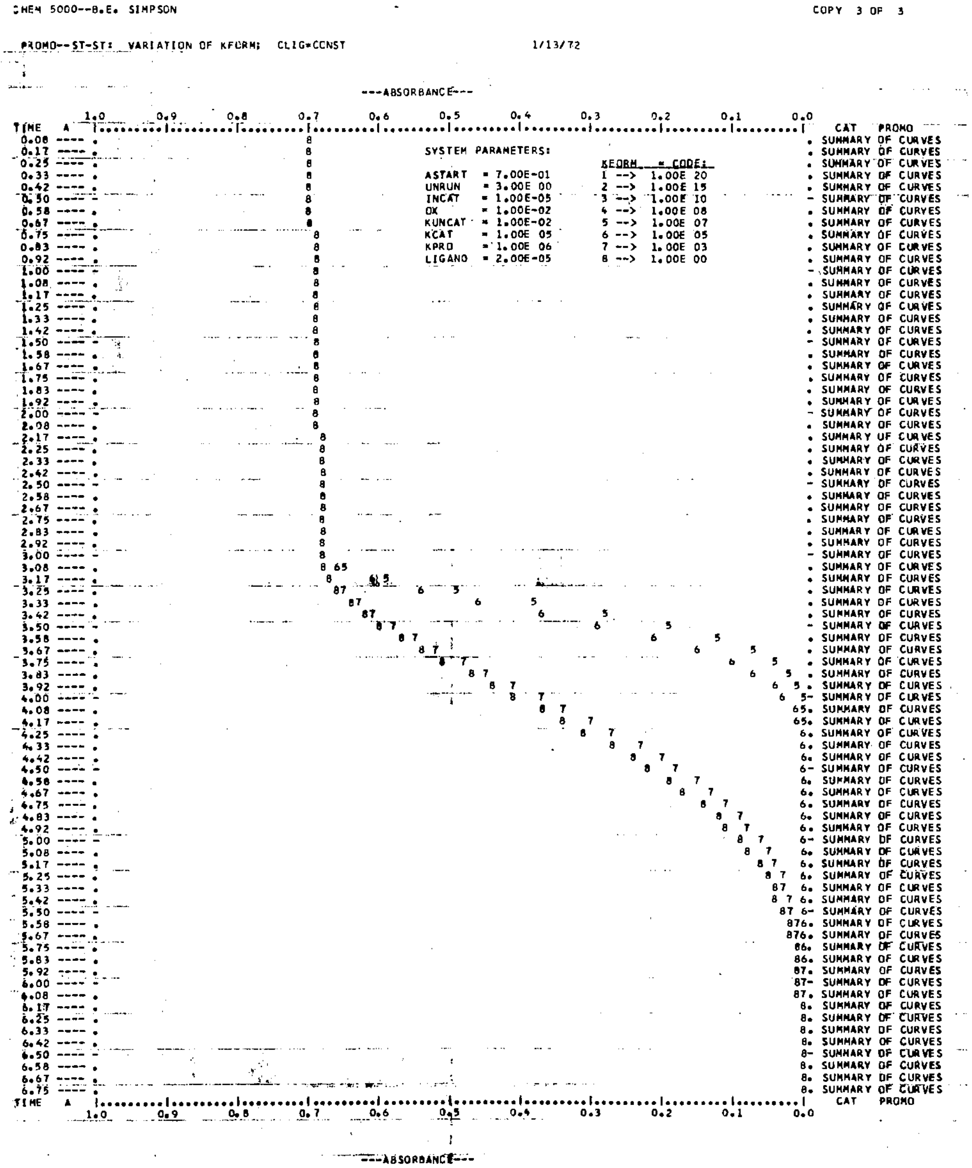
KCAT     = 1.00E 05

KPRO     = 5.00E 00

KFORM    = 1.00E 20

KEQ      = 1.00E 08
```

Figure 17. Computer Simulation of Hypothetical System; Addition of Rate-Increasing Complexing Agent Assuming Pre-equilibrium Condition and True Catalysis. Effect Varying Initial Ligand Concentration



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CHEM 5000--B.E. SIMPSON                                             COPY 3 OF 3

PROMO--ST-ST:  VARIATION OF KFORM;  CLIG=CCNST                1/13/72

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UNRUN   = 3.00E 00                2 -->  1.00E 15
INCAT   = 1.00E-05                3 -->  1.00E 10
OX      = 1.00E-02                4 -->  1.00E 08
KUNCAT  = 1.00E-02                5 -->  1.00E 07
KCAT    = 1.00E 05                6 -->  1.00E 05
KPRO    = 1.00E 06                7 -->  1.00E 03
LIGANO  = 2.00E-05                8 -->  1.00E 00
```
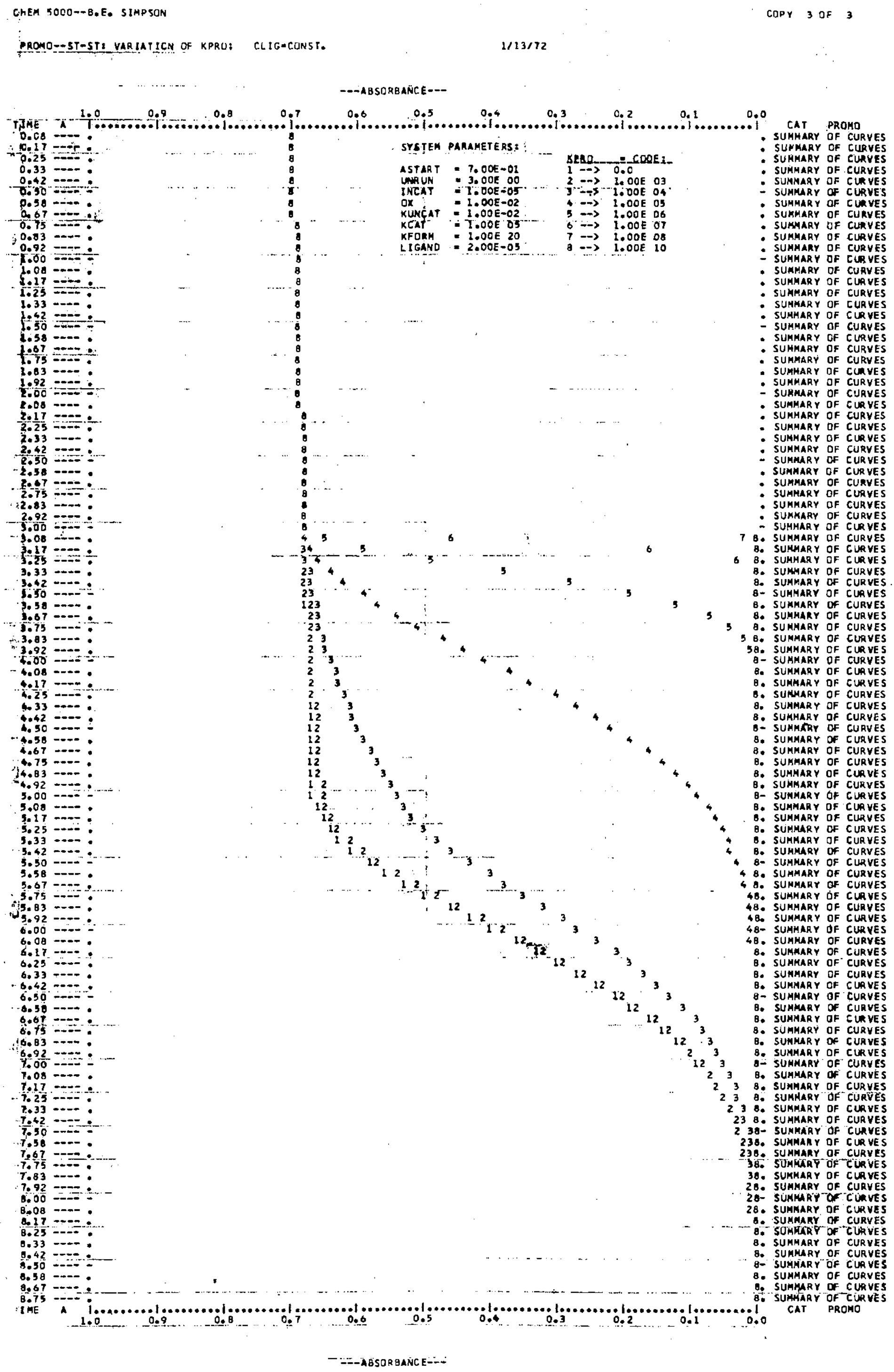

Figure 18. Computer Simulation of Hypothetical System; Addition of Rate-Increasing Complexing Agent Assuming Steady-State Condition and True Catalysis. Effect of Varying K_f



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ChEM 5000--B.E. SIMPSON                                                    COPY  3 OF  3

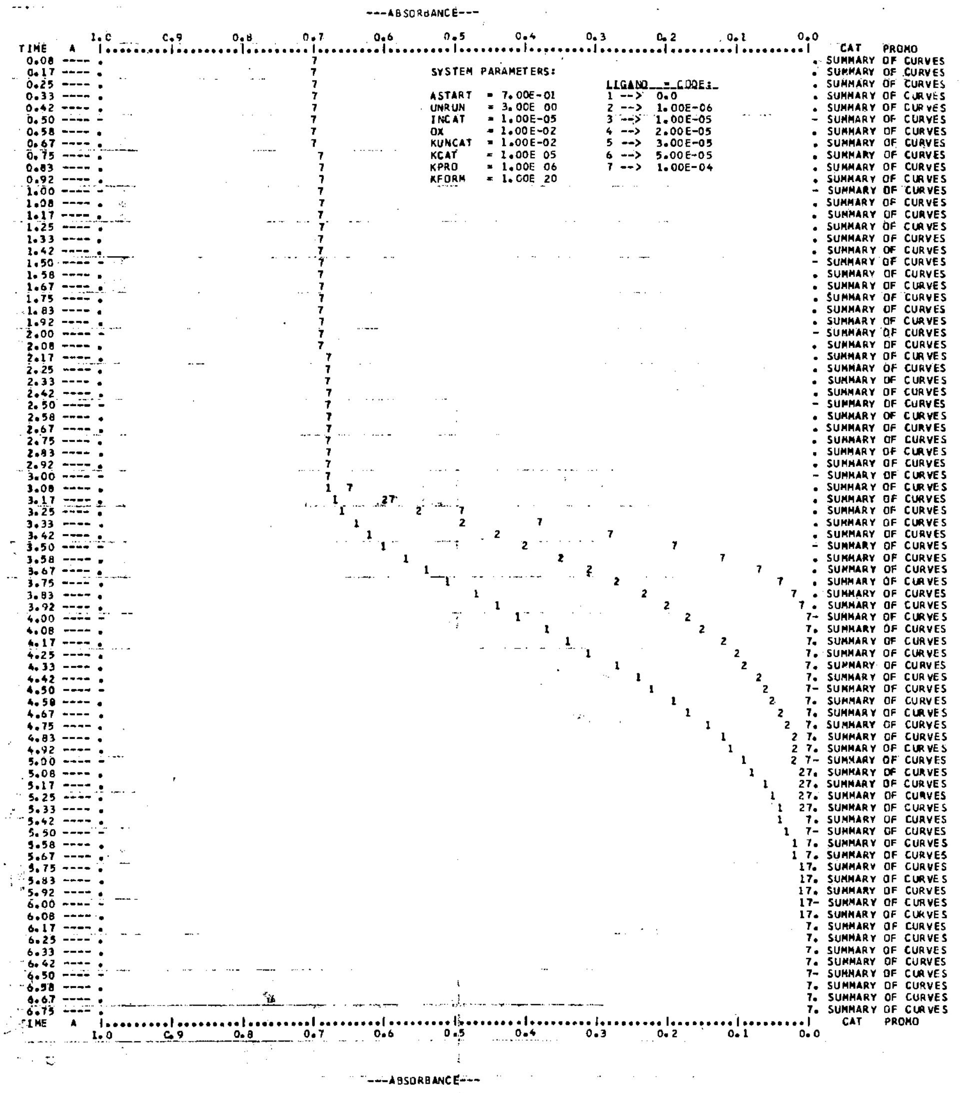
PROMO--ST-ST: VARIATICN OF KPRO:   CLIG=CONST.                 1/13/72

                    SYSTEM PARAMETERS:
                                                   KPRO     = CODE:
                    ASTART   = 7.00E-01            1 -->  0.0
                    UNRUN    = 3.00E 00            2 -->  1.00E 03
                    INCAT    = 1.00E-05            3 -->  1.00E 04
                    OX       = 1.00E-02            4 -->  1.00E 05
                    KUNCAT   = 1.00E-02            5 -->  1.00E 06
                    KCAT     = 1.00E 05            6 -->  1.00E 07
                    KFORM    = 1.00E 20            7 -->  1.00E 08
                    LIGAND   = 2.00E-05            8 -->  1.00E 10
```

Figure 19. Computer Simulation of Hypothetical System; Addition of Rate-Increasing Complexing Agent Assuming Steady-State Condition and True Catalysis. Effect of Varying k_p

```
CHEM 5000--B.E. SIMPSON                                                    COPY 3 OF 3

PROMO--ST-ST:  VARIATION OF LIGAND;  CLIG=CONSTANT                1/13/72
```



```
SYSTEM PARAMETERS:

ASTART   = 7.00E-01
UNRUN    = 3.00E 00
INCAT    = 1.00E-05
OX       = 1.00E-02
KUNCAT   = 1.00E-02
KCAT     = 1.00E 05
KPRO     = 1.00E 06
KFORM    = 1.00E 20

LIGAND  = CODE:
1 --> 0.0
2 --> 1.00E-06
3 --> 1.00E-05
4 --> 2.00E-05
5 --> 3.00E-05
6 --> 5.00E-05
7 --> 1.00E-04
```

Figure 20. Computer Simulation of Hypothetical System; Addition of Rate-Increasing Complexing Agent Assuming Steady-State Condition and True Catalysis. Effect of Varying Initial Ligand Concentration

TABLE II

COMPARISON OF RESULTS OBTAINED ASSUMING TRUE CATALYSIS WITH THOSE OBTAINED ASSUMING PROMOTION

Parameter Varied	Condition Assumed	Reaction Rate Comparison			
		Catalysis	Ref. Fig:	Promotion	Ref. Fig:
		Faster than Promotion When:		*Faster than Catalysis When:*	
KEQ	Pre-eq.	KEQ large compared to 1/(Dr)	12	KEQ small compared to 1/(Dr)	2,3
KFORM	Pre-eq.	K_f larger than $1/(C)_o$	13	Never faster	4
	St-St	K_f larger than $1/(C)_o$	18	Never faster	9
KPRO	Pre-eq.	k_p larger than ε/k_c	14	k_p smaller than ε/k_c	5,6
	St-St	Never faster	19	k_p smaller than k_c	10
CLIG	Pre-eq.	Always faster	15,16,17	Never faster	7,8
	St-St	C_L much smaller than $(C)_o$	20	Never faster	11

The most drastic and, consequently, the most interesting difference in rates between true catalysis and promotion effects is observed in the case of variation of initial ligand concentration. This rather pronounced difference in effects may be explained by looking at two key expressions. Equations 3-80 and 3-99 give the amount of catalyst available for reaction by the normal catalytic cycle when assuming the pre-equilibrium and steady-state mechanisms, respectively. These expressions can in turn be analyzed in terms of a common expression:

$$\text{Term} = [C]_o - C_L \ .$$

As was mentioned in earlier discussion, as long as $[C]_o < C_L$, almost all of the available catalyst is tied up in the complex, CxL. If this is the case, the $\text{rate}_c \approx 0$ and $\text{rate}_{\text{overall}} = \text{rate}_L$ (rate_L = rate due to ligand effect). It can be seen, then, that if $\frac{dC_L}{dt} = 0$ and C_L is therefore not decreasing as the reaction proceeds, catalyst will be tied up longer by a given amount of ligand added at $t = 0$. If, for a given system, the rate due to ligand effects is faster than the rate due to the normal catalytic cycle, then we would expect the faster rate to persist for a longer time if C_L is not destroyed. This accounts for the observed effect in the simulated curves. If we had chosen a system in which $\text{rate}_L < \text{rate}_c$, the opposite effect would be observed; i.e., the promotion effect would give the fastest overall rate since the slower rate (rate_L) would not be allowed to persist for as long since C_L is being destroyed as the reaction proceeds.

It is noteworthy to mention that the curves observed assuming the steady-state condition and true catalysis, most closely resemble those shown in the literature (9).

Determination of Constants

The second phase of this study of catalytic titrations involved the elucidation of rate constants for the catalyzed and uncatalyzed portions of a given reaction from absorbance versus time data. The basic principles of the method used are the same regardless of the mechanism chosen: that is, estimates of rate constants may be obtained by plotting the instantaneous rate of a reaction, measured as the derivative of an absorbance versus time curve against some function of time and absorbance. That particular function to be used depends upon the system under study and the form of the differential equations describing the system. For this reason, a hypothetical system very similar to that described earlier (see pages 9-11 this work) was used to develop the computer programs necessary to obtain estimates of rate constants. Applications of a modified version of the program described here to a real system are discussed in the next chapter.

Consider a generalized, simplified rate expression of the following form:

$$\text{RATE} = \text{UNCATALYZED RATE} + \text{CATALYZED RATE} \qquad (3\text{-}108)$$

where:

$$\text{UNCAT RATE} = \frac{dA}{dt} = -k_u A\ , \qquad (3\text{-}109)$$

$$\text{CAT RATE} = \frac{dA}{dt} = -k_c A(C)_o, \qquad (3\text{-}110)$$

$(C)_o$ = amount of catalyst added at time = t or

$(C)_o$ = Ct = (catalyst addition rate in moles/liter·min) (time) and

A = absorbance of the monitored species.

It was assumed throughout this development for the sake of simplicity and clarity of illustration that k_u and k_c represented true first and second order rate constants, respectively, and that the rate of the reaction was independent of any parameters other than those given in the rate expression.

Looking first at the uncatalyzed part, it can be seen that if dA/dt is plotted as a function of A, the slope of the resulting straight line will be equal to $- k_u$. Now, taking the overall rate equation and rearranging, we get:

$$\frac{dA}{dt} + k_u A = - k_c ACt \tag{3-111}$$

Here again, knowing k_u, we can plot the quantity $(\frac{dA}{dt} + k_u A)$ versus ACt and, again, obtain the slope, $-k_c$, and thus the catalyzed rate constant.

It was obvious that for this procedure to work, a reliable method of determining the derivative, dA/dt, must be used. Such a method was found in the literature (16). The method essentially consists of the following. An odd number of ordinate points is used in a "convoluting smooth" to obtain the derivative of the central point of those taken. The value of the derivative is found using the following relationship:

$$\text{derivative of central point} = \frac{\sum_{i=-m}^{m} C_i Y_i}{\Delta X \cdot N}$$

where:

Y = f(X),

m = number of points taken,

C_i = convoluting integers, and

N = normalizing factor.

The constants C_i and the normalizing factor N are given in tables in the reference (16).

An equally important factor, of course, is the least-squares fitting routine. The method used is the same as that outlined in an article by Sullivan, Rydberg, and Miller (17). A set of normal equations is generated and then solved by matrix inversion. The most useful portion of their work was the inclusion of a data weighting feature and a method of obtaining statistical parameters by using the diagonal elements of the inverted matrix arising from the solution of the set of normal equations.

Weighted least squares minimizes the function:

$$S = \sum_{i=1}^{I} W_i \left(Y_{i(calc)} - Y_{i(obs)}\right)^2 \tag{3-113}$$

where:

S = "sum of squares",

I = no. of data points,

W_i = weights of each individual data point,

Y_{obs} = observed or experimental ordinate value, and

Y_{calc} = ordinate value calculated from results of fit.

In the present work, weights for each point were based on indeterminate errors from two sources: (1) instrumental error and (2) error in reading the chart paper from which the data was obtained. This may be represented as:

$$\text{TOTAL ERROR} = \text{INSTRUMENTAL ERROR} + \text{CHART READING ERROR} \quad (3\text{-}114)$$

An expression for instrumental error may be arrived at in the same manner as that used by Willard, Merit, and Dean (18). According to these authors:

$$\frac{\Delta C}{C} = \frac{0.4343\ \Delta T}{T \log T} \quad (3\text{-}115)$$

where:

C = concentration of monitored species,

ΔC = error in C,

T = transmittance, and

ΔT = photometric error

But, since:

$$A = -\log T \quad (3\text{-}116)$$

where: A = absorbance, we have:

$$\frac{\Delta C}{C} = \frac{0.4343\ \Delta T}{-A\cdot 10^{-A}} = \frac{0.4343\cdot 10^{A}\cdot \Delta T}{-A} \quad (3\text{-}117)$$

From Beer's Law:

$$C = \frac{A}{\varepsilon b} \text{ or } \Delta C = \frac{\Delta A}{\varepsilon b} \quad (3\text{-}118)$$

where:

ε = molar absorptivity and b = path length = 1 cm.

Then, ignoring the negative sign since error is absolute, the final expression for the relative error due to instrumental error is:

$$\text{rel. error} = \frac{\Delta A}{A} = \frac{0.4343 \cdot 10^{A} \cdot \Delta T}{A} \qquad (3\text{-}119)$$

If the absolute error in chart reading is represented by ΔR, the overall expression for relative error becomes:

$$\text{TOTAL ERROR} = \frac{1}{A}(.4343 \cdot 10^{A} \cdot \Delta T + \Delta R) \qquad (3\text{-}120)$$

A plot of total error versus absorbance with $\Delta T = .005$ and $\Delta R = .002$ is shown in Figure 21. A weighting function which gives almost equal weight to those points occurring in the flat portion of the curve is:

$$W_i = [\frac{P}{100} - (\text{total rel. error})] \cdot 10 \qquad (3\text{-}121)$$

where:

P = maximum acceptable per cent error.

A plot of W_i versus A with $P = 10\%$ is also shown in Figure 21. This is the weighting expression used for the determination of system parameters.

"Data" for a test run was provided by simulating a curve using the following parameters:

A_o = initial absorbance = 0.7

k_u = uncatalyzed rate constant = 10^{-4}/min.

k_c = catalyzed rate constant = 10^{5}L/M·min.

C = catalyst addition rate = 10^{-5}M/L·min.

Values of absorbance thus obtained for the overall (that is, uncat + cat) portions of the curve were read into a program which does the following:

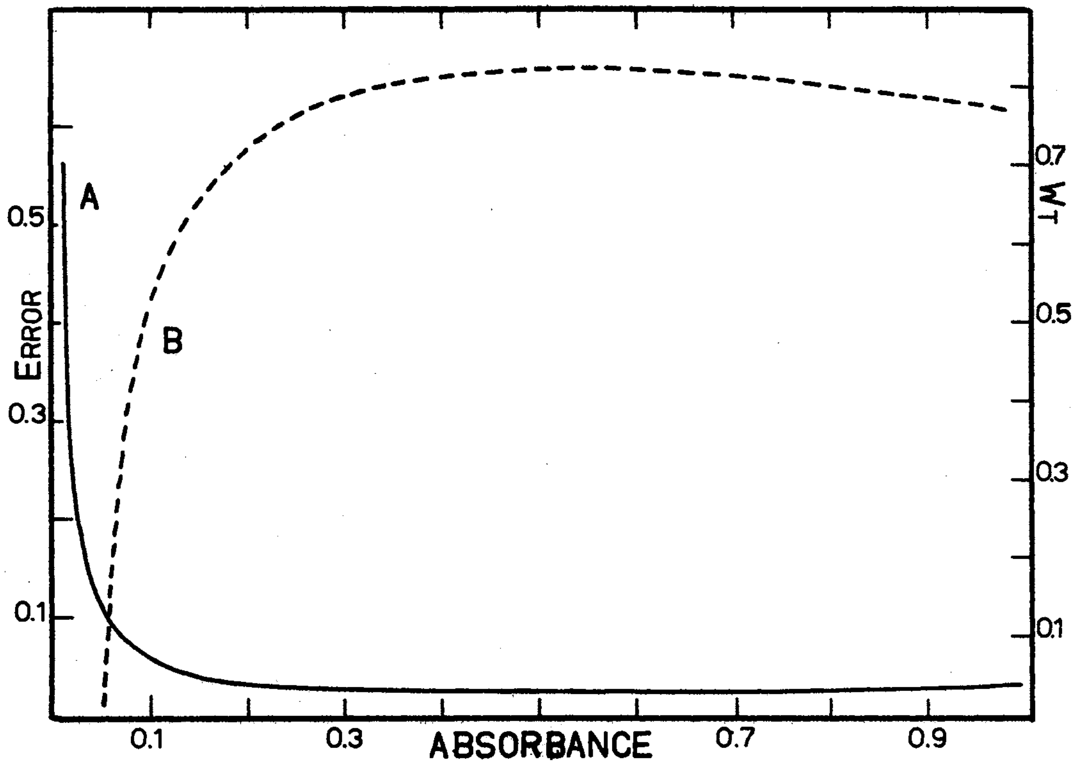


Figure 21. Error Curves for Absorbance Region 0 to 1. Curve A: Relative Error in Measurement as Function of Absorbance. Curve B: Weight Assigned to Individual Data Points Derived From Corresponding Absorbance Value

i) determines dA/dt,

ii) computes the corresponding independent and dependent variables,

iii) does a least squares fit of the function thus obtained, and

iv) prints out the slope of the line and goodness of fit parameters.

The points obtained from the program along with the best least squares line are plotted in Figure 22. The value found by the program for the catalyzed rate constant was:

$$k_c = 1.02 \times 10^5 .$$

Compared to the 'true' value used in the simulation, this number contains an error of + 2.0%.

A complete listing of the source program along with a flow diagram and definition of all FORTRAN variables is given in Appendix D.

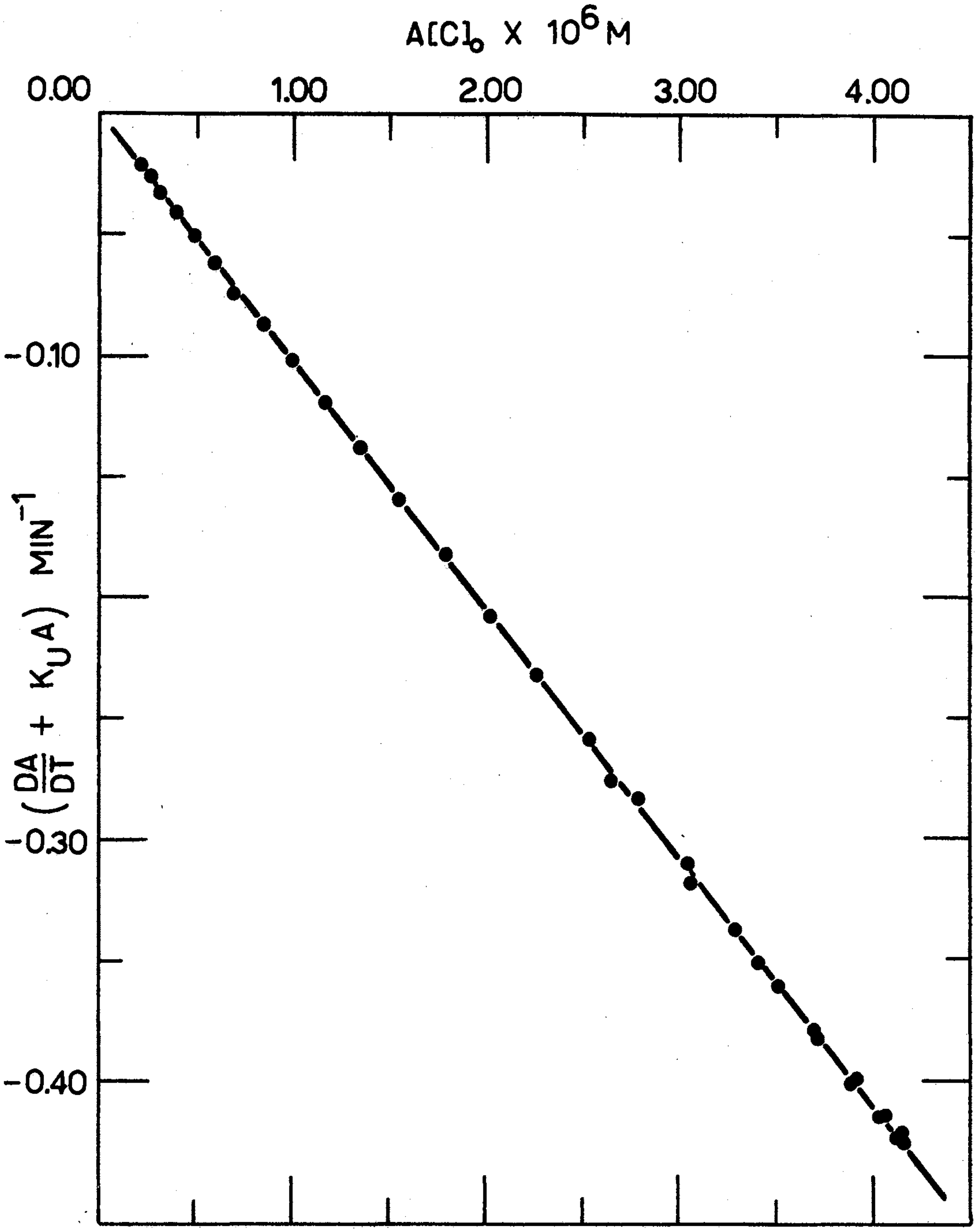


Figure 22. Determination of Rate Constants Using a Computer Simulated Catalytic Titration Curve as Data

CHAPTER IV

ANALYSIS OF A REAL SYSTEM

Catalyzed Oxidation of a Dye

The system selected for analysis was the Mn(II) catalyzed oxidation of malachite green cation (MG+) by periodate ions. This system was chosen for study primarily due to its relatively broad use in analytical applications (19,20). First, a set of criteria had to be set aside to decide when a given mechanism adequately "describes" the system under study. The criteria used were these: (1) values found for any rate constant must remain constant under variation of at least one major system variable (such as initial dye concentration, oxidizing agent concentration, catalyst addition rate, etc.) and (2) constants found with the program described in Chapter III must reproduce the experimental curve from which they were derived when used in the simulation program also described in Chapter III. Any mechanism which led to the satisfaction of these two points was considered to adequately describe the behavior of the system under study.

Selection of a Simplified Mechanism

The logical place to start the search for a suitable mechanism to describe the Mn(II) catalyzed oxidation was with those mechanistic assumptions discussed previously in this work in Chapter III. As has been pointed out earlier, assumption of pre-equilibrium kinetics leads to a rate expression of the form:

$$\frac{dA}{dt} = -k_u A - k_c A[\mathrm{Mn(II)}]_t \qquad (4\text{-}1)$$

where:

$[\mathrm{Mn(II)}]_t$ = amt. of catalyst added at time = t

Since the value of k_u was known from previous work (23), and was equal to 1.5×10^{-3} min^{-1}, the contribution from the uncatalyzed reaction would be small when compared to that from the catalyzed portion. Since in this work the uncatalyzed reaction was almost imperceptible over a period of three minutes and rough calculations confirmed the order of magnitude of the reported value, the uncatalyzed contribution has been neglected in the determination of catalyzed rate constants for the sake of simplicity.

A set of experimental titration curves was obtained, the absorbance values were read and punched onto IBM data cards, and the instantaneous rate, dA/dt, was plotted as a function of the absorbance times the catalyst concentration. The plots were straight lines, but the resulting constants did not meet criterion #1, i.e.,--the values were a function of initial dye concentration. Consideration of a reverse reaction in the rate determining step succeeded in producing a better fit of the data, but failed to compensate for the dependence of rate constants upon initial dye concentration.

The possibility of a chain mechanism was also considered using the following equations to describe the system:

$$2\ \mathrm{MG}^{+} + \mathrm{IO}_4^{-} \xrightarrow{k_o} \mathrm{IO}_3^{-} + 2\mathrm{MG}^{++}\!\cdot$$

$$MG^{+\!+}\!\!\cdot + Mn^{II} \overset{k_1}{\rightarrow} Mn^{III} + MG^{+}$$

$$MG^{+} + Mn^{III} \overset{k_2}{\rightarrow} Mn^{II} + \text{Products}$$

$$MG^{+\!+}\!\!\cdot \overset{k_3}{\rightarrow} \text{Products}'$$

This mechanism was ruled out "on paper", however, when the derived rate equation proved to be independent of catalyst concentration, which was definitely unrealistic.

These results led to the consideration of the steady-state approximation in the reaction kinetics in hopes of obtaining a mechanism which better described the system. The apparent reliance of the observed rate upon initial dye concentration prompted the inclusion of possible reverse reactions in the development of the overall rate expressions.

Use of the steady-state approximation led to the development of a mechanism which met both of the established criteria. Complete derivation of the final expression follows.

Development of Expressions for the Selected System

The reaction path considered was:

$$Mn(II) + \frac{1}{2}\,IO_4^{-} + H^{+} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Mn(III) + \frac{1}{2}\,IO_3^{-} + \frac{1}{2}\,H_2O \qquad (4\text{-}2)$$

$$Mn(III) + MG^{+} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Mn(II) + P \qquad (4\text{-}3)$$

It was felt that Mn(III) was a reasonable choice for the reaction intermediate and was preferred over any higher oxidation states for several reasons. First, it is well known that acetate stabilizes the +3 oxi-

$$\mathrm{MG}^{++}\cdot + \mathrm{Mn}^{II} \xrightarrow{k_1} \mathrm{Mn}^{III} + \mathrm{MG}^{+}$$

$$\mathrm{MG}^{+} + \mathrm{Mn}^{III} \xrightarrow{k_2} \mathrm{Mn}^{II} + \text{Products}$$

$$\mathrm{MG}^{++}\cdot \xrightarrow{k_3} \text{Products}'$$

This mechanism was ruled out "on paper", however, when the derived rate equation proved to be independent of catalyst concentration, which was definitely unrealistic.

These results led to the consideration of the steady-state approximation in the reaction kinetics in hopes of obtaining a mechanism which better described the system. The apparent reliance of the observed rate upon initial dye concentration prompted the inclusion of possible reverse reactions in the development of the overall rate expressions.

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<u>Development of Expressions for the Selected System</u>

The reaction path considered was:

$$\mathrm{Mn(II)} + \frac{1}{2}\,\mathrm{IO_4}^- + \mathrm{H}^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Mn(III)} + \frac{1}{2}\,\mathrm{IO_3}^- + \frac{1}{2}\,\mathrm{H_2O} \tag{4-2}$$

$$\mathrm{Mn(III)} + \mathrm{MG}^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{Mn(II)} + \mathrm{P} \tag{4-3}$$

It was felt that Mn(III) was a reasonable choice for the reaction intermediate and was preferred over any higher oxidation states for several reasons. First, it is well known that acetate stabilizes the +3 oxi-

$$\mathrm{MG}_{\cdot}^{++} + \mathrm{Mn}^{\mathrm{II}} \xrightarrow{k_1} \mathrm{Mn}^{\mathrm{III}} + \mathrm{MG}^{+}$$

$$\mathrm{MG}^{+} + \mathrm{Mn}^{\mathrm{III}} \xrightarrow{k_2} \mathrm{Mn}^{\mathrm{II}} + \text{Products}$$

$$\mathrm{MG}_{\cdot}^{++} \xrightarrow{k_3} \text{Products}'$$

This mechanism was ruled out "on paper", however, when the derived rate equation proved to be independent of catalyst concentration, which was definitely unrealistic.

These results led to the consideration of the steady-state approximation in the reaction kinetics in hopes of obtaining a mechanism which better described the system. The apparent reliance of the observed rate upon initial dye concentration prompted the inclusion of possible reverse reactions in the development of the overall rate expressions.

Use of the steady-state approximation led to the development of a mechanism which met both of the established criteria. Complete derivation of the final expression follows.

<u>Development of Expressions for the Selected System</u>

The reaction path considered was:

$$\mathrm{Mn(II)} + \tfrac{1}{2}\,\mathrm{IO_4}^- + \mathrm{H}^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Mn(III)} + \tfrac{1}{2}\,\mathrm{IO_3}^- + \tfrac{1}{2}\,\mathrm{H_2O} \qquad (4\text{-}2)$$

$$\mathrm{Mn(III)} + \mathrm{MG}^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{Mn(II)} + \mathrm{P} \qquad (4\text{-}3)$$

It was felt that Mn(III) was a reasonable choice for the reaction intermediate and was preferred over any higher oxidation states for several reasons. First, it is well known that acetate stabilizes the +3 oxi-

$$\text{Rate} = -(k_2[\text{Dr}] + k_{-2}[\text{Dx}])[\text{Cx}] + k_{-2}[\text{C}]_o[\text{Dx}] \qquad (4\text{-}11)$$

Substitution of Equation 4-9 for [Cx] led to:

$$\text{Rate} = \frac{-(k_2[\text{Dr}] + k_{-2}[\text{Dx}])(k_1[\text{Ox}]^{\frac{1}{2}} + k_{-2}[\text{Dx}])[\text{C}]_o}{k_{-1}[\text{R}]^{\frac{1}{2}} + k_1[\text{Ox}]^{\frac{1}{2}} + (k_2[\text{Dr}] + k_{-2}[\text{Dx}])} + k_{-2}[\text{Dx}][\text{C}]_o \qquad (4\text{-}12)$$

Proceeding with the algebra, the first term to the right of the equals sign was divided by $(k_2[\text{Dr}] + k_{-2}[\text{Dx}])$. This gave:

$$\text{Rate} = \frac{-(k_1[\text{Ox}]^{\frac{1}{2}} + k_{-2}[\text{Dx}])[\text{C}]_o}{\dfrac{k_{-1}[\text{R}]^{\frac{1}{2}} + k_1[\text{Ox}]^{\frac{1}{2}}}{(k_2[\text{Dr}] + k_{-2}[\text{Dx}])} + 1} + k_{-2}[\text{Dx}][\text{C}]_o \qquad (4\text{-}12)$$

Since it was assumed that $k_1 \geq k_{-1}$ (the validity of this assumption can be seen later) and from stoichiometric considerations $[\text{R}] \leq [\text{Dr}]_o$, the term $k_{-1}[\text{R}]^{\frac{1}{2}}$ was neglected in comparison to $k_1[\text{Ox}]^{\frac{1}{2}}$. This simplification was entirely justified, since $[\text{Ox}]_o = 5 \times 10^{-3}$ and $[\text{Dr}]_o \leq 2 \times 10^{-5}$. This simplification was applied and $[\text{C}]_o$ factored out to arrive at:

$$\text{Rate} = -\,[\text{C}]_o \left[\frac{(k_1[\text{Ox}]^{\frac{1}{2}} + k_{-2}[\text{Dx}])}{\dfrac{k_1[\text{Ox}]^{\frac{1}{2}}}{(k_2[\text{Dr}] + k_{-2}[\text{Dx}]} + 1} - k_{-2}[\text{Dx}] \right] \qquad (4\text{-}14)$$

Clearing fractions inside the brackets gave:

$$\text{Rate} = -[\text{C}]_o \left[\frac{k_1[\text{Ox}]^{\frac{1}{2}} + k_{-2}[\text{Dx}] - \dfrac{k_1[\text{Ox}]^{\frac{1}{2}}\, k_{-2}[\text{Dx}]}{(k_2[\text{Dr}] + k_{-2}[\text{Dx}])} - k_{-2}[\text{Dx}]}{\dfrac{k_1[\text{Ox}]^{\frac{1}{2}}}{(k_2[\text{Dr}] + k_{-2}[\text{Dx}])} + 1} \right] \qquad (4\text{-}15)$$

The $k_{-2}[Dx]$ terms in the numerator cancelled and $k_1[Ox]^{\frac{1}{2}}$ was factored out to give:

$$\text{Rate} = - k_1[Ox]^{\frac{1}{2}}[C]_o \left[\frac{1 - \dfrac{k_{-2}[Dx]}{(k_2[Dr] + k_{-2}[Dx])}}{1 + \dfrac{k_1[Ox]^{\frac{1}{2}}}{(k_2[Dr] + k_{-2}[Dx])}} \right] \qquad (4\text{-}16)$$

Again clearing fractions in both the numerator and denominator inside the brackets and cancelling out common terms led to:

$$\text{Rate} = - k_1[Ox]^{\frac{1}{2}}[C]_o \left[\frac{k_2[Dr]}{k_1[Ox]^{\frac{1}{2}} + k_2[Dr] + k_{-2}[Dx]} \right] \qquad (4\text{-}17)$$

Mass balance requires $[Dx] = [Dr]_o - [Dr]$. This substitution gave the final overall catalyzed rate expression:

$$\text{Rate} = \frac{- k_1k_2[Ox]^{\frac{1}{2}}[Dr][C]_o}{k_1[Ox]^{\frac{1}{2}} + k_2[Dr] + k_{-2}[Dr]_o - k_{-2}[Dr]} \qquad (4\text{-}18)$$

Testing Validity of Simplified Mechanism

Determination of Constants

Rate constants were obtained using the program described in Chapter III. The required function of absorbance to be plotted versus a function of the derivative was obtained by algebraic manipulation of the rate expression, Equation 4-18.

Equation 4-18 was first re-written in the following manner:

$$\frac{\text{Rate}}{[\text{C}]_o} = \frac{-\,k_1k_2[\text{Ox}]^{\frac{1}{2}}[\text{Dr}]}{k_1[\text{Ox}]^{\frac{1}{2}} + k_{-2}[\text{Dr}]_o + k_2[\text{Dr}] - k_{-2}[\text{Dr}]} \tag{4-19}$$

Grouping similar terms and inversion of both sides of the equation gave:

$$\frac{[\text{C}]_o}{\text{Rate}} = \frac{(k_1[\text{Ox}]^{\frac{1}{2}} + k_{-2}[\text{Dr}]_o) + (k_2 - k_{-2})[\text{Dr}]}{-\,k_1k_2[\text{Ox}]^{\frac{1}{2}}[\text{Dr}]} \tag{4-20}$$

Dividing both terms in the numerator of the right-hand side by the denominator led to:

$$\frac{[\text{C}]_o}{\text{Rate}} = \frac{(k_1[\text{Ox}]^{\frac{1}{2}} + k_{-2}[\text{Dr}]_o)}{-\,k_1k_2[\text{Ox}]^{\frac{1}{2}}[\text{Dr}]} + \frac{(k_2 - k_{-2})}{-\,k_1k_2[\text{Ox}]^{\frac{1}{2}}} \tag{4-21}$$

Conversion to absorbance by application of Beer's Law considering a 1 cm path length led to:

$$\frac{[\text{C}]_o}{\text{rate}} = \frac{(k_1\ \varepsilon[\text{Ox}]^{\frac{1}{2}} + k_{-2}\ A_o)}{-\,k_1k_2\ \varepsilon[\text{Ox}]^{\frac{1}{2}}} \cdot \frac{1}{A} + \frac{(k_2 - k_{-2})}{-\,k_1k_2\ \varepsilon[\text{Ox}]^{\frac{1}{2}}} \tag{4-22}$$

The form of equation suggested a plot of 1/A versus $[\text{C}]_o$/rate should be a straight line with slope = $\dfrac{(k_1\varepsilon[\text{Ox}]^{\frac{1}{2}} + k_{-2}\ A_o)}{-\,k_1k_2\ \varepsilon[\text{Ox}]^{\frac{1}{2}}}$ and intercept = $\dfrac{-\,(k_2 - k_{-2})}{k_1k_2\ \varepsilon[\text{Ox}]^{\frac{1}{2}}}$.

A new set of titration curves were obtained according to the procedure outlined in Chapter II using the fastest chart speed possible on the Cary 14 (8 inches/min) with hopes of improving resolution and accuracy of chart reading. The data was recorded, punched on IBM data cards, and read into the program for determining rate constants. Figure 23 shows selected plots of 1/A vs $[C]_o$/rate and serves to illustrate the variation of slope with changing initial dye concentration and the relatively constant value of the intercept.

Consideration of the expressions for the slope and intercept showed the dependence of the slope upon initial absorbance. Letting C_1 = intercept and C_2 = slope, the expression for the slope was written as:

$$C_2 = \frac{k_1 \ \varepsilon[Ox]^{\frac{1}{2}} + k_{-2} \ A_o}{- \ k_1 k_2 \ \varepsilon[Ox]^{\frac{1}{2}}} \tag{4-23}$$

or:

$$C_2 = - \frac{1}{k_2} - \frac{k_{-2} \ A_o}{k_1 k_2 \ \varepsilon[Ox]^{\frac{1}{2}}} \tag{4-24}$$

Since:

$$C_1 = \frac{k_2 - k_{-2}}{- \ k_1 k_2 \ \varepsilon[Ox]^{\frac{1}{2}}} \tag{4-25}$$

an expression was obtained for k_1:

$$k_1 = \frac{k_2 - k_{-2}}{- \ C_1 k_2 \ \varepsilon[Ox]^{\frac{1}{2}}} \tag{4-26}$$

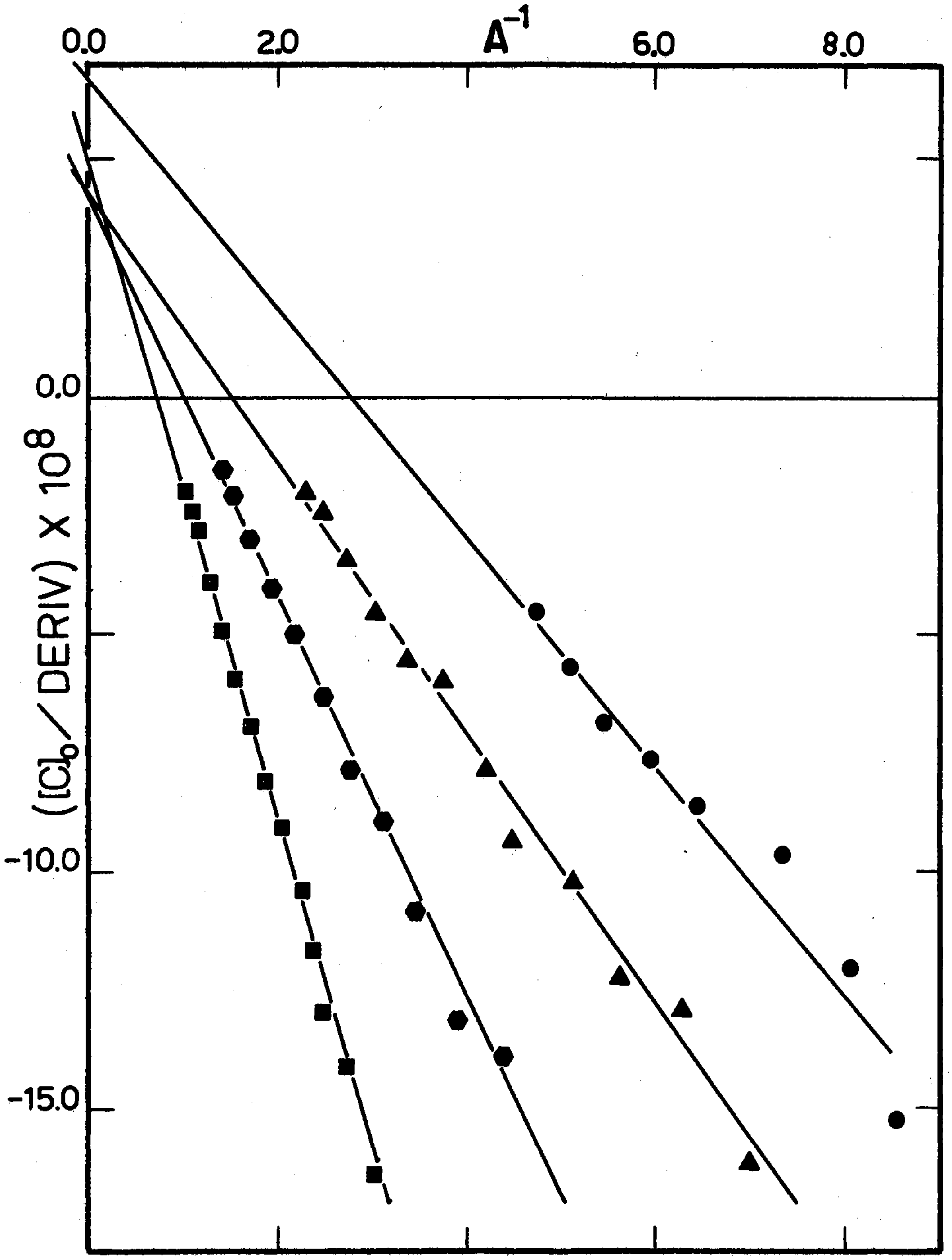

Figure 23. Variation of Slope as a Function of Initial Dye Concentration (See Appendix E, p. 124)

O = 3.75 x 10^{-6} M

Δ = 7.77 x 10^{-6} M

⬡ = 1.27 x 10^{-5} M

◻ = 1.68 x 10^{-5} M

Substitution of the expression for k_1 into Equation 4-24 led to:

$$C_2 = -\frac{1}{k_2} + \frac{\dfrac{k_{-2} A_o}{(k_2 - k_{-2})}}{C_1} \qquad (4\text{-}27)$$

or finally:

$$C_2 = \frac{k_{-2}}{(k_2 - k_{-2})} \cdot C_1 A_o - \frac{1}{k_2} \qquad (4\text{-}28)$$

A plot of C_2 versus $C_1 A_o$ proved to be a straight line with intercept equal to $- 1/k_2$. This offered a method for the determination of k_2. Figure 24 shows the plot used in the determination of k_2, the forward rate constant for the reaction represented by Equation 4-5. Further, solving Equation 4-28 for k_{-2} gave:

$$k_{-2} = \frac{C_2 k_2 + 1}{C_1 A_o + C_2 + \frac{1}{k_2}} \qquad (4\text{-}29)$$

This provided a method for obtaining a second constant, k_{-2}. Substitution of the values thus obtained for k_2 and k_{-2} into Equation 4-26, along with the mean value of all C_1 values gave the value for the third constant, k_1. Complete listings of computer print-out of all the least squares fits of both raw data and for the determination of k_2 are given in Appendix E. A brief summary of the values found and their standard deviations is given in Table III.

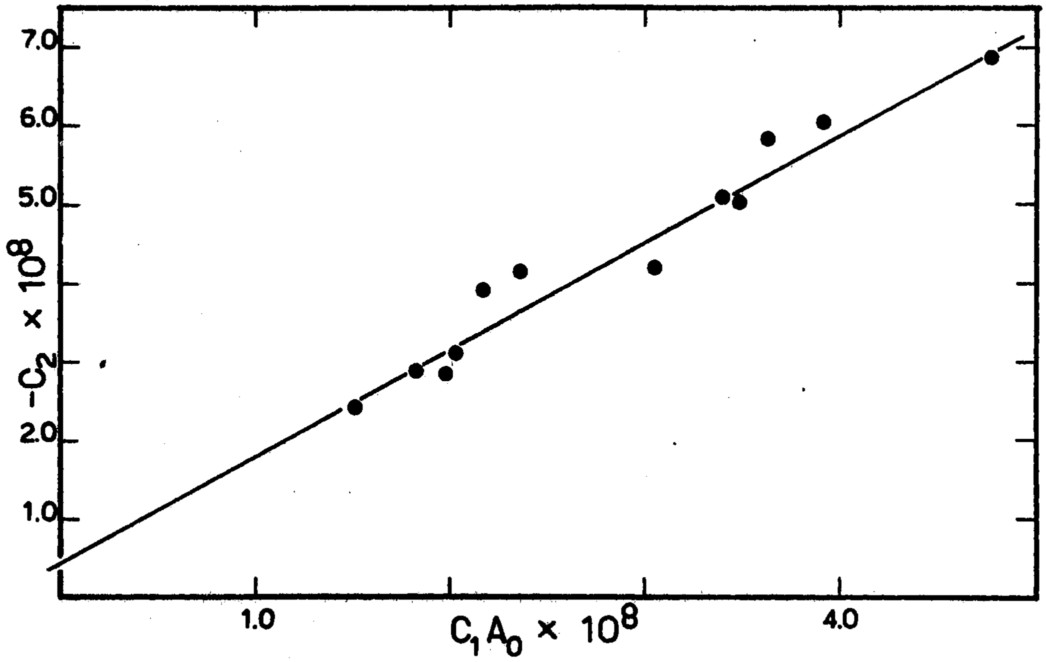

Figure 24. Determination of K_2, the Forward Rate Constant for the Reaction Represented by Equation 4-5. Data Points Can be Found in Appendix E, p. 138

TABLE III

SUMMARY OF RATE CONSTANTS FOUND

Rate Constant	Value Found	Relative Standard Deviation (%)
k_1	$1.36 \times 10^4\ M^{-\frac{1}{2}}\ sec^{-1}$	20.1
k_2	$2.24 \times 10^8\ M^{-1}\ sec^{-1}$	66.2
k_{-2}	$8.43 \times 10^8\ M^{-1}\ sec^{-1}$	7.58

It should be noted at this point that the large standard deviations reported here and in the NTA results to follow in the next section can be attributed to several factors, the most significant being the inherent error in using the intercept of a linear plot in the determination of parameters. Any statistics text, such as the one by Snedecor and Cochran (26) points out the poorer precision associated with the intercept of a linear plot when extrapolating long distances. Unfortunately, due to the nature of the modified rate equations, this offers the only means of obtaining an estimate of the rate constant, k_2. Since the value found for k_2 is in turn used in the determination of the remaining system parameters, the error introduced here is carried throughout the determinations. The value reported for the standard deviation of k_{-2} is that of the slope of the linear plot mentioned above, since this is the basis of the determination of this constant. The statistical information reported for k_1 was obtained by calculating the sample standard deviation of the individual intercepts (C_1 in Equation 4-25). A recent review presents a detailed analysis of the problems encountered in using linear plots in the estimation of various parameters (27).

The assumption made earlier in the derivation of the rate expression can now be verified; i.e.--that $k_1 \geq k_{-1}$. The equilibrium constant for Equation 4-4 can be estimated from the standard potentials of the half-reactions and appears to be on the order of 10^6. Since $K_{eq} = k_1/k_{-1}$, the values of K_{eq} and k_1 require k_{-1} to be much, much less than k_1. The simplification made in Equation 4-14 appears as indeed valid under these conditions.

Computer Simulation of Experimental Curves

The curves used to obtain the constants discussed in the preceding section were simulated using the constants thus determined. Figure 25 shows selected curves at varying initial dye concentrations. A reasonable good fit was obtained, especially in the earlier portions of the curves. Handling of the observed induction period will be discussed in the following chapter.

Summary: Selection of a Simplified Mechanism

The steady-state approximation in the kinetics of the Mn(II) catalyzed oxidation of MG+ by periodate ion leads to an overall rate expression which satisfies both of the established criteria: (1) the constants determined are independent of initial dye concentration and (2) simulated curves match those experimental curves from which the constants were obtained.

MN(III)--PERIODATE SYSTEM: SIMULATION 35.02,03,08, & 09 6/14/72

DATA SET = 35.09

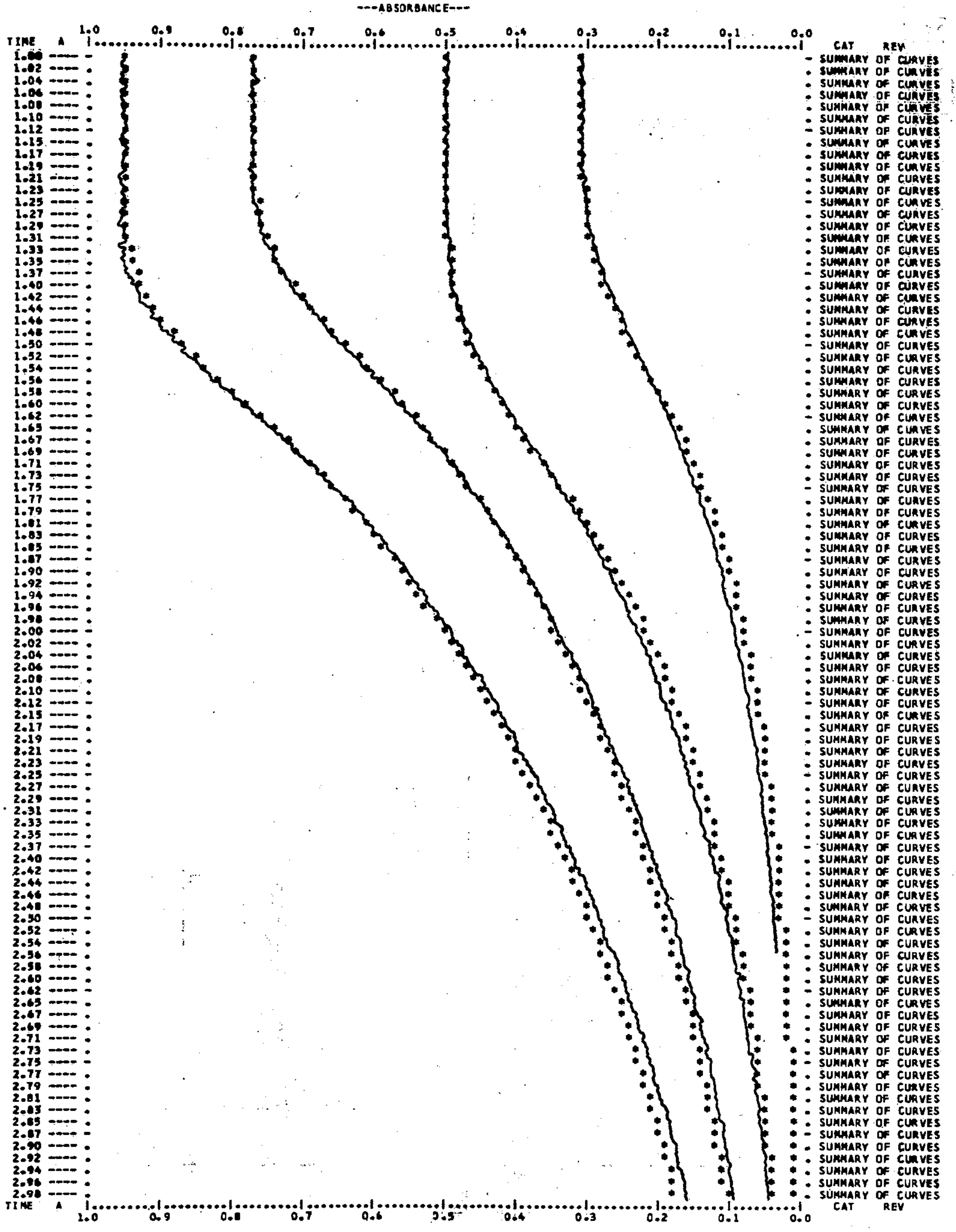

Figure 25. Computer Simulation of Experimental Curves Using Constants Obtained From Original Absorbance Versus Time Data. Solid Lines Represent Actual Experimental Curves While Asterisks Show Simulation Results. Experimental Conditions are Given in Appendix E, p. 124

The Modifying Effect of NTA on the Mn(II)
Catalyzed Oxidation of Malachite
Green Cation by Periodate Ions

Selection of a Simplified Mechanism

It was known that the addition of NTA (nitrilotriacetic acid) to the Mn(II)-MG+-periodate system noticeably increased the rate of the reaction (9,11,21,23). The problem was to select a simplified mechanism which could be used to describe what was occurring in the system. The large formation constant of the Mn(III)-NTA complex (28) suggested strongly the possibility that this was the active species. The mechanism selected, then, for describing the NTA effect, was exactly the same as that used when NTA was not present.

Development of Expressions for the Selected Mechanism

In this case, the reaction path was considered to be the following:

$$C + Ox \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Cx + R \qquad (4\text{-}30)$$

$$Cx + L \xrightarrow{\text{very fast}} CxL \qquad (4\text{-}31)$$

$$CxL + Dr \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} CL + Dx \qquad (4\text{-}32)$$

where:

L = NTA

This set of equations describing the mechanism of reaction was treated in exactly the same manner as was done with the same system without NTA, with the exception that the term [Cx] is replaced everywhere it appears with the term [CxL]. This substitution was valid due to the relatively large formation constant reported for the Mn(III)-NTA complex (28) and the magnitude of the difference between this value, $K_F = 1.8 \times 10^{20}$, and that for the formation of the Mn(III)-Acetate complex which is probably no larger than 10^{14} (see Appendix F for method of estimation). With an acetate concentration of about 0.5 M, due to the use of an acetate buffer, equilibrium calculations showed that virtually all of any Mn(III) present in the system would be complexed by the NTA as long as the formation constant for the Mn(III)-Acetate complex was no greater than about 10^{14}. Since all runs were done with an excess of NTA present, the limiting reagent in the formation of the complex was Cx, the concentration of Mn(III). Constants were also determined in an identical manner with the pertinent results summarized in Table IV. Complete listings of all computer print-out of the least square fits are given in Appendix G.

TABLE IV

SUMMARY OF RATE CONSTANTS DETERMINED FOR NTA EFFECT

Rate Constant	Value	Relative Standard Deviation (pph)
k_1*	4.20×10^5 $M^{-\frac{1}{2}}$ sec^{-1}	37.7
k_2*	3.07×10^8 M^{-1} sec^{-1}	24.7
k_{-2}*	5.47×10^9 M^{-1} sec^{-1}	11.8

Figure 26 shows the results of computer simulation of the curves used to obtain the constants given above. All showed a good match when compared to the experimental curves.

Summary: Selection of Simplified Mechanism Describing NTA Effect

Making the steady-state approximation on the time-rate of change of Mn(III)-NTA complex concentration leads to an overall rate equation which meets both of the established criteria. The constants were not seen to vary with changes in dye concentration and the curves simulated by the computer matched the experimental curves. Again, the handling of the induction period will be discussed in the following chapter.

```
CHEM 5CC0--B.E. SIMPSON                                                              COPY  2 OF  2

MN(II)--PERIODATE SYSTEM:  SIMULATION:  MG-34 (NTA ADDED)              6/12/72

DATA SET =      34.14
```

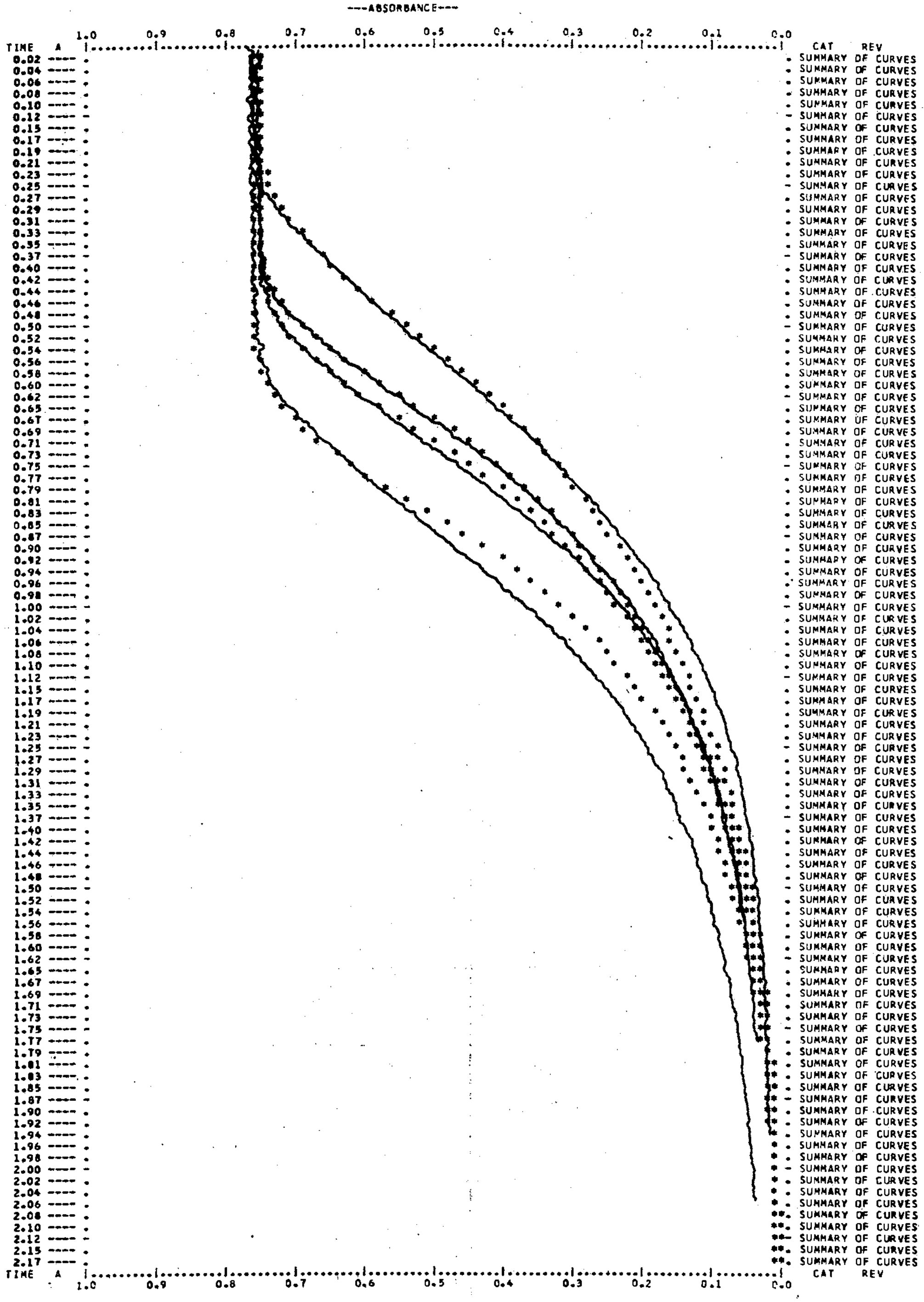

Figure 26. Computer Simulation of Experimental Curves Using Constants Obtained From Original Absorbance Versus Time Data. Solid Lines Represent Actual Experimental Curves While Asterisks Show Simulation Results. Experimental Conditions are Given in Appendix G, p. 146

CHAPTER V

SUMMARY OF RESULTS, DISCUSSIONS, AND SUGGESTIONS FOR FURTHER STUDY

Results

Most numerical results have already been presented in the text of the thesis and in the various appendices. Summarizing statements only will be presented here.

The overall goals of the study have been accomplished: i.e.--development of computer programs to determine system parameters and simulate catalytic titration curves and the application of these programs to the study of a real system. In addition, new equipment necessary to adapt catalytic titrations to the Cary 14 spectrophotometer were designed, built, and tested. The utility of using experimentally determined instantaneous derivatives to derive information from catalytic titration was demonstrated as was the application of simple, first order, linear least squares methods to the study of reaction kinetics. Further, it was shown that the programs developed can be used in attempts to test mechanistic assumptions, and, indeed, were used to show how the steady-state approximation can be used to describe a real system: namely, the Mn(II) catalyzed oxidation of MG+ by periodate ion both with and without the presence of a particular complexing agent, NTA.

Discussion

One problem encountered in the study was the treatment of the induction period which was observed after introduction of the catalyst. This period of time varied from a few seconds in the case of large NTA concentration to over a minute in other cases. The only correlation with any physical or chemical variable was the dependence upon NTA concentration as has already been observed by Mottola and Harrison (11). In the absence of complexing agent, however, the length of the induction period seemed to be independent of everything and would sometimes vary from one run to the next by as much as 10 - 20 seconds. Part of this variation could be attributed to error in determining exactly when the catalyst solution actually entered the system, as this was accomplished by means of a mark on the tip of the buret and a stopwatch. Error from this source, however, could not possibly contribute more than ± 3 seconds.

In the realm of possible explanations, two extremes exist: (1) the catalyst is tied up by some agent present in the system for a given amount of time, then released suddenly into the system after a period of time or (2) a given amount of catalyst equal to the rate of catalyst times the length of induction period is tied up by some agent and is never released during the reaction. The latter extreme would essentially mean that, as far as catalyst added to the system is concerned, time = 0 at the point where the break first occurs in the curve. This extreme was ruled out, since the plot of $-C_2$ vs. C_1A_o shown in Figure 24 (see page 83, this work) did not give a slope greater than 1.0, as is required by Equation 4-28. That is, the term $\frac{k_{-2}}{k_2 - k_{-2}}$ must be larger than 1.0 if $k_{-2} > k_2$. The negative slope of the C_2 vs. C_1A_o verifies that $k_{-2} > k_2$, due to the term $(k_2 - k_{-2})$.

On the other hand, possibility number one gave quite good fits with the exception of the early parts of the curves. The real problem in accepting this assumption as it stood, however, was the failure in attempts to simulate experimental curves. Simulated curves showed a sharp break at the point where catalyst first became available while actual experimental curves exhibited a gentle are (see Figure 25). Simulation, then, seemed to indicate that after a certain time, the catalyst available for reaction was indeed equal to the total amount of catalyst added, $[C]_o$, but before that time was represented by some other function. Figure 27 shows a plot of available catalyst concentration versus time superimposed over a typical absorbance versus time catalytic titration curve. In the figure, T_1 represents the time when catalyst first becomes available to the system and T_2 represents the time when the available catalyst concentration becomes equal to the total amount of catalyst added to the system. The broken line represents the amount of catalyst actually added to the system at any time. Time equals zero when the buret containing catalyst is turned on. The portion of the available catalyst curve between T_1 and T_2 was approximated empirically with the following parabolic function:

$$C = a(t - T_1)^2 \qquad (5\text{-}1)$$

If $C = k_a t$ at $t = T_2$, where k_a = catalyst addition rate, then solving equation 5-1 for the constant, a, gave:

$$a = \frac{C}{(T_2 - T_1)^2} = \frac{k_a T_2}{(T_2 - T_1)^2} \qquad (5\text{-}2)$$

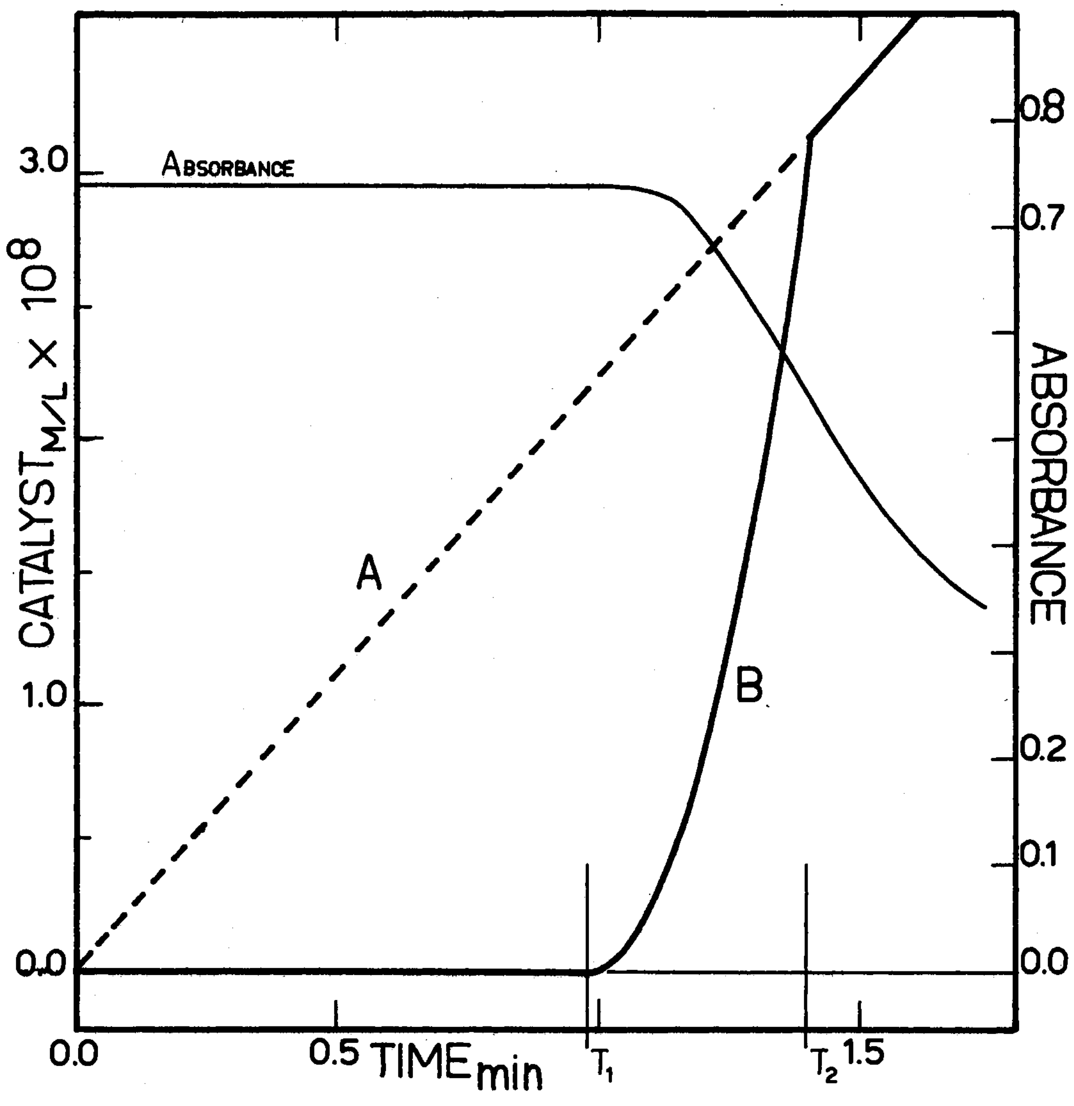

Figure 27. Available Catalyst Concentration. Curve A: Catalyst Actually Added to System. Curve B: Catalyst Available to System for Participation in Reaction. Corresponding Absorbance is Also Shown

This led to the final expression used to empirically explain the available catalyst concentration:

$$C = \frac{k_a T_2}{(T_2 - T_1)^2} (t - T_1)^2 \Bigg|_{t = T_1}^{t = T_2} \qquad (5\text{-}3)$$

The only valid defense of this approach is the fact that use of this expression led to an improved linearity in the plots of 1/A vs. $[C]_0$/rate and gave an almost perfect match of simulated and experimental curves in many cases. Both T_1 and T_2 can be determined directly from experimental curves: T_1 being that time when the first deviation from the uncatalyzed reaction is observed and T_2 being the time at the point of inflection of the catalytic titration curve. The computer output given in Appendix E and referred to earlier (page 83, this work) gives the values of T_1 and T_2 used in each case.

Other empirical functions were considered, namely an exponential function of the form:

$$C = b\,e^{a(t - T_1)} \qquad (5\text{-}4)$$

but were abandoned when they failed to give an improvement in linearity better than that achieved with the parabolic assumption.

It should be mentioned that the correction employed using T_1 and T_2 was necessary only in the case of simulation, since constants can be determined, if need be, from only the latter portions of a titration curve. For the sake of consistency, however, these corrections were included in both simulation and constant determination programs.

Suggestions for Further Work

One of the most obvious places where further study would be profitable would be in the area of the induction period. Various types of experiments done with various ligand and buffer systems similar to those conducted by Rudenko and co-authors (20) could lead to a better understanding of what is taking place. The seeming independence of the induction upon initial dye concentration and its aforementioned reliance upon NTA concentration would indicate the answer to the induction period problem lies somewhere in the formation of some metal-ligand complex which, for some reason, decays rapidly after a period of time equal to the induction period. Better knowledge of the oxidation potentials of the various reactions occurring in the system could be the key to understanding the "avalanche" change of available catalyst concentration from zero to the maximum possible in a period of a few seconds. Further, the effect caused by increasing NTA concentration would seem to be a result of mass action; as if the NTA were "taking away" the catalyst from some other species which was keeping it from participating in the catalytic cycle.

Another area where further work is called for is in the study of the effect of different ligands upon the system, especially one which inhibits the course of the reaction. A study of the pH dependence of inhibition or rate-increase would also serve to provide more information as to the "true" mechanism of ligand modification.

In conclusion, the primary analytical reasons for undertaking this study may be pin-pointed as follows. First, a study of this type can lead to better understanding of a widely used analytical system, and, consequently, to improved methods of analysis. Secondly, the area of catalytic titration curves deserves attention. Since the introduction of these methods (1, 9, 11, 21, 22, 23), a computer study such as this present work has not been undertaken. Use of the digital computer to characterize the reactions used in catalytic end-point determination can lead to better methods of end-point determination and a more lucid interpretation of what is occurring at the theoretical equivalence point.

Third, and finally, a study such as this seems to lend itself to the tracing of metal chelate catalysis, promotion, and inhibition which is of much importance not only in the area of analytical chemistry, but also in bio-chemical applications in which oxygen and nitrogen containing ligands play an important role. It is hoped that the computer programs, methods of analysis, and technical apparatus presented in this work will make a valid contribution to the above mentioned areas.

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APPENDIXES

APPENDIX A

CHECK OF INTEGRATION TECHNIQUE

Check of Simulation

In order to check the accuracy of the simulated curves, a differential rate equation was solved rigorously and the resulting function of time, t, plotted. The test equation used was that developed in Chapter III to express the rate of the reaction assuming the pre-equilibrium mechanism:

$$\text{Rate} = \text{uncatalyzed rate} + \text{catalyzed rate}$$

$$= \frac{dA}{dt} = -k_uA - k_cA(C)_o \qquad \text{(A-1)}$$

where:

A = absorbance

$k_u = k_{uncat}(Ox)$ = constant (since (Ox) is constant),

$k_c = k_2$ = catalyzed rate constant, and

$(C)_o = Ct$ = (catalyst addition rate)(time).

Proceeding with the solution:

$$\frac{dA}{dt} = -k_uA - k_cACt \qquad \text{(A-2)}$$

$$\frac{dA}{A} = -k_udt - k_cCtdt \qquad \text{(A-3)}$$

$$\int \frac{dA}{A} = -k_u \int dt - k_c C \int tdt \tag{A-4}$$

$$\ln A + \ln B = -k_u t - \tfrac{1}{2}k_c Ct^2 \tag{A-5}$$

where: ln B contains all constants of integration

$$\ln AB = -k_u t - \tfrac{1}{2}k_c Ct^2 \tag{A-6}$$

$$AB = e^{-k_u t} \cdot e^{-\frac{1}{2}k_c Ct^2} \tag{A-7}$$

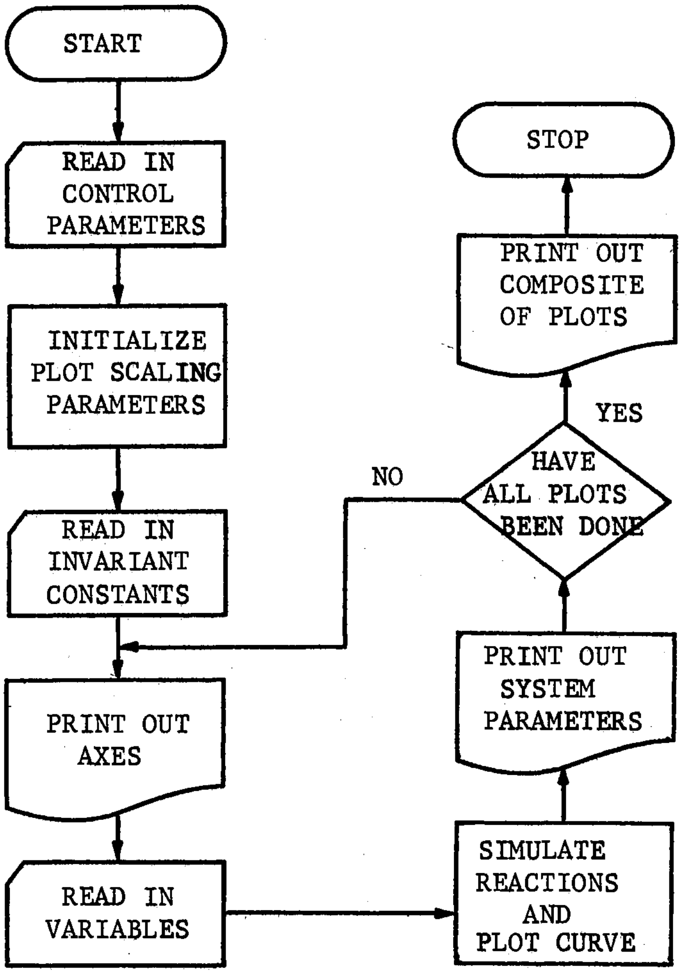
At $t = 0$, $B = \frac{1}{A} = \frac{1}{A_o}$, therefore:

$$A = A_o(e^{-k_u t} \cdot e^{-\frac{1}{2}k_c Ct^2}) \tag{A-8}$$

Comparison of the curve plotted with this function with one simulated using the same parameters showed that they are identical. This favorable comparison shows that the integration technique used in the simulation does a good job of producing a curve, given a differential equation expressing the rate.

APPENDIX B

FLOW DIAGRAM AND SOURCE PROGRAM FOR SIMULATION


START
READ IN CONTROL PARAMETERS
INITIALIZE PLOT SCALING PARAMETERS
READ IN INVARIANT CONSTANTS
PRINT OUT AXES
READ IN VARIABLES
SIMULATE REACTIONS AND PLOT CURVE
PRINT OUT SYSTEM PARAMETERS
HAVE ALL PLOTS BEEN DONE
NO
YES
PRINT OUT COMPOSITE OF PLOTS
STOP

```
C      GIVEN THE SYSTEM PARAMETERS, THIS PROGRAM SIMULATES A CATALYTIC TITRATION
C      CURVE BY PRODUCING A PLOT OF ABSORBANCE VS. TIME.  THE PRINTOUT IS A
C      1:1 REPRODUCTION OF THE STRIPCHART FROM THE CARY 14 SPECTROPHOTOMETER.
C      VALUES OF TIME, ABSORBANCE, AND CONTRIBUTIONS OF BOTH THE FORWARD AND
C      REVERSE REACTIONS TO THE OVERALL RATE ARE ALSO TABULATED FOR EACH POINT.
C
C      A BREAKDOWN OF THE PROGRAM SEGMENTS AND THEIR FUNCTION FOLLOWS:
C
C        MAIN: 1) READS IN THE NUMBER OF PLOTS TO BE DONE.
C              2) CALLS ALL OTHER SUB-PROGRAMS.
C              3) HANDLES TIME INCREMENTING AND KEEPS TRACK OF THE DEPENDENT
C                 VARIABLE.
C
C        AINPUT: 1) READS IN ALL PARAMETERS WHICH DO NOT VARY WITH SUCCESSIVE
C                   PLOTS.
C
C        BINPUT: 1) READS IN THOSE PARAMETERS WHICH CHANGE WITH SUCCESSIVE PLOTS.
C
C        AXIS: 1) READS IN AND PRINTS OUT THE LABEL FOR EACH PLOT.
C              2) PRINTS OUT ORDINATE AXES BEFORE AND AFTER EACH PLOT.
C
C        PLOT: 1) DOES THE ACTUAL PLOTTING OF POINTS.
C              2) PRINTS OUT TIME, ABSORBANCE, FORWARD REACTION CONTRIBUTION,
C                 AND REVERSE REACTION CONTRIBUTION.
C
C        AMODEL: 1) DEFINES THE SYSTEM MODEL.
C                2) CONTAINS THE INTEGRATION TECHNIQUE.
C
C        OUTPUT: 1) PRINTS OUT THE SYSTEM PARAMETERS.
C
C        CHART:  "SAVES" EACH INDIVIAUAL PLOT AND PRINTS OUT A COMPOSITE GRAPH.
C
C      SEE SUB-PROGRAMS FOR FURTHER COMMENTS AND DEFINITION OF VARIABLES.
C
C      DEFINITION OF VARIABLES APPEARING IN MAIN PROGRAM:
C
C        A:  ABSORBANCE AT ANY TIME
C        A1:  CORRECTED ABSORBANCE (EQUALS A -1.0 IF A.GT.1.D)
C        ASTART:  INITIAL ABSORBANCE OF THE DYE IN SOLUTION
C        ADELT:  INCREMENT IN ABSORBANCE PER UNIT OF TIME RESULTING FROM PROGRESS
C                OF REACTION
C        CAT:  FORWARD CONTRIBUTION TO THE OVERALL RATE
C        CATCON:  CATALYST CONCENTRATION AVAILABLE TO THE SYSTEM AT ANY TIME
C        CATREV:  CONTRIBUTION TO OVERALL RATE FROM REVERSE REACTION
C        CHECK:  VARIABLE USED TO DETERMINE MAGNITUDE OF STEP SIZE IN INTEGRATION
C                ROUTINE(USED ONLY WHEN KPRO.GT.0)
C        CLIG:  CONCENTRATION OF LIGAND AT ANY TIME (USED ONLY WHEN CONTRIBU-
C               TION EXPECTED FROM BOTH LIGAND EFFECT AND NORMAL PATH)
C        CLIG1:  INITIAL CONENTRATION OF LIGAND ADDED TO SYSTEM (USED UNDER SAME
C                CONDITIONS AS CLIG)
C        DELTIM:  VALUE COMPUTED FROM "TDELT" WHEN VARIABLE STEP SIZE REQUIRED
C                 BY THE PROGRAM
C        EPS:  MOLAR ABSORPTIVITY OF THE DYE BEING USED
C        IGRID:  ARRAY FOR SAVING THE INDIVIDUAL PLOTS
C        INCAT:  RATE OF CATALYST ADDITION IN MOLES/LITER.MIN
C        ISCALE:  DESIRED SCALE OF PLOT IN INCHES PER MINUTE
C        KEQ:  EQUILIBRIUM CONSTANT (USED ONLY WHEN PRE-EQUILIBRIUM MECH ASSUMED)
C        KFORM:  FORMATION CONSTANT OF COMPLEX OF LIGAND WITH CATALYST
C                (USED ONLY WHEN CONTRIBUTION EXPECTED FROM BOTH LIGAND EFFECT
C                AND NORMAL CATALYTIC CYCLE)
C        KICK:  VARIABLE USED TO ADJUST STEP SIZE IN INTEGRATION ROUTINE
C        KNEG2:  RATE CONSTANT FOR REVERSE REACTION IN SECOND STEP OF MECHANISM
C        KPRO:  RATE CONSTANT FOR PROMOTION REACTION (USED ONLY WHEN A CONTRIBU-
C               TION FROM BOTH LIGAND EFFECT AND NORMAL CATALYTIC CYCLE IS
C               EXPECTED)
C        KUNCAT:  RATE CONSTANT FOR UNCATALYZED REACTION
C        K1: RATE CONSTANT FOR FIRST STEP IN REACTION MECHANISM
C        K2:  RATE CONSTANT FOR FORWARD REACTION IN SECOND STEP OF MECHANISM
C        LABEL:  ANY LABEL UP TO 80 CHARACTERS LONG TO BE PRINTED WITH PLOT
C        MAXTIM:  MAXIMUM TIME ALLOWED FOR A GIVEN PLOT
C        OX:  CONCENTRATION OF OXIDIZING AGENT IN MOLES/LITER
C        PROMO:  RATE CONTRIBUTION DUE TO PROMOTION OF THE LIGAND (USED ONLY
C                WHEN CONTRIBUTION EXPECTED FROM BOTH LIGAND AND NORMAL CYCLES)
C        REF:  DATA IDENTIFIER
C        SAVE,SAVE1,SAVE2,SAVE3:  VARIABLES USED TO SAVE THE VALUES OF GIVEN
C                                 PARAMETERS WHICH MUST BE SET TO ZERO DURING ANY
C                                 UNCATALYZED PORTION OF THE REACTION.
C        STD:  ARRAY CONTAINING VALUES ASSIGNED TO VARIABLES IN "VAR"
C        TERM:  VARIABLE NEED IN SYSTEM MODEL--CALCULATED IN MAIN PROGRAM TO SAVE
C               EXECUTION TIME
C        TDELT:  TIME INCREMENT USED IN THE INTEGRATION ROUTINE
C        TIME:  TIME FROM INTRODUCTION OF CATALYST INTO SYSTEM
C        T1:  TIME WHEN CATALYST FIRST BECOMES AVAILABLE TO THE SYSTEM
C        T2:  TIME WHEN TOTAL ANALYTICAL CATALYST CONCENTRATION IS AVAILABLE
C        UNRUN:  THE NUMBER OF MINUTES OF UNCATALYZED REACTION TO BE SIMULATED
C        VAR:  ARRAY CONTAINING STANDARD VALUES OF GIVEN PARMETERS TO BE VARIED
C              DURING A RUN
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 KUNCAT,K1,K2,KNEG2,KEQ,INCAT,KPRO,KFORM
      REAL*4 LABEL,VAR,STD
      COMMON OX,CLIG,CLIG1,EPS,TDELT,INCAT,ASTART,KUNCAT,K1,K2,KNEG2,
     $KPRO,KFORM,KEQ,UNRUN,DELTIM,T1,T2,ISCALE,MAXTIM
      DIMENSION IGRID(200,10),STD(10),VAR(10,2),LABEL(20)
      DATA IGRID/2000*101/
       A1=1.01
      DO 15 IREAD=1,10
   15 READ(5,253)VAR(IREAD,1),VAR(IREAD,2),STD(IREAD)
      READ(5,251)NSETS,NUMCOP
      CALL AINPUT
      SCALE=ISCALE
      MAX=MAXTIM*6*ISCALE
      MAXUN=(UNRUN+0.0001)*6*ISCALE
      INNER1=24/ISCALE
      LOCATE=1
      DO 1000 ISETS=1,NSETS
      LINES=1
      READ(5,252)NUMRUN,LABEL
      DO 111 IRUN=1,NUMRUN
      CATCON=0.0D0
      CAT=0.0D0
      PROMO=0.0D0
      CATREV=0.D0
        K=0
      KK=0
        WRITE(6,300)                                                    C
      CALL BINPUT(REF)
      CALL AXIS(LABEL,REF,LOCATE)
      TERM=K1*EPS*DSQRT(OX)
      A=ASTART
      TIME=0.0D0
      SAVE=TERM
      SAVE1=KPRO
      SAVE2=KNEG2
      SAVE3=K2
      TERM=0.D0
      KPRO=0.0D0
      KNEG2=0.D0
      K2=0.D0
      IF(MAXUN.EQ.0)GO TO 9
      INNER=INNER1
      TDELT=DELTIM
    6 DO 7 ILOOP=1,MAXUN
      DO 8 IDELT=1,INNER
      TIME=TIME+TDELT
      CALL AMODEL(A,CATCON,UNCAT,CAT,CATREV,PROMO,ADELT,TIME,TERM)
    8 A=A+ADELT
      CALL PLOT(A,K,TIME,CAT,CATREV)
      A1=A
      IF(A1.GT.1.D0)A1=A1-1.D0
      IGRID(ILOOP,IRUN)=101.49999-A1*100.
    7 CONTINUE
```

```
    9 MLOOP=MAXUN+1
      TERM=SAVE
      KPRO=SAVE1
      KNEG2=SAVE2
      K2=SAVE3
      CHECK=KPRO
      IF(K2.GT.KPRO)CHECK=K2
       KICK=(DLOG10(CHECK)-6.0D0)
      IF(KICK.LT.1)KICK=1
      IF(KICK.GT.10)KICK=10
      KICK=2
      INNER=INNER1*KICK
      TDELT=DELTIM/KICK
      DO 10 ILOOP=MLOOP,MAX
      DO 11 IDELT=1,INNER
      TIME=TIME+TDELT
      CATCON=INCAT*T2*(TIME-T1)**2/(T2-T1)**2
      IF(TIME.LT.T1)CATCON=0.D0
      IF(TIME.GE.T2)CATCON=INCAT*TIME
      CALL AMODEL(A,CATCON,UNCAT,CAT,CATREV,PROMO,ADELT,TIME,TERM)
      A=A+ADELT
      IF(ADELT.GT.0.0D0)GO TO 12
   11 CONTINUE
      CALL PLOT(A,K,TIME,CAT,CATREV)
      IF((DABS(A1-A).LT.1.D-4).AND.((TIME-UNRUN).GT.4.D0))GO TO 12
      IF(A.LT.0.005D0)GO TO 12
      A1=A
      IF(A1.GT.1.D0)A1=A1-1.D0
      IGRID(ILOOP,IRUN)=101.49999-A1*100.
   10 CONTINUE
   12 IF(ILOOP.GT.LINES)LINES=ILOOP
      CALL PLOT(A,K,TIME,CAT,CATREV)
      CALL AXIS(LABEL,REF,LOCATE)
      CALL OUTPUT(IRUN,INNER)
  111 CONTINUE
      IF(NUMCOP.EQ.0)GO TO 1000
      DO 112 KOPY=1,NUMCOP
      WRITE(6,301)KOPY,NUMCOP
      CALL AXIS(LABEL,REF,LOCATE)
      CALL CHART(IGRID,NUMRUN,LINES,SCALE,VAR,STD,KOPY)
      CALL AXIS(LABEL,REF,LOCATE)
  112 CONTINUE
      DO 1001 ISTUFF=1,LINES
      DO 1001 JSTUFF=1,NUMRUN
      IGRID(ISTUFF,JSTUFF)=101
 1001 CONTINUE
 1000 CONTINUE
      WRITE(6,300)
      STOP
  251 FORMAT(2I3)
  252 FORMAT(I3/20A4)
  253 FORMAT(2A4,E10.3)
  300    FORMAT(1H1,'CHEM 5000--B.E. SIMPSON'//)
  301 FORMAT(1H1,'CHEM 5000--B.E. SIMPSON',T115,'COPY',I3,' OF',I3//)
      END
```

```
      SUBROUTINE AINPUT
C
C       THIS SUB-PROGRAM READS IN THOSE VARIABLES WHICH ARE CONSTANT FOR A
C       GIVEN SET OF DATA.  VARIABLE NAMES ARE THE SAME AS THOSE LISTED IN
C       THE MAIN PROGRAM.
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 KUNCAT,K1,K2,KNEG2,KEQ,INCAT,KPRO,KFORM
      COMMON OX,CLIG,CLIG1,EPS,TDELT,INCAT,ASTART,KUNCAT,K1,K2,KNEG2,
     $KPRO,KFORM,KEQ,UNRUN,DELTIM,T1,T2,ISCALE,MAXTIM
      READ(5,252)ISCALE,MAXTIM,DELTIM,INCAT,KUNCAT,OX,EPS,KPRO,KFORM,
     $KEQ,UNRUN,K1,K2,KNEG2
      CLIG1=0.D0
      CLIG=0.D0
  252 FORMAT(2I3/(E10.3))
      RETURN
      END


      SUBROUTINE BINPUT(REF)
C
C       THIS SUB-PROGRAM READS IN THOSE VARIABLES WHICH CHANGE WITH SUCCESSIVE
C       PLOTS.  SEE MAIN PROGRAM COMMENTS FOR VARIABLE NAMES DEFINITION.
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 KUNCAT,K1,K2,KNEG2,KEQ,INCAT,KPRO,KFORM
      COMMON OX,CLIG,CLIG1,EPS,TDELT,INCAT,ASTART,KUNCAT,K1,K2,KNEG2,
     $KPRO,KFORM,KEQ,UNRUN,DELTIM,T1,T2,ISCALE,MAXTIM
      READ(5,250)REF,ASTART,T1,T2
  250 FORMAT(F10.0/F10.0/2F10.0)
      RETURN
      END


      SUBROUTINE OUTPUT(IRUN,INNER)
C
C       THIS SUB-PROGRAM PRINTS OUT SELECTED SYSTEM PARAMETERS.  SEE MAIN
C       PROGRAM FOR VARIABLE NAME DEFINITION.
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 KUNCAT,K1,K2,KNEG2,KEQ,INCAT,KPRO,KFORM
      REAL*4 KSTAR
      COMMON OX,CLIG,CLIG1,EPS,TDELT,INCAT,ASTART,KUNCAT,K1,K2,KNEG2,
     $KPRO,KFORM,KEQ,UNRUN,DELTIM,T1,T2,ISCALE,MAXTIM
      KODE=IRUN
      IF(KODE.EQ.10)KODE=0
      WRITE(6,350)TDELT,INNER,INCAT,ASTART,KUNCAT,KPRO,K1,K2,KNEG2
     $,KEQ,KFORM,OX,UNRUN,KODE
  350 FORMAT(1H1,10X,'SYSTEM PARAMETERS:'///
     $11X,'TDELT=',1PD13.6//
     $11X,'NUMBER OF ITERATIONS FOR EACH POINT=',I3//
     $11X,'INCAT=',D13.6//
     $11X,'ASTART=',D13.6//
     $11X,'KUNCAT=',D13.6//
     $11X,'KPRO=',D13.6//
     $11X,'K1=',D13.6//
     $11X,'K2=',D13.6//
     $11X,'K-2=',D13.6//
     $11X,'KEQ=',D13.6//
     $11X,'KFORM=',D13.6//
     $11X,'OX=',D13.6//
     $11X,'NUMBER OF MINUTES OF UNCATALYZED REACTION=',0PF6.3//
     $11X,'THE CODE FOR THIS REACTION ON THE COMPOSITE',/11X,'GRAPH AT',
     $' THE END OF THIS SET OF OUTPUT IS:  >>>---> ',I2)
      RETURN
      END
```

```
C
      SUBROUTINE AXIS(TITLE,REF,LOCATE)
C
C       THIS SUB-PROGRAM PRINTS THE PROPER LABELS AND AXES FOR EACH PLOT.
C
C
         DIMENSION TITLE(20)
      GO TO (20,30),LDCATE
   20    WRITE(6,295)TITLE,REF
         WRITE(6,296)
          WRITE(6,297)
         WRITE(6,305)
      LOCATE=2
      GO TO 40
   30 WRITE(6,305)
         WRITE(6,297)
         WRITE(6,296)
      LOCATE=1
   40 RETURN
  295 FORMAT(1X,20A4,//1X,'DATA SET = ',F10.2)
  296    FORMAT(///,1X,T50,' ---ABSORBANCE---'/)
  297    FORMAT(11X,'1.0         0.9',
     $   '         0.8        0.7        0.6        0.5        0.4        0.3',
     $   '         0.2        0.1        0.0')
  305    FORMAT(1X,'TIME    A    |.........|.........|.........|',
     $   '.........|.........|.........|.........|.........|.........|',
     $   '.........|     CAT     REV ')
      END
C
      SUBROUTINE PLOT(A,K,TIME,UNCAT,CAT)
C
C       THIS SUB-PROGRAM TAKES ABSORBANCE VALUES FROM THE MAIN PROGRAM AND
C       PLOTS THEM ON A SCALE MATCHING THE PRINTOUT OF THE CARY 14 .
C
C
      REAL*8 A,TIME,UNCAT,CAT,B
         DIMENSION PLT(102)
         DATA PLT,STAR,BLANK,DOT,BAR/102*' ','*',' ','.','-'/
      B=A
      IF(B.GT.1.00)B=B-1.00
         K=K+1
         INDEX=101.49999-B*100.
         IF(INDEX.GT.101)INDEX=101
         IF(INDEX.LT.2)INOEX=2
         PLT(INDEX)=STAR
         IF(K.EQ.6)GO TO 495
         PLT(1)=DOT
         PLT(102)=DOT
         GO TO 496
  495    PLT(1)=BAR
         PLT(102)=BAR
         K=0
  496    WRITE(6,201)TIME,A,PLT,UNCAT,CAT
  201 FORMAT(1X,F5.2,1X,F5.3,102A1,1PD9.2,1X,1PD9.2)
         PLT(INOEX)=BLANK
      RETURN
      END
```

```
C
      SUBROUTINE CHART(IGRID,NUMRUN,LINE ,SCALE,VAR,STD,KOPY)
C
C       THIS SUB-PROGRAM ACCEPTS ARRAY IGRID FROM THE MAIN PROGRAM CONTAINING
C       ALL THE PREVIOUS PLOTS IN THIS DATA SET AND PRINTS A COMPOSIT GRAPH.
C
C
      REAL*8 SCALE
      DIMENSION IGRID(200,10),GRID(102),VAL(10),STD(10),VAR(10,2),
     $STAR(10)
      DATA GRID,STAR,BLANK,DOT,BAR/102*' ',10*'*',' ','.','-'/                C
      IF(KOPY.GT.1)GO TO 10
      DO 11 J=7,10
   11 CONTINUE
   10 DENOM=6.*SCALE
      TIME=0.0
      K=0
      LINES=LINE-1
      DO 300 I=1,LINES
      TIME=TIME+1./DENOM
      K=K+1
      DO 200 J=1,NUMRUN
  200 GRID(IGRID(I,J))=STAR(J)
      IF(K.EQ.6)GO TO 205
      GRID(1)=DOT
      GRID(102)=DOT
      GO TO 206
  205 GRID(1)=BAR
      GRID(102)=BAR
      K=0
  206 WRITE(6,301)TIME,GRID
      WRITE(6,410)TIME,GRID
  410 FORMAT(1H+,F5.2,1X,'---- ',102A1)
  299 DO 300 J=1,NUMRUN
  300 GRIO(IGRID(I,J))=BLANK
      RETURN
  301 FORMAT(1X,F5.2,1X,'---- ',102A1,' SUMMARY OF CURVES')
      ENO
```

```
C
C
      SUBROUTINE AMODEL
     $(A,CATCON,UNCAT,CAT,CATREV,PROMO,ADELT,TIME,TERM)
C
C         THIS MODEL DESCRIBES THE MALACHITE GREEN--PERIODATE SYSTEM
C         CATALYZED BY MN(II).  THE STEADY-STATE APPROXIMATION WAS MADE
C         LEADING TO THE EXPRESSIONS DENOTED BELOW BY "CAT" AND "CATREV".
C
C                                       DATE SUB-PROBRAM WRITTEN:  1 MAY 72
C
C        DEFINITION OF VARIABLE NAMES APPEARING IN THIS SUB-PROGRAM AND NOT
C        ALREADY DEFINED IN THE MAIN PROGRAM:
C
C          APRIME:  EQUALS ABSORBANCE--NECESSARY FOR TRAPEZOIDAL INTEGRATION TO
C                   AVOID ALTERING THE VALUE OF "A" FROM THE MAIN PROGRAM
C          CATIN:  GIVES AMOUNT OF CATALYST NOT TIED UP BY LIGAND (USED ONLY
C                  WHEN CONTRIBUTIONS EXPECTED FROM BOTH LIGAND AND NORMAL PATHS)
C          CATOX:  AMOUNT OF CATALYTIC SPECIES AVAILABLE IN OXIDIZED FORM
C          CONCAT:  AVAILABLE CATALYST CONCENTRATION( EQUAL TO CATCON IN MAIN
C                   PROGRAM BUT NECESSARY TO DO TRAPEZOIDAL INTRGRATION WITHOUT
C                   ALTERING THE VALUE OF CATCON
C          DELIG:  CHANGE IN TOTAL LIGAND CONCENTRATION PER UNIT OF TIME
C                  RESULTING FROM PROGRESS OF THE REACTION (USED ONLY WHEN
C                  CONTRIBUTIONS EXPECTED FROM BOTH LIGAND AND NORMAL PATHS)
C          UNCAT:  CONTRIBUTION OF UNCATALYZED REACTION TO OVERALL RATE
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 KUNCAT,K1,K2,KNEG2,KEQ,INCAT,KPRO,KFORM
      COMMON OX,CLIG,CLIG1,EPS,TDELT,INCAT,ASTART,KUNCAT,K1,K2,KNEG2,
     $KPRO,KFORM,KEQ,UNRUN,DELTIM,T1,T2,ISCALE,MAXTIM
      CONCAT=CATCON
      APRIME=A
      DO 10 I=1,2
      SIGN=1.000
      UNCAT=-(KUNCAT*APRIME)
      IF(K2.EQ.0.D0)GO TO 111
      IF((1.D0/KFORM+CLIG-CONCAT).LT.0.000)SIGN=-1.D0
      CATIN=(DSQRT((1.D0/KFORM+CLIG-CONCAT)**2+4.D0*CONCAT/KFORM)
     $-SIGN*DSQRT((1.D0/KFORM+CLIG-CONCAT)**2))/2.D0
      TERM1 = TERM + KNEG2*(ASTART - APRIME)                              C
      CATOX = TERM1*CONCAT/(K2*APRIME + TERM1)                           C
      CAT = - K2*APRIME*CATOX                                            C
      CATREV = KNEG2*(ASTART - APRIME)*(CONCAT - CATOX)                  C
      PROMO=-(KPRO*APRIME*(CONCAT-CATIN))
  111 IF(I.EQ.2)GO TO 11
      DELIG=PROMO*TDELT/EPS
      CLIG=CLIG+DELIG                                                    C
      X1 = UNCAT + CAT + CATREV + PROMO
      CONCAT=INCAT*T2*(TIME+TDELT-T1)**2/(T2-T1)**2
      IF(TIME.LT.T1)CONCAT=0.D0
      IF(TIME.GE.T2)CONCAT=INCAT*(TIME+TDELT)
   10 APRIME=APRIME+TDELT*X1
   11 ADELT = TDELT*(X1 + UNCAT + CAT + CATREV + PROMO)/2.D0
      RETURN
      END
```

APPENDIX C

DETAILED DERIVATION OF EQUATIONS

Complete derivations of cases discussed in the text of this report. Derivations are in the same order as the discussions appear in the paper.

Pre-equilibrium Condition (Case 1)

$$2C + Ox = 2Cx + R \qquad \text{(C-1)}$$

$$Cx + Dr = Dx + C \qquad \text{(C-2)}$$

$$K_{eq} = [Cx]^2[R]/[C]^2[Ox] \qquad \text{(C-3)}$$

Solving for $[Cx]^2$:

$$[Cx]^2 = K_{eq}[C]^2[Ox]/[R] \qquad \text{(C-4)}$$

From stoichiometric considerations:

$$[Ox] = [Ox]_o - \tfrac{1}{2}[Cx]$$

$$[C] = [C]_o - [Cx]$$

$$[Cx] = 2[R]$$

Now, let: $X = [Cx]$, $C = [C]_o$, $\emptyset = [Ox]_o$, and $K = K_{eq}$

Substituting the above relations into Equation C-4 gives:

$$X^2 = \frac{K(C - X)^2(\emptyset - \frac{1}{2}X)}{\frac{1}{2}X} \qquad \text{(C-5)}$$

Multiplying both sides by X and the right-hand side by $\frac{2}{2}$ gives:

$$\begin{aligned} X^3 &= K(C - X)^2(2\emptyset - X) \\ &= (KC^2 - 2KCX + KX^2)(2\emptyset - X) \\ &= 2\emptyset KC^2 - 4\emptyset KCX + 2\emptyset KX^2 - KX^3 \\ &\qquad - KC^2X + 2KCX^2 \end{aligned}$$

Collecting terms:

$$(K + 1)X^3 = 2K(\emptyset + C)X^2 - KC(C + 4\emptyset)X + 2\emptyset KC^2$$

Dividing both sides by K and transferring to the left side:

$$(1 + \frac{1}{K})X^3 - 2(C + \emptyset)X^2 + C(C + 4\emptyset)X - 2C^2\emptyset = 0 \qquad \text{(C-6)}$$

Conversion back to the original variables gives the final equation expressing the activated catalyst concentration, [Cx], in a cubic polynomial:

$$(1 + \frac{1}{K})[Cx]^3 - 2([C]_o + [Ox]_o)[Cx]^2 + [C]_o([C]_o + 4[Ox]_o)[Cx] - 2[C]_o^2[Ox]_o = 0 \qquad \text{(C-7)}$$

Pre-equilibrium Condition (Case 2)

$$C + 2Ox = Cx + 2R \qquad \text{(C-8)}$$

$$Cx + Dr = Dx + C \qquad \text{(C-9)}$$

$$K_{eq} = [Cx][R]^2/[C][Ox]^2 \qquad \text{(C-10)}$$

Solving for [Cx]:

$$[Cx] = K_{eq}[C][Ox]^2/[R]^2 \qquad \text{(C-11)}$$

From stoichiometric considerations:

$$[Ox] = [Ox]_2 - 2[Cx] \qquad \text{(C-12)}$$

$$[C] = [C]_o - [Cx] \qquad \text{(C-13)}$$

$$[R] = 2[Cx] \qquad \text{(C-14)}$$

Again, letting: $X = [Cx]$, $C = [C]_o$, $\emptyset = [Ox]_o$, and $K = K_{eq}$ and substituting into Equation C-11 gives:

$$X = \frac{K(C - X)(\emptyset - 2X)^2}{4X^2} \qquad \text{(C-15)}$$

Multiplying both sides by $4X^2/K$:

$$\begin{aligned} \frac{4X^3}{K} &= (C - X)(\emptyset - 2X)^2 \\ &= (C - X)(\emptyset^2 - 4\emptyset X + 4X^2) \\ &= C\emptyset^2 - 4C\emptyset X + 4CX^2 \\ &\qquad - \emptyset^2 X + 4\emptyset X^2 - 4X^3 \end{aligned}$$

Collection of terms and transferring to the left side gives the final form of the expression for [Cx]:

$$4(1 + \frac{1}{K})X^3 - 4(C + \emptyset)X^2 + (4C + \emptyset)\emptyset X - C\emptyset^2 = 0 \qquad \text{(C-16)}$$

Or, in terms of the original variables:

$$4(1 + \frac{1}{K})[Cx]^3-4([C]_o+[Ox]_o)[Cx]^2 + (4[C]_o+[Ox]_o)[Ox]_o[Cx]-[C]_o[Ox]_o^2 = 0 \tag{C-17}$$

Steady-State Condition (Case 1)

$$2C + Ox \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Cx + R \tag{C-18}$$

$$2Cx + Dr \xrightarrow{k_2} 2C + Dx \tag{C-19}$$

Equation C-18 represents the rate-determining step.

$$\text{rate} = -\frac{d[Dr]}{dt} = -\frac{d[Ox]}{dt} = k_1[Ox][C]^2 - k_{-1}[Cx]^2[R] \tag{C-20}$$

Making the steady-state approximation:

$$\frac{1}{2}\frac{d[Cx]}{dt} = k_1[Ox][C]^2 - k_{-1}[Cx]^2[R] - k_2[Cx][Dr] = 0 \tag{C-21}$$

From Equation C-21 we get the following two relationships:

$$k_1[Ox][C]^2 = k_{-1}[Cx]^2[R] + k_2[Cx][Dr] \tag{C-22}$$

and, using the quadratic formula:

$$[Cx] = \frac{-k_2[Dr] + \sqrt{(k_2[Dr])^2 + 4k_1k_{-1}[R][Ox][C]^2}}{2k_{-1}[R]} \tag{C-23}$$

Substitution of Equation C-22 into Equation C-20 gives:

$$\text{rate} = -k_2[Cx][Dr] \tag{C-24}$$

Taking the following stoichiometric relations:

$$[R] = [Dr]_o - [Dr] \tag{C-25}$$

$$[Ox] = [Dr] - [Dr]_o + [Ox]_o \tag{C-26}$$

and Equation C-23 in Equation C-24 gives the final rate expression:

$$\text{rate} = -k_2[Dr]\left(\frac{-k_2[Dr] + \sqrt{(k_2[Dr])^2 + 4k_1k_{-1}[R][Ox][C]^2}}{2k_{-1}[R]}\right) \tag{C-27}$$

Steady-State Mechanism (Case 2)

$$C + 2Ox \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} Cx + 2R \tag{C-28}$$

$$Cx + Dr \overset{k_2}{\rightarrow} C + Dx \tag{C-29}$$

$$\text{rate} = \frac{-d[Dr]}{dt} = -\frac{1}{2}\frac{d[Ox]}{dt} = k_1[Ox]^2[C] - k_{-1}[Cx][R]^2 \tag{C-30}$$

Making the steady-state approximation:

$$\frac{d[Cx]}{dt} = k_1[Ox]^2[C] - k_{-1}[Cx][R]^2 - k_2[Cx][Dr] = 0 \tag{C-31}$$

Rearrangement of Equation C-31 gives the following two relations:

$$k_1[Ox]^2[C] = k_{-1}[Cx][R]^2 + k_2[Cx][Dr] \tag{C-32}$$

and, using the quadratic formula:

$$[Cx] = \frac{k_1[Ox]^2[C]}{k_{-1}[R]^2 + k_2[Dr]} \qquad (C\text{-}33)$$

Substitution of Equation C-32 into Equation C-30 gives:

$$\text{rate} = -2(k_2[Cx][Dr]) \qquad (C\text{-}34)$$

Replacing [Cx] by Equation C-33

$$\text{rate} = \frac{-2k_1k_2[Ox]^2[Dr][C]}{k_{-1}[R]^2 + k_2[Dr]} \qquad (C\text{-}35)$$

but, since k_2 is much greater than k_{-1} and

$$[Ox] = [Ox]_o - 2[Dr]_o + 2[Dr]$$

we have:

$$\text{rate} = -2k_1([Ox]_o - 2[Dr]_o + 2[Dr])^2[C]_o, \qquad (C\text{-}36)$$

the final expression for the catalyzed rate.

Special Case: 3 Different Species

$$C + Dr + Ox \underset{k-1}{\overset{k_1}{\rightleftharpoons}} Q \qquad (C\text{-}37)$$

$$Q \overset{k_2}{\rightleftharpoons} C + Dx + R \qquad (C\text{-}38)$$

Pre-equilibrium Mechanism

$$K_{eq} = [Q]/[C][Dr][Ox] \qquad (C\text{-}39)$$

Solving for [Q] gives:

$$[Q] = K_{eq}[C][Dr][Ox] \tag{C-40}$$

Stoichiometric considerations give:

$$[Ox] = [Ox]_o - [Q] \tag{C-41}$$

$$[C] = [C]_o - [Q] \tag{C-42}$$

$$[Dr] = [Dr]_o - [Q] \tag{C-43}$$

Letting $Q = [Q]$, $C = [C]_o$, $D = [Dr]_o$, $\emptyset = [Ox]_o$, and $K = K_{eq}$ and substituting into Equation C-40 gives:

$$Q = K(C - Q)(D - Q)(\emptyset - Q) \tag{C-44}$$

$$Q/K = (CD - (C + D)Q + Q^2)(\emptyset - Q)$$

$$\begin{aligned} \frac{Q}{K} = {} & CD\emptyset - \emptyset(C + D)Q + \emptyset Q^2 \\ & - CDQ + (C + D)Q^2 - Q^3 \end{aligned}$$

Collection of terms and transferring to the left side gives:

$$Q^3 - (\emptyset + C + D)Q^2 + (\emptyset(C + D) + CD + \frac{1}{K})Q - CD\emptyset = 0 \tag{C-45}$$

Substitution of the original variables gives Equation 3-38 in text.

Steady-State Condition

Referring to Equations C-37 and C-38

$$\text{rate} = -\frac{d[Dr]}{dt} = -k_{-1}[Q] + k_1[C][Dr][Ox] \tag{C-46}$$

Making the steady-state approximation:

$$\frac{d[Q]}{dt} = k_1[C][Dr][Ox] - k_2[Q] - k_{-1}[Q] = 0 \qquad \text{(C-47)}$$

Equation C-47 yields the following two relations:

$$k_1[C][Dr][Ox] = k_2[Q] + k_{-1}[Q] \quad \text{and} \qquad \text{(C-48)}$$

$$[Q] = \frac{k_1[C][Dr][Ox]}{k_2 + k_{-1}} \qquad \text{(C-49)}$$

Substitution of Equation C-48 into Equation C-46 gives:

$$\text{rate} = -k_2[Q] \qquad \text{(C-50)}$$

Equation C-49 in Equation C-50 gives:

$$\text{rate} = \frac{-k_1k_2[C][Dr][Ox]}{k_2 + k_{-1}} \qquad \text{(C-51)}$$

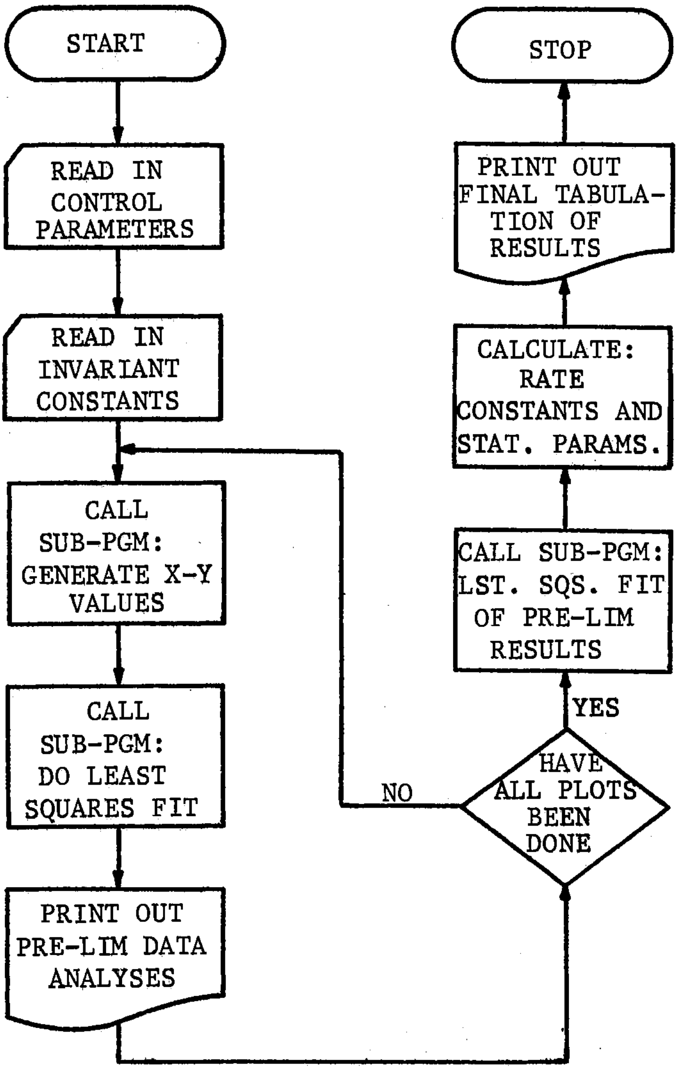
But, since k_2 is much greater than k_{-1}, $[C] = [C]_o$ and $[Ox] = [Ox]_o - [Dr]_o + [Dr]$, we have finally:

$$\text{rate} = -\,k_1[Dr][C]_o([Ox]_o - [Dr]_o + [Dr]) \qquad \text{(C-52)}$$

This is the final expression for the catalyzed rate when considering the collision of three different species and assuming the steady-state mechanism.

APPENDIX D

FLOW DIAGRAM AND SOURCE PROGRAM FOR DETERMINATION OF SYSTEM PARAMETERS


START
READ IN CONTROL PARAMETERS
READ IN INVARIANT CONSTANTS
CALL SUB-PGM: GENERATE X-Y VALUES
CALL SUB-PGM: DO LEAST SQUARES FIT
PRINT OUT PRE-LIM DATA ANALYSES
HAVE ALL PLOTS BEEN DONE
NO
YES
CALL SUB-PGM: LST. SQS. FIT OF PRE-LIM RESULTS
CALCULATE: RATE CONSTANTS AND STAT. PARAMS.
PRINT OUT FINAL TABULATION OF RESULTS
STOP

```
C
C         THIS PROGRAM ACCEPTS ABSORBANCE VS. TIME DATA AND CALCULATES RATE
C         CONSTANTS BY DOING A LEAST SQUARES FIT OF THE MODIFIED RATE EQUATION.
C
C         A BREAKDOWN OF THE INDIVIDUAL PROGRAM SEGMENTS AND THEIR FUNCTION
C         FOLLOWS:
C
C           MAIN:  1)  READS IN PARAMETERS WHICH DO NOT VARY FROM RUN TO RUN
C                  2)  CALLS ALL OTHER SUB-PROGRAMS
C                  3)  COLLECTS RESULTS OF LEAST SQUARES FITS AND CALCULATES
C                      MEAN VALUES AND STATISTICAL PARAMETERS FOR THE RATE
C                      CONSTANTS DETERMINED
C
C           POINTS:  1)  READS IN ABSORBANCE VS. TIME DATA AND OTHER CONTROL
C                        PARAMETERS
C                    2)  CALCULATES THE DERIVATIVE OF EACH POINT
C                    3)  GENERATES THE ABSCISSA AND ORDINATE VALUES FOR THE
C                        LEAST SQUARES ROUTINE
C                    4)  PRINTS OUT INPUT PARAMETERS, DERIVATIVES, AND WEIGHTS
C
C           FIT:  CALCULATES ORDINATE VALUES PREDICTED BY THE FITTED EQUATION
C
C           OUTPUT:  GENERATES THE OUTPUT OF THE LEAST SQUARES ROUTINE
C
C           MTXGEN:  GENERATES THE AURMENTED MATRIX NECESSARY TO DO GAUSSIAN
C                    ELIMINATION
C
C           WEIGHT:  1)  SOLVES THE SYSTEM OF SIMULTANEOUS EQUATIONS NECESSARY
C                        TO DO LINEAR LEAST SQUARES FITTING
C                    2)  GENERATES THE INVERSE OF THE AUGMENTED MATRIX NECESSARY
C                        TO CALCULATE STATISTICAL PARAMETERS
C
C         DEFINITION OF VARIABLES APPEARING IN MAIN PROGRAM:
C
C           AKNEG2:  REVERSE RATE CONSTANT FOR REACTION OF CATALYST WITH DYE
C           AK1:  FORWARD RATE CONSTANT FOR THE OXIDATION OF CATALYST
C           AK2:  FORWARD RATE CONSTANT FOR THE REACTION OF OXIDIZED CATALYST
C                 WITH DYE
C           AMTX:  ARRAY CONTAINING THE AUGMENTED MATRIX GENERATED BY "MTXGEN"
C           ASTART:  INITIAL ABSORBANCE
C           CATIN:  CATALYST ADDITION RATE IN MOLES/LITER.MIN
C           CONST:  ARRAY CONTAINING RESULTS OF THE LEAST SQUARE FITTING
C           DEV:  ARRAY CONTAINING THE ABSOLUTE DEVIATION OF EACH OBSERVED
C                 ORDINATE VALUE FROM THE CORRESPONDING CALCULATED VALUE
C           EPS:  MOLAR ABSORPTIVITY OF THE DYE BEING USED
C           LABEL:  ANY 80 CHARACTER LABEL TO BE PRINTED AT THE TOP OF EACH TABLE
C           N:  NUMBER OF POINTS CONTAINED IN ARRAYS X,Y, AND W
C           OMEGA:  SUM OF THE SQUARES OF THE VALUES IN "DEV"
C           OX:  CONCENTRATION OF THE OXIDIZING AGENT IN MOLES/LITER
C           PCTDEV:  ARRAY CONTAINING THE RELATIVE DEVIATIONS OF EACH OBSERVED
C                    ORDINATE VALUE FROM THE CALCULATED VALUE
C          RCONST:  ARRAY CONTAINING CALCULATED RATE CONSTANTS (USED ONLY WHEN
C                   INDIVIDUAL CONSTANTS ARE CALCULATED, THEN AVERAGED)
C           SD:  ARRAY CONTAINING THE STANDARD DEVIATIONS OF THE RESULTS OF THE
C                LEAST SQUARE FITTING
C           SOLN:  ARRAY CONTAINING SOLUTIONS TO THE SIMULTANEOUS EQUATIONS
C                  SOLVED BY SUB-PROGRAM WEIGHT
C           TABLE:  ARRAY CONTAINING DATA IDENTIFIER, INITIAL DYE CONCENTRATION,
C                   AND CATALYST ADDITION RATE
C           T1:  TIME WHEN CATALYST FIRST BECOMES AVAILABLE TO SYSTEM
C           T2:  TIME WHEN AVAILABLE CATALYST EQUALS TOTAL ANALYTICAL CATALYST
C                CONCENTRATION
C           W:  ARRAY CONTAINING THE WEIGHTS OF EACH CORRESPONDING ORDINATE POINT
C           WINV:  ARRAY CONTAINING THE DIAGONAL ELEMENTS OF THE INVERSE OF
C                  THE AUGMENTED MATRIX
C           WTFAC:  DIAGONAL ELEMENT OF THE INVERSE OF THE AUGMENTED MATRIX
C                   CORRESPONDING TO "SOLN(I)"
C           X:  ARRAY CONTAINING ABSCISSA VALUES FOR LEAST SQUARE FITTING
C           Y:  ARRAY CONTAINING ORDINATE VALUES FOR LEAST SQUARE FITTING
C           YCAL:  ARRAY CONTAINING ORDINATE VALUES CALCULATED FROM RESULTS
C                  OF LEAST SQUARE FITTING
C
```

```
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON X(100),Y(100),W(100),N
      DIMENSION SOLN(6),AMTX(6,7),YCAL(100),RCONST(20,2),SD(20,2)
     $,WINV(6),CONST(20,2),PCTDEV(100),DEV(100)
      REAL*4 LABEL(20),TABLE(20,3)
      DATA MFIT/1/
C                                                                 /2/TIFM ATAD
                                                             DO 3000 MASTER=1,2
      READ(5,997)NUMRUN,AKUN,CRIT,EPS,OX
      DO 1000 KOUNT=1,NUMRUN
      READ(5,995)TABLE(KOUNT,1)
      READ(5,998)LABEL
      LOOP=1
      CALL POINTS
     $(LOOP,ASTART,CATIN,EPS,OX,T1,T2,LABEL)
      CALL MTXGEN(MFIT,AMTX,NROW)
      CALL WEIGHT(MFIT,AMTX,WINV,SOLN,KODE)
      IF(KODE.EQ.1)GO TO 1010
      CALL FIT(YCAL,PCTDEV,DEV,OMEGA,SOLN,MFIT)
      DO 2001 ISTAT=1,2
      KEY=ISTAT
      CONST(KOUNT,ISTAT)=SOLN(ISTAT)
      WTFAC=DABS(WINV(KEY))
 2001 SD(KOUNT,ISTAT)=DSQRT(OMEGA*WTFAC)
      CALL OUTPUT(LABEL,YCAL,PCTDEV,DEV,OMEGA,SOLN,WINV,MFIT)
      GO TO 1020
 1010 WRITE(6,350)MFIT,LOOP
C
C     END INSERT * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
 1020 CONTINUE
      TABLE(KOUNT,2)=ASTART/EPS
      TABLE(KOUNT,3)=CATIN
 1000 CONTINUE
      DO 1070 I=1,NUMRUN
      ABSORB=TABLE(I,2)*EPS
      X(I)=ABSORB*CONST(I,1)
      W(I)=1.D-8*(.1D0-((2.1715D-3*1.D1**ABSORB+2.D-3)/ABSORB))/SD(I,2)
 1070 Y(I)=CONST(I,2)
      READ(5,998)LABEL
      N = NUMRUN
      CALL MTXGEN(MFIT,AMTX,NROW)
      CALL WEIGHT(MFIT,AMTX,WINV,SOLN,KODE)
      IF(KODE.EQ.1)GO TO 1095
      CALL FIT(YCAL,PCTDEV,DEV,OMEGA,SOLN,MFIT)
      CALL OUTPUT(LABEL,YCAL,PCTDEV,DEV,OMEGA,SOLN,WINV,MFIT)
      WTFAC=DABS(WINV(1))
      AK2=-1.D0/SOLN(1)
      SD2=DSQRT(OMEGA*WTFAC)*AK2/(-SOLN(1))
      WRITE(6,352)
      C2 = 1.D-8*SOLN(2) + SOLN(1)
      AKNEG2=(C2*AK2 + 1.D0)/(1.D-8 + C2 - SOLN(1))
      WTFAC=DABS(WINV(2))
      SD3=DSQRT(OMEGA*WTFAC)*AKNEG2/(-SOLN(2))
      SUM1=0.D0
      DO 1081 I=1,NUMRUN
      SUM1=SUM1 + CONST(I,1)
 1081 CONTINUE
      C1BAR=SUM1/NUMRUN
      AK1=(AKNEG2-AK2)/(C1BAR*AK2*EPS*DSQRT(OX))
      SUMSQ1=0.D0
      DO 1090 I=1,NUMRUN
      SUMSQ1=SUMSQ1 + (C1BAR-CONST(I,1))**2
 1090 CONTINUE
      REALN=NUMRUN - 1
      RELSD1=DSQRT(SUMSQ1/REALN)*1.D2/C1BAR
      SD1=AK1*RELSD1/1.D2
      RELSD2=1.D2*SD2/AK2
      RELSD3=1.D2*SD3/AKNEG2
      WRITE(6,355)AK1,SD1,RELSD1,AK2,SD2,RELSD2,AKNEG2,SD3,RELSD3
      GO TO 1099
```

```
 1095 WRITE(6,356)
 1099 WRITE(6,351)
3000                                                     CONTINUE
      STOP
  997 FORMAT(I3,4E10.3)
  995 FORMAT(F10.0)
  998 FORMAT(20A4)
  350 FORMAT(1H1,'SINGULAR MATRIX ENCOUNTERED FOR DEGREE ',I2//
     $1X,'LOOP= ',I3)
  351 FORMAT(1H1,'END OF OUTPUT')
  352 FORMAT(1H1,T8,'DETERMINATION OF SYSTEM PARAMETERS--SUMMARY OF',
     $' RESULTS'////)
  355 FORMAT(////1X,T8,'MEAN VALUES OF RATE CONSTANTS:'///
     $1X,T12,'CONSTANT        VALUE          STD DEV       REL STD DEV(PPH)'/
     $/1X,T15,'K1'      ,T24,2(1PD11.4,3X),0PF10.5/
     $/1X,T15,'K2'      ,T24,2(1PD11.4,3X),0PF10.5/
     $/1X,T15,'K-2'     ,T24,2(1PD11.4,3X),0PF10.5/       )
  356 FORMAT(///1X,'************************ SINGULAR MATRIX ENCOUNTERED
     $ ON THIS STEP **********************************************')
      END
```

```
      SUBROUTINE POINTS
     $(LOOP,ASTART,CATIN,EPS,DX,T1,T2,LABEL)
C
C         THIS SUB-PROGRAM GENERATES THE ABSCISSA AND ORDINATE VALUES FOR THE
C         LEAST SQUARES ROUTINE.
C
C         DEFINITION OF VARIABLES NOT APPEARING IN THE MAIN PROGRAM:
C
C            ABSB:  ARRAY CONTAINING INPUT ABSORBANCE VALUES
C            ABSORB:  ABSORBANCE FOR THE I'TH POINT
C            DCHECK:  VARIABLE USED IN FINDING POINT WITH LARGEST DERIVATIVE
C            DEL:  EQUALS TDELT (NECESSARY WHEN VARIABLE STEP SIZE USED)
C            DERIV:  ARRAY CONTAINING CALCULATED DERIVATIVE VALUES FOR EACH POINT
C            SLOPE:  CHANGE IN INPUT ABSORBANCE PER UNIT OF TIME (USED AS A ROUGH
C                    CHECK ON THE DERIVATIVE VALUE FOR EACH POINT)
C            TDELT:  TIME INCREMENT BETWEEN INPUT ABSORBANCE VALUES
C            TSTART:  TIME CORRESPONDING TO FIRST INPUT ABSORBANCE VALUE
C
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*4 LABEL(20)
      COMMON X(100),Y(100),W(100),N
      DIMENSION ABSB(100), DERIV(100)
      IF(LOOP.GT.1)GO TO 15                                               C
      JUMP=5
      READ(5,100)NUM,KDROP
      READ(5,2999)T1
      READ(5,101)TDELT,TSTART,CATIN,ASTART,(ABSB(K),K=1,NUM)
      DEL=TDELT
      IF(KDROP.EQ.0)GO TO 12
      NUM=NUM - KDROP
      TSTART=TSTART + KDROP*TDELT
      DO 13 I=1,NUM
   13 ABSB(I) = ABSB(I + KDROP)
   12 CONTINUE
```

```
       TIME=TSTART + JUMP*DEL
      NSTOP=NUM - 2*JUMP
      N = NSTOP
      WRITE(6,302)LABEL
      DCHECK=0.D0
      DO 30 I=1,NSTOP
      ABSORB=ABSB(I + JUMP)
      SLOPE=(ABSORB - ABSB(I + JUMP -1))/DEL
      W(I)=1.D1*(0.1D00-((2.1715D-3*1.D1**ABSORB + 2.D-3)/ABSORB))
      IF(W(I).LT.0.D0)W(I)=0.D0
      DERIV(I)=
     $      (300.*ABSB(I)-294.*ABSB(I+1)-532.*ABSB(I+2)-503.*ABSB(I+3)
     $-296.*ABSB(I+4)+296.*ABSB(I+6)+503.*ABSB(I+7)+532.*ABSB(I+8)
     $+294.*ABSB(I+9)-300.*ABSB(I+10))/(5148.*DEL)
      IF(DERIV(I).GT.DCHECK)GO TO 25
      DCHECK=DERIV(I)
      T2=TIME
   25 JUMP1=1+JUMP
      WRITE(6,301)I,TIME,ABSB(JUMP1 ),DERIV(I),SLOPE,W(I)
   30 TIME=TIME + DEL
      WRITE(6,354)NUM,KDROP,TDELT,TSTART,CATIN,ASTART,T1,T2
   15 TIME=TSTART + JUMP*DEL
    6 TIME = TSTART + JUMP*DEL
      DO 40 I=1,NSTOP
      ABSORB=ABSB(I + JUMP)
      X(I) =  1.D0/ABSORB
      CATCON=CATIN*T2*(TIME-T1)**2/(T2-T1)**2
      IF(TIME.LT.T1)CATCON=0.D0
      IF(TIME.GE.T2)CATCON=CATIN*TIME
      Y(I)=CATCON/DERIV(I)
   40 TIME = TIME + DEL
   11 RETURN
  100 FORMAT(2I3)
  101 FORMAT(4E10.3/(8F10.0))
  301 FORMAT(4X,I3,5(3X,F10.5))
  302 FORMAT(1H1,T5,20A4///1X,T5,'DETERMINATION OF DERIVATIVE USING ',
     $'11-POINT CUBIC SMOOTH'///1X,T5,'NO.         TIME        ',
     $            'ABSORBANCE   DERIVATIVE        SLOPE           WEIGHT'/)
  354 FORMAT(///1X,T5,'VALUES OF OTHER INPUT PARAMETERS:'//1X,T5,
     $'NUM=',I4,3X,'KDROP=',I3,3X,'TDELT= ',1PD11.4,3X,'TSTART= ',D11.4,
     $//1X,T5,'CATIN= ',D11.4,3X,'ASTART= ',0PF6.3,3X,'T1= ',F7.4,
     $3X,'T2= ',F7.4)
 2999 FORMAT(2F10.0)
      END
```

```
      SUBROUTINE MTXGEN(M,G,MP1)
C
C         THIS SUB-PROGRAM TAKES THE X(I) AND Y(I) VALUES AND BUILDS THE
C         AUGMENTED MATRIX NECESSARY TO DO GAUSSIAN ELIMINATION.
C
C         PARAMETERS REQUIRED:
C
C                 M=THE DEGREE OF THE POLYNOMIAL TO BE FIT.
C
C         VALUES RETURNED:
C
C                 G=THE AUGMENTED MATRIX CONTAINING THE COEFFICIENTS OF THE
C                 SIMULTANEOUS EQUATIONS TO BE SOLVED.
C
C                 MP1=THE NUMBER OF SIMULTANEOUS EQUATIONS TO BE SOLVED.
C
C         NOTE:  THIS SUB-PROGRAM WAS WRITTEN BY T.E. BAILEY.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON X(100),Y(100),W(100),N
      DIMENSION G(6,7),SUMX(11),SUMY(6)
       MP2=M+2
      MP1=M+1
      M2P1=M*2+1
      SUMX(1)=0.D0
      DO 9 I=1,N
    9 SUMX(1)=SUMX(1)+W(I)
      DO 7 I=2,M2P1
    7 SUMX(I)=0.
      DO 8 I=1,MP1
    8 SUMY(I)=0.
      DO 1 I=2,M2P1
      DO 1 K=1,N
    1 SUMX(I)=SUMX(I)+W(K)*X(K)**(I-1)
      DO 2 K=1,N
    2 SUMY(1)=SUMY(1)+W(K)*Y(K)
      DO 3 I=2,MP1
      DO 3 K=1,N
    3 SUMY(I)=SUMY(I)+W(K)*Y(K)*X(K)**(I-1)
C   GENERATE THE AUGMENTED MATRIX.
      INDEX=0
      DO 5 J=1,MP1
      DO 4 I=1,MP1
    4 G(I,J)=SUMX(I+INDEX)
    5 INDEX=INDEX+1
      DO 6 I=1,MP1
    6 G(I,MP2)=SUMY(I)
C   THE AUGMENTED MATRIX IS NOW GENERATED AND READY FOR SOLUTION.
      RETURN
      END
```

```
      SUBROUTINE WEIGHT(MFIT,AUG,WINV,SOLN,KODE)
C
C         THIS SUB-PROGRAM ACCEPTS AN AUGMENTED MATRIX FROM THE MAIN PROGRAM
C        CONSTITUTING A SET OF SIMULTANEOUS LINEAR EQUATIONS AND RETURNS THE
C        SOLUTIONS TO THE EQUATIONS ALONG WITH AN ARRAY(WINV) CONTAINING THE
C        DIAGONAL ELEMENTS OF THE INVERSE OF THE AUGMENTED MATRIX.
C
C        SEE MAIN PROGRAM FOR VARIALBE DEFINITION
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION AUG(6,7),VAL(6,13),WINV(6),SOLN(6)
      KODE=0
      NSIZE=MFIT+1
      NIDENT=NSIZE+1
      NNSIZE=2*NSIZE+1
      DO 7 I=1,NSIZE
      DO 7 J=NIDENT,NNSIZE
      VAL(I,J)=0.D0
      IF(I.EQ.(J-NSIZE))VAL(I,J)=1.D0
    7 CONTINUE
      DO 8 I=1,NSIZE
      DO 8 J=1,NSIZE
    8 VAL(I,J)=AUG(I,J)
      DO 11 I=1,NSIZE
   11 VAL(I,NNSIZE)=AUG(I,NIDENT)
      DO 1 IA=1,NSIZE
      CK=0.D0
      DO 10 IR=IA,NSIZE
      IF(DABS(VAL(IR,IA)).LE.DABS(CK))GO TO 10
      CK=VAL(IR,IA)
      KR=IR
   10 CONTINUE
      DO 20 J=1,NNSIZE
      R=VAL(KR,J)
      VAL(KR,J)=VAL(IA,J)
   20 VAL(IA,J)=R
      GPIVT=VAL(IA,IA)
      IF(DABS(GPIVT).LT.1.D-60)GO TO 30
      DO 2 N1=1,NNSIZE
    2 VAL(IA,N1)=VAL(IA,N1)/GPIVT
      DO 3 N2=1,NSIZE
      IF(N2.EQ.IA)GO TO 3
      D=VAL(N2,IA)
      DO 4 N3=1,NNSIZE
    4 VAL(N2,N3)=VAL(N2,N3)-VAL(IA,N3)*D
    3 CONTINUE
    1 CONTINUE
      DO 9 I=1,NSIZE
      SOLN(I)=VAL(I,NNSIZE)
    9 WINV(I)=VAL(I,(I+NSIZE))
      GO TO 40
   30 KODE=1
   40 RETURN
      END
```

```
      SUBROUTINE FIT(YCAL,PCTDEV,DEV,OMEGA,C,M)
C
C        THIS SUB-PROGRAM CALCULATES THE ORDINATE VALUES PREDICTED BY THE
C        FITTED EQUATION.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON X(100),Y(100),W(100),N
      DIMENSION C(6),YCAL(100),PCTDEV(100),DEV(100)
      DO 1 I=1,N
      YCAL(I)=C(1)
      DO 1 K=1,M
    1 YCAL(I)=YCAL(I)+C(K+1)*X(I)**K
      SUMCHI=0.0
      SUMSQ=0.0
      DO 10 I=1,N
      DEV(I)=Y(I)-YCAL(I)
      PCTDEV(I)=DEV(I)*100./YCAL(I)
   10 SUMSQ = SUMSQ + W(I)*DEV(I)**2
      RN=N
       IF(N.EQ.2)RN=3.D0
      RM=M +1
      OMEGA = SUMSQ/(RN-RM)
      RETURN
       END
```

```
      SUBROUTINE OUTPUT(LABEL,YCALC,PCTDEV,DEV,OMEGA,C,WINV,M)
C
C        THIS SUB-PROGRAM GENERATES THE OUTPUT OF THE LEAST SQUARES PORTION
C        OF THE PROGRAM.  SPECIFICLY, IT PRINTS OUT:
C
C                   X(I)=THE ABSCISSA VALUE FED INTO THE LEAST SQUARES PORTION.
C
C                   Y(I)=Y(OBS)=ORDINATE VALUE FED INTO THE LEAST SQUARES PORTION
C                   OF THE PROGRAM.
C
C                   YCALC(I)=THE ORDINATE VALUE CALCULATED FROM THE EQUATION
C                   GENERATED BY THE LEAST SQUARES SEGMENT.
C
C                   DEV(I)=THE DEVIATION OF Y(OBS) FROM THE FITTED CURVE.
C
C                   PCTDEV=PER CENT DEVIATION OF Y(OBS) FROM THE FITTED CURVE.
C
C                   CHISQ(I)=TERM CONTRIBUTING TO THE OVERALL CHI SQUARED
C                   GOODNESS OF FIT CRITERION:  CHISQ(I)=DEV**2/ABS(YCALC(I)).
C
C                   OMEGA=THE SAMPLE VARIANCE OF THE LEAST SQUARES FIT.
C
C                   SUMCHI=THE SUM OF THE INDIVIDUAL CHI SQUARED TERMS: A MEASURE
C                   OF THE GOODNESS OF FIT OF THE CURVE TO THE DATA.
C
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON X(100),Y(100),W(100),N
      DIMENSION C(6),YCALC(100),PCTDEV(100),DEV(100),WINV(6)
      REAL*4 LABEL(20)
      WRITE(6,10)LABEL
      DO 1 I=1,N
    1 WRITE(6,11)X(I),Y(I),YCALC(I),DEV(I),PCTDEV(I),W(I)
      MPI=M+1
      WRITE(6,14)OMEGA
      WRITE(6,15)M
      DO 20 I=1,MPI
      WTFAC=DABS(WINV(I))
      SDOP=DSQRT(OMEGA*WTFAC)
      RELSDO=SDOP*1.D2/C(I)
   20 WRITE(6,16)I,C(I),SDOP,RELSDO
      RETURN
   10 FORMAT(1H1////1H ,10X,20A4////1H ,14X,'X          Y(OBS)',
     $'      Y(CALC)',
     $'       DEV(Y)     % DEV(Y)     WEIGHT(Y)'/)
   11 FORMAT(1H ,9X,3(1PD10.3,2X),D10.3,2X,0PF10.5,2X,F11.4)
   14 FORMAT(///15X,'GODONESS OF FIT:        GAUSS CRITERION,  OMEGA=',1X
     $,1PD10.3)                                                         C
   15 FORMAT(///1X,T15,'CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF ',
     $'DEGREE ',I1,' :'///1X,T20,'CONSTANT      VALUE        STD DEV   ',
     $'REL STD DEV(PPH) '/)
   16 FORMAT(1X,T23,'C(',I1,')',T30,2(1PD11.4,2X),0PF10.4/)
      END
```

APPENDIX E

COMPLETE LISTING OF OUTPUT FROM DETERMINATION OF SYSTEM PARAMETERS PROGRAM--NO NTA PRESENT

```
MN(II)--PERIODATE SYSTEM: 34.01  INCLUDES ALLOWANCE FOR INDUCTION PERIOD 6/6/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.       TIME      ABSORBANCE   DERIVATIVE      SLOPE        WEIGHT

  1      1.00817      0.21100     -0.26013     -0.19200      0.73792
  2      1.02900      0.20300     -0.30724     -0.38400      0.73077
  3      1.04983      0.19700     -0.33960     -0.28800      0.72496
  4      1.07067      0.19000     -0.35701     -0.33600      0.71772
  5      1.09150      0.18300     -0.35244     -0.33600      0.70986
  6      1.11233      0.17400     -0.33608     -0.43200      0.69876
  7      1.13317      0.16800     -0.33117     -0.28800      0.69065
  8      1.15400      0.16200     -0.31992     -0.26800      0.68190
  9      1.17483      0.15500     -0.30424     -0.33600      0.67078
 10      1.19567      0.14900     -0.30219     -0.28800      0.66038
 11      1.21650      0.14200     -0.30907     -0.33600      0.64709
 12      1.23733      0.13600     -0.28794     -0.28800      0.63456
 13      1.25817      0.13100     -0.26465     -0.24000      0.62320
 14      1.27900      0.12400     -0.23807     -0.33600      0.60572
 15      1.29983      0.12000     -0.20672     -0.19200      0.59478
 16      1.32067      0.11700     -0.19421     -0.14400      0.58608
 17      1.34150      0.11200     -0.19000     -0.24000      0.57050
 18      1.36233      0.10900     -0.18075     -0.14400      0.56046
 19      1.38317      0.10500     -0.17752     -0.19200      0.54615
 20      1.40400      0.10000     -0.17619     -0.24000      0.52662
 21      1.42483      0.09700     -0.16960     -0.14400      0.51392
 22      1.44567      0.09500     -0.16804     -0.09600      0.50500
 23      1.46650      0.09100     -0.15897     -0.19200      0.48597
 24      1.48733      0.08600     -0.15545     -0.24000      0.45965
 25      1.50817      0.08400     -0.15500     -0.09600      0.44823
 26      1.52900      0.08100     -0.15249     -0.14400      0.43003
 27      1.54983      0.07800     -0.13841     -0.14400      0.41042
 28      1.57067      0.07500     -0.14379     -0.14400      0.38922
 29      1.59150      0.07200     -0.14498     -0.14400      0.36624


VALUES OF OTHER INPUT PARAMETERS:

NUM=  39   KOROP=  0   TDELT=  2.0833D-02   TSTART=  9.0400D-01

CATIN=  2.2400D-08   ASTART=  0.225   T1=  0.8620   T2=  1.0707
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MN(II)--PERIODATE SYSTEM: 34.01  INCLUDES ALLOWANCE FOR INDUCTION PERIOD 6/6/72

     X            Y(OBS)      Y(CALC)       DEV(Y)     % DEV(Y)     WEIGHT(Y)

4.739D 00   -4.524D-08  -4.755D-08   2.314D-09   -4.86665       0.7379
4.926D 00   -5.000D-08  -5.207D-08   2.069D-09   -3.97376       0.7308
5.076D 00   -5.719D-08  -5.569D-08  -1.494D-09    2.68243       0.7250
5.263D 00   -6.718D-08  -6.022D-08  -6.961D-09   11.56024       0.7177
5.464D 00   -6.937D-08  -6.508D-08  -4.289D-09    6.58946       0.7099
5.747D 00   -7.414D-08  -7.192D-08  -2.221D-09    3.08889       0.6988
5.952D 00   -7.665D-08  -7.688D-08   2.339D-10   -0.30430       0.6906
6.173D 00   -8.080D-08  -8.221D-08   1.409D-09   -1.71396       0.6819
6.452D 00   -8.650D-08  -8.895D-08   2.453D-09   -2.75720       0.6708
6.711D 00   -8.863D-08  -9.523D-08   6.602D-09   -6.93289       0.6604
7.042D 00   -8.817D-08  -1.032D-07   1.506D-08  -14.59313       0.6471
7.353D 00   -9.626D-08  -1.107D-07   1.448D-08  -13.07821       0.6346
7.634D 00   -1.065D-07  -1.175D-07   1.104D-08   -9.39096       0.6232
8.065D 00   -1.203D-07  -1.279D-07   7.605D-09   -5.94374       0.6057
8.333D 00   -1.408D-07  -1.344D-07  -6.402D-09    4.76171       0.5948
8.547D 00   -1.523D-07  -1.396D-07  -1.271D-08    9.10627       0.5861
8.929D 00   -1.582D-07  -1.488D-07  -9.323D-09    6.26410       0.5705
9.174D 00   -1.688D-07  -1.548D-07  -1.406D-08    9.08232       0.5605
9.524D 00   -1.745D-07  -1.632D-07  -1.130D-08    6.92566       0.5462
1.000D 01   -1.785D-07  -1.747D-07  -3.761D-09    2.15240       0.5266
1.031D 01   -1.882D-07  -1.822D-07  -5.963D-09    3.27257       0.5139
1.053D 01   -1.927D-07  -1.875D-07  -5.247D-09    2.79902       0.5050
1.099D 01   -2.066D-07  -1.987D-07  -7.994D-09    4.02432       0.4860
1.163D 01   -2.143D-07  -2.141D-07  -2.225D-10    0.10393       0.4596
1.190D 01   -2.208D-07  -2.208D-07  -1.417D-11    0.00642       0.4482
1.235D 01   -2.246D-07  -2.315D-07   6.857D-09   -2.96248       0.4300
1.282D 01   -2.508D-07  -2.429D-07  -7.897D-09    3.25063       0.4104
1.333D 01   -2.447D-07  -2.553D-07   1.064D-08   -4.16766       0.3892
1.389D 01   -2.459D-07  -2.688D-07   2.287D-08   -8.50884       0.3662


    GOODNESS OF FIT:        GAUSS CRITERION,  OMEGA=  4.394D-17


   CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

        CONSTANT      VALUE        STD DEV    REL STD DEV(PPH)

          C(1)     6.7032D-08   5.2887D-09      7.8898

          C(2)    -2.4177D-08   6.2448D-10     -2.5829
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MN(III)--PERIODATE SYSTEM: 34.02  INCLUDES ALLOWANCE FOR INDUCTION PERIOD 6/6/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.       TIME      ABSORBANCE   DERIVATIVE     SLOPE        WEIGHT

  1     0.97917      0.43500     -0.42532     -0.38400     0.81811
  2     1.00000      0.42800     -0.46491     -0.33600     0.81734
  3     1.02083      0.41600     -0.51990     -0.57600     0.81588
  4     1.04167      0.40300     -0.56065     -0.62400     0.81409
  5     1.06250      0.39400     -0.58519     -0.43200     0.81270
  6     1.08333      0.38200     -0.59875     -0.57600     0.81065
  7     1.10417      0.36600     -0.59388     -0.76800     0.80755
  8     1.12500      0.35500     -0.60416     -0.52800     0.80514
  9     1.14583      0.34500     -0.60568     -0.48000     0.80273
 10     1.16667      0.33000     -0.56955     -0.72000     0.79871
 11     1.18750      0.31900     -0.54324     -0.52800     0.79541
 12     1.20833      0.30700     -0.53693     -0.57600     0.79143
 13     1.22917      0.29700     -0.49277     -0.48000     0.78778
 14     1.25000      0.28800     -0.47139     -0.43200     0.78421
 15     1.27083      0.27700     -0.48947     -0.52800     0.77945
 16     1.29167      0.26700     -0.47924     -0.48000     0.77469
 17     1.31250      0.25900     -0.46211     -0.38400     0.77056
 18     1.33333      0.24600     -0.42389     -0.62400     0.76317
 19     1.35417      0.23800     -0.38430     -0.38400     0.75814
 20     1.37500      0.23300     -0.35633     -0.24000     0.75479
 21     1.39583      0.22500     -0.34048     -0.38400     0.74909
 22     1.41667      0.21800     -0.33900     -0.33600     0.74370
 23     1.43750      0.21000     -0.36862     -0.38400     0.73706
 24     1.45833      0.20300     -0.36155     -0.33600     0.73077
 25     1.47917      0.19500     -0.32342     -0.38400     0.72296
 26     1.50000      0.18800     -0.30504     -0.33600     0.71554
 27     1.52083      0.18200     -0.28691     -0.28800     0.70869
 28     1.54167      0.17800     -0.28237     -0.19200     0.70384
 29     1.56250      0.17200     -0.28113     -0.28800     0.69612
 30     1.58333      0.16400     -0.28849     -0.38400     0.68489
 31     1.60417      0.15900     -0.27776     -0.24000     0.67726
 32     1.62500      0.15300     -0.27039     -0.28800     0.66741
 33     1.64583      0.14800     -0.24696     -0.24000     0.65857
 34     1.66667      0.14300     -0.23074     -0.24000     0.64907
 35     1.68750      0.13900     -0.23585     -0.19200     0.64096

VALUES OF OTHER INPUT PARAMETERS:

NUM=  45   KDROP=  0   TDELT=  2.0833D-02   TSTART=  8.7500D-01

CATIN=  2.2400D-08   ASTART=  0.466   T1=  0.7510   T2=  1.1458
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MN(II)--PERIODATE SYSTEM: 34.02  INCLUDES ALLOWANCE FOR INDUCTION PERIOD 6/6/72

     X           Y(OBS)      Y(CALC)       DEV(Y)     % DEV(Y)     WEIGHT(Y)

2.299D 00   -2.015D-08   -2.270D-08    2.545D-09   -11.21161        0.8181
2.356D 00   -2.196D-08   -2.376D-08    1.806D-09    -7.60141        0.8173
2.404D 00   -2.306D-08   -2.567D-08    2.616D-09   -10.19047        0.8159
2.481D 00   -2.481D-08   -2.787D-08    3.062D-09   -10.98517        0.8141
2.538D 00   -2.730D-08   -2.948D-08    2.180D-09    -7.39436        0.8127
2.618D 00   -3.037D-08   -3.174D-08    1.370D-09    -4.31685        0.8107
2.732D 00   -3.458D-08   -3.498D-08    4.062D-10    -1.16099        0.8075
2.817D 00   -3.812D-08   -3.738D-08   -7.333D-10     1.96145        0.8051
2.899D 00   -4.238D-08   -3.970D-08   -2.677D-09     6.74234        0.8027
3.030D 00   -4.588D-08   -4.344D-08   -2.449D-09     5.63789        0.7987
3.135D 00   -4.897D-08   -4.640D-08   -2.568D-09     5.53415        0.7954
3.257D 00   -5.041D-08   -4.987D-08   -5.376D-10     1.07794        0.7914
3.367D 00   -5.587D-08   -5.298D-08   -2.892D-09     5.45926        0.7878
3.472D 00   -5.940D-08   -5.596D-08   -3.435D-09     6.13690        0.7842
3.610D 00   -5.816D-08   -5.987D-08    1.717D-09    -2.86700        0.7795
3.745D 00   -6.037D-08   -6.371D-08    3.334D-09    -5.23317        0.7747
3.861D 00   -6.362D-08   -6.699D-08    3.366D-09    -5.02516        0.7706
4.065D 00   -7.046D-08   -7.277D-08    2.314D-09    -3.17966        0.7632
4.202D 00   -7.893D-08   -7.665D-08   -2.285D-09     2.98106        0.7581
4.292D 00   -8.644D-08   -7.920D-08   -7.234D-09     9.13396        0.7548
4.444D 00   -9.183D-08   -8.353D-08   -8.303D-09     9.93966        0.7491
4.587D 00   -9.361D-08   -8.758D-08   -6.032D-09     6.88777        0.7437
4.762D 00   -8.735D-08   -9.253D-08    5.177D-09    -5.59448        0.7371
4.926D 00   -9.035D-08   -9.719D-08    6.834D-09    -7.03167        0.7308
5.128D 00   -1.024D-07   -1.029D-07    4.669D-10    -0.45366        0.7230
5.319D 00   -1.102D-07   -1.083D-07   -1.822D-09     1.68152        0.7155
5.495D 00   -1.187D-07   -1.133D-07   -5.435D-09     4.79721        0.7087
5.618D 00   -1.223D-07   -1.168D-07   -5.497D-09     4.70598        0.7038
5.814D 00   -1.245D-07   -1.224D-07   -2.140D-09     1.74876        0.6961
6.098D 00   -1.229D-07   -1.304D-07    7.462D-09    -5.72268        0.6849
6.289D 00   -1.294D-07   -1.358D-07    6.469D-09    -4.76221        0.6773
6.536D 00   -1.346D-07   -1.428D-07    8.207D-09    -5.74602        0.6674
6.757D 00   -1.493D-07   -1.491D-07   -1.952D-10     0.13094        0.6586
6.993D 00   -1.618D-07   -1.558D-07   -6.010D-09     3.85770        0.6491
7.194D 00   -1.603D-07   -1.615D-07    1.222D-09    -0.75689        0.6410

    GOODNESS OF FIT:        GAUSS CRITERION,  OMEGA=  1.341D-17


   CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

        CONSTANT      VALUE        STD DEV    REL STD DEV(PPH)

          C(1)     4.2481D-08    2.1763D-09      5.1231

          C(2)    -2.8352D-08    4.9475D-10     -1.7450
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MN(II)--PERIODATE SYSTEM: 34.03  INCLUDES ALLOWANCE FOR INDUCTION PERIOD 6/6/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.        TIME       ABSORBANCE   DERIVATIVE       SLOPE          WEIGHT

  1       1.17917       0.70800     -0.48725     -0.48000        0.81517
  2       1.20000       0.69900     -0.58807     -0.43200        0.81605
  3       1.22083       0.68300     -0.66294     -0.76800        0.81749
  4       1.24167       0.67000     -0.70381     -0.62400        0.81855
  5       1.26250       0.65400     -0.74685     -0.76800        0.81973
  6       1.28333       0.63800     -0.77067     -0.76800        0.82076
  7       1.30417       0.62400     -0.80232     -0.67200        0.82154
  8       1.32500       0.60600     -0.83031     -0.86400        0.82236
  9       1.34583       0.58700     -0.83725     -0.91200        0.82300
 10       1.36667       0.57100     -0.85433     -0.76800        0.82335
 11       1.38750       0.55100     -0.86554     -0.96000        0.82355
 12       1.40833       0.53700     -0.82754     -0.67200        0.82351
 13       1.42917       0.51800     -0.78769     -0.91200        0.82321
 14       1.45000       0.50000     -0.75673     -0.86400        0.82266
 15       1.47083       0.48500     -0.72800     -0.72000        0.82198
 16       1.49167       0.47400     -0.71347     -0.52800        0.82135
 17       1.51250       0.45800     -0.67643     -0.76800        0.82022
 18       1.53333       0.44200     -0.66939     -0.76800        0.81881
 19       1.55417       0.42800     -0.66092     -0.67200        0.81734
 20       1.57500       0.41600     -0.63337     -0.57600        0.81588
 21       1.59583       0.40400     -0.56477     -0.57600        0.81423
 22       1.61667       0.39100     -0.53423     -0.62400        0.81221
 23       1.63750       0.38000     -0.51802     -0.52800        0.81029
 24       1.65833       0.37000     -0.50063     -0.48000        0.80837
 25       1.67917       0.36200     -0.47709     -0.38400        0.80670
 26       1.70000       0.34900     -0.46257     -0.62400        0.80372
 27       1.72083       0.34000     -0.47027     -0.43200        0.80145
 28       1.74167       0.33100     -0.46908     -0.43200        0.79899
 29       1.76250       0.32200     -0.44123     -0.43200        0.79634
 30       1.78333       0.31200     -0.42480     -0.48000        0.79314
 31       1.80417       0.30200     -0.42562     -0.48000        0.78965
 32       1.82500       0.29500     -0.40447     -0.33600        0.78701
 33       1.84583       0.28800     -0.38192     -0.33600        0.78421
 34       1.86667       0.27700     -0.37495     -0.52800        0.77945
 35       1.88750       0.27100     -0.37104     -0.28800        0.77665
 36       1.90833       0.26400     -0.35263     -0.33600        0.77318
 37       1.92917       0.25600     -0.32858     -0.38400        0.76894
 38       1.95000       0.24800     -0.32786     -0.38400        0.76436
 39       1.97083       0.24300     -0.34603     -0.24000        0.76133
 40       1.99167       0.23700     -0.33391     -0.28800        0.75748
 41       2.01250       0.22800     -0.32461     -0.43200        0.75128
 42       2.03333       0.22000     -0.31611     -0.38400        0.74528
 43       2.05417       0.21500     -0.31792     -0.24000        0.74128


VALUES OF OTHER INPUT PARAMETERS:

NUM=  53   KDROP=  0    TDELT=  2.0833D-02   TSTART=  1.0750D 00

CATIN=  2.2400D-08   ASTART=  0.737   T1=  0.9600   T2=  1.3875
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MN(II)--PERIODATE SYSTEM: 34.03  INCLUDES ALLOWANCE FOR INDUCTION PERIOD 6/6/72

    X            Y(OBS)      Y(CALC)        DEV(Y)      % DEV(Y)     WEIGHT(Y)

1.412D 00  -1.676D-08  -1.774D-08   9.789D-10    -5.51664       0.8152
1.431D 00  -1.666D-08  -1.851D-08   1.850D-09    -9.99378       0.8160
1.464D 00  -1.745D-08  -1.991D-08   2.460D-09   -12.35564       0.8175
1.493D 00  -1.917D-08  -2.111D-08   1.935D-09    -9.16765       0.8186
1.529D 00  -2.084D-08  -2.264D-08   1.800D-09    -7.95366       0.8197
1.567D 00  -2.306D-08  -2.425D-08   1.183D-09    -4.87738       0.8208
1.603D 00  -2.511D-08  -2.572D-08   6.146D-10    -2.38930       0.8215
1.650D 00  -2.729D-08  -2.772D-08   4.322D-10    -1.55931       0.8224
1.704D 00  -3.024D-08  -2.996D-08  -2.778D-10     0.92730       0.8230
1.751D 00  -3.292D-08  -3.196D-08  -9.568D-10     2.99352       0.8234
1.815D 00  -3.591D-08  -3.463D-08  -1.278D-09     3.68986       0.8235
1.862D 00  -3.812D-08  -3.662D-08  -1.506D-09     4.11166       0.8235
1.931D 00  -4.064D-08  -3.948D-08  -1.160D-09     2.93839       0.8232
2.000D 00  -4.292D-08  -4.240D-08  -5.238D-10     1.23539       0.8227
2.062D 00  -4.526D-08  -4.499D-08  -2.631D-10     0.58474       0.8220
2.110D 00  -4.683D-08  -4.700D-08   1.691D-10    -0.35975       0.8214
2.183D 00  -5.009D-08  -5.009D-08   6.925D-12    -0.01382       0.8202
2.262D 00  -5.131D-08  -5.341D-08   2.099D-09    -3.93072       0.8188
2.336D 00  -5.267D-08  -5.651D-08   3.841D-09    -6.79685       0.8173
2.404D 00  -5.570D-08  -5.934D-08   3.641D-09    -6.13556       0.8159
2.475D 00  -6.329D-08  -6.234D-08  -9.548D-10     1.53164       0.8142
2.558D 00  -6.779D-08  -6.579D-08  -1.994D-09     3.03097       0.8122
2.632D 00  -7.081D-08  -6.890D-08  -1.909D-09     2.77089       0.8103
2.703D 00  -7.420D-08  -7.188D-08  -2.318D-09     3.22441       0.8084
2.762D 00  -7.884D-08  -7.439D-08  -4.456D-09     5.99027       0.8067
2.865D 00  -8.232D-08  -7.871D-08  -3.616D-09     4.59368       0.8037
2.941D 00  -8.197D-08  -8.189D-08  -7.881D-11     0.09624       0.8014
3.021D 00  -8.317D-08  -8.524D-08   2.075D-09    -2.43414       0.7990
3.106D 00  -8.948D-08  -8.879D-08  -6.893D-10     0.77632       0.7963
3.205D 00  -9.404D-08  -9.296D-08  -1.072D-09     1.15284       0.7931
3.311D 00  -9.495D-08  -9.742D-08   2.466D-09    -2.53165       0.7896
3.390D 00  -1.011D-07  -1.007D-07  -3.572D-10     0.35470       0.7870
3.472D 00  -1.083D-07  -1.042D-07  -4.088D-09     3.92474       0.7842
3.610D 00  -1.115D-07  -1.100D-07  -1.561D-09     1.41983       0.7795
3.690D 00  -1.139D-07  -1.133D-07  -6.394D-10     0.56427       0.7766
3.788D 00  -1.212D-07  -1.174D-07  -3.808D-09     3.24330       0.7732
3.906D 00  -1.315D-07  -1.224D-07  -9.133D-09     7.46289       0.7689
4.032D 00  -1.332D-07  -1.277D-07  -5.557D-09     4.35298       0.7644
4.115D 00  -1.276D-07  -1.312D-07   3.572D-09    -2.72349       0.7613
4.219D 00  -1.336D-07  -1.355D-07   1.915D-09    -1.41271       0.7575
4.386D 00  -1.389D-07  -1.425D-07   3.635D-09    -2.55093       0.7513
4.545D 00  -1.441D-07  -1.492D-07   5.119D-09    -3.43120       0.7453
4.651D 00  -1.447D-07  -1.536D-07   8.907D-09    -5.79725       0.7413


  GOODNESS OF FIT:        GAUSS CRITERION,  OMEGA=  7.567D-18


 CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

      CONSTANT      VALUE        STD DEV   REL STD DEV(PPH)

         C(1)    4.1521D-08   1.3944D-09      3.3584

         C(2)   -4.1959D-08   4.9211D-10     -1.1728
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RH(III)--PERIODATE SYSTEM: 34.04  INCLUDES ALLOWANCE FOR INDUCTION PERIOD 6/6/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.      TIME      ABSORBANCE   DERIVATIVE      SLOPE        WEIGHT

  1     1.10417     0.97500     -0.35501     -0.38400     0.76923
  2     1.12500     0.97000     -0.39392     -0.24000     0.77046
  3     1.14583     0.95900     -0.43624     -0.52800     0.77311
  4     1.16667     0.95100     -0.46475     -0.38400     0.77499
  5     1.18750     0.94000     -0.50971     -0.52800     0.77752
  6     1.20833     0.93000     -0.53076     -0.48000     0.77976
  7     1.22917     0.91700     -0.54819     -0.62400     0.78258
  8     1.25000     0.90700     -0.58781     -0.48000     0.78468
  9     1.27083     0.89300     -0.63659     -0.67200     0.78754
 10     1.29167     0.88200     -0.68240     -0.52800     0.78970
 11     1.31250     0.86500     -0.71942     -0.81600     0.79291
 12     1.33333     0.85000     -0.73011     -0.72000     0.79561
 13     1.35417     0.83300     -0.74284     -0.81600     0.79852
 14     1.37500     0.82000     -0.74736     -0.62400     0.80065
 15     1.39583     0.80400     -0.75147     -0.76800     0.80313
 16     1.41667     0.79000     -0.75429     -0.67200     0.80520
 17     1.43750     0.77000     -0.75685     -0.96000     0.80796
 18     1.45833     0.75700     -0.74974     -0.62400     0.80965
 19     1.47917     0.74000     -0.72521     -0.81600     0.81171
 20     1.50000     0.72800     -0.71445     -0.57600     0.81308
 21     1.52083     0.71100     -0.68602     -0.81600     0.81487
 22     1.54167     0.69800     -0.66730     -0.62400     0.81614
 23     1.56250     0.68300     -0.61791     -0.72000     0.81749
 24     1.58333     0.67000     -0.59620     -0.62400     0.81855
 25     1.60417     0.66000     -0.58855     -0.48000     0.81931
 26     1.62500     0.64800     -0.60975     -0.57600     0.82014
 27     1.64583     0.63500     -0.62984     -0.62400     0.82094
 28     1.66667     0.62000     -0.63246     -0.72000     0.82174
 29     1.68750     0.60600     -0.61287     -0.67200     0.82236
 30     1.70833     0.59500     -0.57641     -0.52800     0.82276
 31     1.72917     0.58300     -0.55703     -0.57600     0.82310
 32     1.75000     0.57400     -0.54439     -0.43200     0.82330
 33     1.77083     0.56100     -0.52225     -0.62400     0.82349
 34     1.79167     0.54900     -0.50327     -0.57600     0.82355
 35     1.81250     0.53800     -0.49981     -0.52800     0.82352
 36     1.83333     0.53000     -0.49138     -0.38400     0.82343
 37     1.85417     0.52200     -0.47404     -0.38400     0.82330
 38     1.87500     0.50900     -0.48114     -0.62400     0.82297
 39     1.89583     0.49700     -0.49238     -0.57600     0.82254
 40     1.91667     0.49000     -0.47222     -0.33600     0.82223
 41     1.93750     0.48000     -0.44483     -0.48000     0.82171
 42     1.95833     0.47000     -0.42831     -0.48000     0.82109
 43     1.97917     0.46100     -0.45069     -0.43200     0.82045
 44     2.00000     0.45400     -0.45776     -0.33600     0.81990
 45     2.02083     0.44200     -0.43516     -0.57600     0.81881
 46     2.04166     0.43300     -0.41734     -0.43200     0.81789
 47     2.06250     0.42400     -0.39532     -0.43200     0.81688
 48     2.08333     0.41800     -0.38750     -0.28800     0.81614
 49     2.10416     0.41000     -0.36360     -0.38400     0.81508
 50     2.12500     0.40200     -0.36691     -0.38400     0.81394
 51     2.14583     0.39400     -0.35261     -0.38400     0.81270
 52     2.16666     0.38500     -0.34267     -0.43200     0.81118
 53     2.18750     0.38100     -0.33269     -0.19200     0.81047
 54     2.20833     0.37300     -0.34106     -0.38400     0.80896
 55     2.22916     0.36700     -0.35277     -0.28800     0.80775
 56     2.25000     0.35800     -0.35810     -0.43200     0.80582
 57     2.27083     0.35000     -0.35368     -0.38400     0.80396
 58     2.29166     0.34300     -0.33346     -0.33600     0.80223
 59     2.31250     0.33700     -0.32104     -0.28800     0.80065
 60     2.33333     0.33100     -0.31863     -0.28800     0.79899
 61     2.35416     0.32400     -0.32928     -0.33600     0.79695
 62     2.37500     0.31600     -0.33099     -0.38400     0.79445
 63     2.39583     0.31000     -0.32995     -0.28800     0.79246
 64     2.41666     0.30200     -0.30947     -0.38400     0.78965
 65     2.43750     0.29700     -0.29930     -0.24000     0.78778
 66     2.45833     0.29100     -0.29804     -0.28800     0.78543
 67     2.47916     0.28400     -0.29453     -0.33600     0.78254
 68     2.50000     0.27900     -0.28986     -0.24000     0.78035

VALUES OF OTHER INPUT PARAMETERS:

NUM=  78   KDROP=  0   TDELT=  2.08330-02   TSTART=  1.00000 00

CATIN=  2.24000-08   ASTART=  1.006   T1=  0.8050   T2=  1.4375
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MN(III)--PERIODATE SYSTEM: 34.04  INCLUDES ALLOWANCE FOR INDUCTION PERIOD 6/6/72


     X           Y(OBS)      Y(CALC)        DEV(Y)     % DEV(Y)     WEIGHT(Y)

1.026D 00   -2.029D-08   -2.288D-08    2.584D-09   -11.29536       0.7692
1.031D 00   -2.092D-08   -2.324D-08    2.315D-09    -9.96377       0.7705
1.043D 00   -2.143D-08   -2.405D-08    2.617D-09   -10.88099       0.7731
1.052D 00   -2.265D-08   -2.465D-08    1.999D-09    -8.10850       0.7750
1.064D 00   -2.310D-08   -2.550D-08    2.394D-09    -9.38822       0.7775
1.075D 00   -2.467D-08   -2.628D-08    1.613D-09    -6.13622       0.7798
1.091D 00   -2.642D-08   -2.733D-08    9.122D-10    -3.33795       0.7826
1.103D 00   -2.712D-08   -2.815D-08    1.039D-09    -3.68894       0.7847
1.120D 00   -2.744D-08   -2.934D-08    1.904D-09    -6.48889       0.7875
1.134D 00   -2.794D-08   -3.030D-08    2.364D-09    -7.80181       0.7897
1.156D 00   -2.882D-08   -3.183D-08    3.014D-09    -9.46960       0.7929
1.176D 00   -3.077D-08   -3.323D-08    2.457D-09    -7.39501       0.7956
1.200D 00   -3.268D-08   -3.488D-08    2.201D-09    -6.30919       0.7985
1.220D 00   -3.499D-08   -3.618D-08    1.194D-09    -3.29895       0.8006
1.244D 00   -3.739D-08   -3.785D-08    4.609D-10    -1.21770       0.8031
1.266D 00   -3.992D-08   -3.936D-08   -5.596D-10     1.42169       0.8052
1.299D 00   -4.254D-08   -4.162D-08   -9.238D-10     2.21960       0.8080
1.321D 00   -4.357D-08   -4.315D-08   -4.184D-10     0.96951       0.8096
1.351D 00   -4.569D-08   -4.524D-08   -4.524D-10     1.00003       0.8117
1.374D 00   -4.703D-08   -4.676D-08   -2.645D-10     0.56550       0.8131
1.406D 00   -4.966D-08   -4.902D-08   -6.396D-10     1.30478       0.8149
1.433D 00   -5.175D-08   -5.082D-08   -9.333D-10     1.83648       0.8161
1.464D 00   -5.664D-08   -5.298D-08   -3.665D-09     6.91785       0.8175
1.493D 00   -5.949D-08   -5.493D-08   -4.561D-09     8.30280       0.8186
1.515D 00   -6.105D-08   -5.648D-08   -4.574D-09     8.09805       0.8193
1.543D 00   -5.970D-08   -5.841D-08   -1.290D-09     2.20854       0.8201
1.575D 00   -5.853D-08   -6.058D-08    2.042D-09    -3.37029       0.8209
1.613D 00   -5.903D-08   -6.319D-08    4.162D-09    -6.58598       0.8217
1.650D 00   -6.168D-08   -6.575D-08    4.071D-09    -6.19247       0.8224
1.681D 00   -6.639D-08   -6.784D-08    1.455D-09    -2.14494       0.8228
1.715D 00   -6.954D-08   -7.022D-08    6.819D-10    -0.97115       0.8231
1.742D 00   -7.201D-08   -7.206D-08    5.722D-11    -0.07940       0.8233
1.783D 00   -7.595D-08   -7.484D-08   -1.118D-09     1.49419       0.8235
1.821D 00   -7.974D-08   -7.751D-08   -2.234D-09     2.88260       0.8236
1.859D 00   -8.123D-08   -8.007D-08   -1.163D-09     1.45283       0.8235
1.887D 00   -8.357D-08   -8.199D-08   -1.582D-09     1.92923       0.8234
1.916D 00   -8.762D-08   -8.398D-08   -3.637D-09     4.33101       0.8233
1.965D 00   -8.729D-08   -8.734D-08    4.393D-11    -0.05031       0.8230
2.012D 00   -8.625D-08   -9.059D-08    4.346D-09    -4.79743       0.8225
2.041D 00   -9.092D-08   -9.257D-08    1.648D-09    -1.77992       0.8222
2.083D 00   -9.757D-08   -9.549D-08   -2.080D-09     2.17821       0.8217
2.128D 00   -1.024D-07   -9.853D-08   -3.890D-09     3.94819       0.8211
2.169D 00   -9.837D-08   -1.014D-07    3.011D-09    -2.97034       0.8205
2.203D 00   -9.787D-08   -1.037D-07    5.809D-09    -5.60271       0.8199
2.262D 00   -1.040D-07   -1.078D-07    3.758D-09    -3.48714       0.8188
2.309D 00   -1.096D-07   -1.110D-07    1.427D-09    -1.28581       0.8179
2.358D 00   -1.169D-07   -1.144D-07   -2.493D-09     2.17936       0.8169
2.392D 00   -1.204D-07   -1.167D-07   -3.732D-09     3.19818       0.8161
2.439D 00   -1.296D-07   -1.199D-07   -9.726D-09     8.11191       0.8151
2.488D 00   -1.297D-07   -1.232D-07   -6.497D-09     5.27187       0.8139
2.538D 00   -1.363D-07   -1.267D-07   -9.615D-09     7.58887       0.8127
2.597D 00   -1.416D-07   -1.308D-07   -1.086D-08     8.30288       0.8112
2.625D 00   -1.473D-07   -1.326D-07   -1.464D-08    11.03384       0.8105
2.681D 00   -1.450D-07   -1.365D-07   -8.524D-09     6.24425       0.8090
2.725D 00   -1.415D-07   -1.395D-07   -2.023D-09     1.45020       0.8078
2.793D 00   -1.407D-07   -1.442D-07    3.480D-09    -2.41319       0.8058
2.857D 00   -1.438D-07   -1.486D-07    4.785D-09    -3.22006       0.8040
2.915D 00   -1.539D-07   -1.526D-07   -1.334D-09     0.87417       0.8022
2.967D 00   -1.613D-07   -1.562D-07   -5.175D-09     3.31369       0.8007
3.021D 00   -1.640D-07   -1.599D-07   -4.170D-09     2.60844       0.7990
3.086D 00   -1.601D-07   -1.643D-07    4.198D-09    -2.55443       0.7969
3.165D 00   -1.607D-07   -1.697D-07    8.982D-09    -5.29276       0.7945
3.226D 00   -1.627D-07   -1.739D-07    1.126D-08    -6.47674       0.7925
3.311D 00   -1.749D-07   -1.798D-07    4.861D-09    -2.70378       0.7896
3.367D 00   -1.824D-07   -1.836D-07    1.183D-09    -0.64455       0.7878
3.436D 00   -1.848D-07   -1.884D-07    3.613D-09    -1.91802       0.7854
3.521D 00   -1.886D-07   -1.942D-07    5.638D-09    -2.90342       0.7825
3.584D 00   -1.932D-07   -1.985D-07    5.321D-09    -2.68052       0.7804


    GOODNESS OF FIT:        GAUSS CRITERION,  OMEGA=  1.649D-17


   CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

        CONSTANT      VALUE        STD DEV    REL STD DEV(PPH)

          C(1)     4.7534D-08   1.5604D-09      3.2827

          C(2)    -6.8649D-08   7.3724D-10     -1.0739
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MN(III)--PERIODATE SYSTEM:  35.02      INDUCTION PERIOD CONSIDERED        6/7/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.      TIME      ABSORBANCE   DERIVATIVE     SLOPE        WEIGHT

  1     1.31217     0.29800     -0.16860     -0.09600     0.78816
  2     1.33300     0.29200     -0.19968     -0.28800     0.78583
  3     1.35383     0.28800     -0.22656     -0.19200     0.78421
  4     1.37467     0.28400     -0.27071     -0.19200     0.78254
  5     1.39550     0.27700     -0.30135     -0.33600     0.77945
  6     1.41633     0.27200     -0.31568     -0.24000     0.77713
  7     1.43717     0.26400     -0.34313     -0.38400     0.77318
  8     1.45800     0.25500     -0.34839     -0.43200     0.76838
  9     1.47883     0.25000     -0.35457     -0.24000     0.76554
 10     1.49967     0.24300     -0.36388     -0.33600     0.76133
 11     1.52050     0.23400     -0.36433     -0.43200     0.75548
 12     1.54133     0.22700     -0.37647     -0.33600     0.75056
 13     1.56217     0.21800     -0.38496     -0.43200     0.74370
 14     1.58300     0.21100     -0.38741     -0.33600     0.73792
 15     1.60383     0.20300     -0.38444     -0.38400     0.73077
 16     1.62467     0.19500     -0.38517     -0.38400     0.72296
 17     1.64550     0.18700     -0.35730     -0.38400     0.71443
 18     1.66633     0.17800     -0.34891     -0.43200     0.70384
 19     1.68717     0.17300     -0.32332     -0.24000     0.69745
 20     1.70800     0.16600     -0.30913     -0.33600     0.68780
 21     1.72883     0.16100     -0.29741     -0.24000     0.68037
 22     1.74967     0.15200     -0.29202     -0.43200     0.66569
 23     1.77050     0.14800     -0.29827     -0.19200     0.65857
 24     1.79133     0.14100     -0.28929     -0.33600     0.64508
 25     1.81217     0.13600     -0.26842     -0.24000     0.63456
 26     1.83300     0.13000     -0.24952     -0.28800     0.62083
 27     1.85383     0.12400     -0.24650     -0.28800     0.60572
 28     1.87467     0.12000     -0.20900     -0.19200     0.59478
 29     1.89550     0.11700     -0.19454     -0.14400     0.58608
 30     1.91633     0.11100     -0.17973     -0.28800     0.56722
 31     1.93717     0.10800     -0.17791     -0.14400     0.55698
 32     1.95800     0.10600     -0.18268     -0.09600     0.54983
 33     1.97883     0.10000     -0.18854     -0.28800     0.52662
 34     1.99967     0.09700     -0.18080     -0.14400     0.51392
 35     2.02050     0.09300     -0.19085     -0.19200     0.49569

VALUES OF OTHER INPUT PARAMETERS:

NUM=  45   KDROP=  0   TDELT=  2.0833D-02   TSTART=  1.2080D 00

CATIN=  2.2400D-08   ASTART=  0.307   T1=  1.1300   T2=  1.5830
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MN(II)--PERIODATE SYSTEM:  35.02      INDUCTION PERIOD CONSIDERED        6/7/72

     X           Y(OBS)       Y(CALC)       DEV(Y)       % DEV(Y)     WEIGHT(Y)

3.356D 00   -3.401D-08   -3.808D-08    4.068D-09    -10.68356       0.7882
3.425D 00   -3.566D-08   -4.022D-08    4.561D-09    -11.34030       0.7858
3.472D 00   -3.821D-08   -4.170D-08    3.488D-09     -8.36421       0.7842
3.521D 00   -3.821D-08   -4.322D-08    5.009D-09    -11.58919       0.7825
3.610D 00   -4.042D-08   -4.598D-08    5.563D-09    -12.09873       0.7795
3.676D 00   -4.488D-08   -4.804D-08    3.167D-09     -6.59166       0.7771
3.788D 00   -4.751D-08   -5.150D-08    3.991D-09     -7.74937       0.7732
3.922D 00   -5.336D-08   -5.566D-08    2.298D-09     -4.12962       0.7684
4.000D 00   -5.930D-08   -5.809D-08   -1.206D-09      2.07677       0.7655
4.115D 00   -6.489D-08   -6.167D-08   -3.219D-09      5.21889       0.7613
4.274D 00   -7.232D-08   -6.659D-08   -5.733D-09      8.60965       0.7555
4.405D 00   -7.766D-08   -7.068D-08   -6.975D-09      9.86719       0.7506
4.587D 00   -8.383D-08   -7.633D-08   -7.499D-09      9.82399       0.7437
4.739D 00   -9.153D-08   -8.106D-08   -1.047D-08     12.91117       0.7379
4.926D 00   -9.345D-08   -8.686D-08   -6.586D-09      7.58195       0.7308
5.128D 00   -9.449D-08   -9.314D-08   -1.343D-09      1.44166       0.7230
5.348D 00   -1.032D-07   -9.996D-08   -3.204D-09      3.20506       0.7144
5.618D 00   -1.070D-07   -1.084D-07    1.380D-09     -1.27356       0.7038
5.780D 00   -1.169D-07   -1.134D-07   -3.488D-09      3.07563       0.6974
6.024D 00   -1.238D-07   -1.210D-07   -2.791D-09      2.30739       0.6878
6.211D 00   -1.302D-07   -1.268D-07   -3.426D-09      2.70219       0.6804
6.579D 00   -1.342D-07   -1.382D-07    3.998D-09     -2.89243       0.6657
6.757D 00   -1.330D-07   -1.437D-07    1.077D-08     -7.49145       0.6586
7.092D 00   -1.387D-07   -1.542D-07    1.545D-08    -10.02118       0.6451
7.353D 00   -1.512D-07   -1.623D-07    1.103D-08     -6.79576       0.6346
7.692D 00   -1.646D-07   -1.728D-07    8.244D-09     -4.77089       0.6208
8.065D 00   -1.685D-07   -1.844D-07    1.590D-08     -8.62272       0.6057
8.333D 00   -2.009D-07   -1.927D-07   -8.213D-09      4.26186       0.5948
8.547D 00   -2.183D-07   -1.993D-07   -1.891D-08      9.48612       0.5861
9.009D 00   -2.388D-07   -2.137D-07   -2.514D-08     11.76199       0.5672
9.259D 00   -2.439D-07   -2.215D-07   -2.243D-08     10.12540       0.5570
9.434D 00   -2.401D-07   -2.269D-07   -1.319D-08      5.81361       0.5498
1.000D 01   -2.351D-07   -2.445D-07    9.386D-09     -3.83913       0.5266
1.031D 01   -2.477D-07   -2.541D-07    6.350D-09     -2.49899       0.5139
1.075D 01   -2.371D-07   -2.679D-07    3.073D-08    -11.47081       0.4957

   GOODNESS OF FIT:        GAUSS CRITERION,  OMEGA=  7.260D-17

  CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

      CONSTANT      VALUE         STD DEV    REL STD DEV(PPH)

         C(1)     6.6166D-08    5.0129D-09      7.5763

         C(2)    -3.1065D-08    8.1099D-10     -2.6106
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MN(II)--PERIODATE SYSTEM:  35.03      INDUCTION PERIOD CONSIDERED          6/7/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.      TIME      ABSORBANCE   DERIVATIVE     SLOPE        WEIGHT

  1     1.39617     0.49200     -0.06777     -0.04800     0.82233
  2     1.41700     0.49000     -0.10748     -0.09600     0.82223
  3     1.43783     0.48800     -0.15101     -0.09600     0.82214
  4     1.45867     0.48400     -0.19954     -0.19200     0.82193
  5     1.47950     0.48000     -0.23027     -0.19200     0.82171
  6     1.50033     0.47300     -0.26460     -0.33600     0.82129
  7     1.52117     0.46800     -0.29785     -0.24000     0.82096
  8     1.54200     0.46200     -0.32305     -0.28800     0.82053
  9     1.56283     0.45600     -0.35769     -0.28800     0.82006
 10     1.58367     0.44600     -0.40402     -0.48000     0.81919
 11     1.60450     0.43800     -0.44649     -0.38400     0.81842
 12     1.62533     0.42900     -0.47680     -0.43200     0.81745
 13     1.64617     0.41800     -0.48272     -0.52800     0.81614
 14     1.66700     0.40700     -0.50651     -0.52800     0.81466
 15     1.68783     0.39800     -0.53149     -0.43200     0.81333
 16     1.70867     0.38600     -0.54572     -0.57600     0.81136
 17     1.72950     0.37600     -0.55062     -0.48000     0.80954
 18     1.75033     0.36100     -0.55562     -0.72000     0.80648
 19     1.77117     0.35200     -0.54792     -0.43200     0.80444
 20     1.79200     0.34000     -0.52923     -0.57600     0.80145
 21     1.81283     0.33000     -0.50927     -0.48000     0.79871
 22     1.83367     0.31900     -0.47848     -0.52800     0.79541
 23     1.85450     0.30900     -0.47378     -0.48000     0.79212
 24     1.87533     0.29900     -0.44792     -0.48000     0.78854
 25     1.89617     0.29100     -0.43313     -0.38400     0.78543
 26     1.91700     0.28200     -0.43555     -0.43200     0.78167
 27     1.93783     0.27200     -0.43217     -0.48000     0.77713
 28     1.95867     0.26400     -0.41933     -0.38400     0.77318
 29     1.97950     0.25500     -0.40203     -0.43200     0.76838
 30     2.00033     0.24500     -0.38672     -0.48000     0.76256
 31     2.02117     0.24000     -0.37120     -0.24000     0.75943
 32     2.04200     0.23200     -0.35596     -0.38400     0.75411
 33     2.06283     0.22400     -0.33909     -0.38400     0.74834
 34     2.08367     0.21600     -0.30994     -0.38400     0.74209
 35     2.10450     0.21100     -0.30015     -0.24000     0.73792
 36     2.12533     0.20500     -0.27249     -0.28800     0.73261
 37     2.14617     0.19900     -0.27925     -0.26800     0.72695
 38     2.16700     0.19500     -0.30068     -0.19200     0.72296
 39     2.18783     0.18600     -0.31071     -0.43200     0.71331
 40     2.20867     0.18100     -0.30832     -0.24000     0.70750
 41     2.22950     0.17300     -0.28936     -0.38400     0.69745
 42     2.25033     0.16800     -0.25599     -0.24000     0.69065
 43     2.27117     0.16400     -0.22708     -0.19200     0.68489
 44     2.29200     0.15800     -0.22284     -0.28800     0.67567
 45     2.31283     0.15500     -0.21628     -0.14400     0.67078
 46     2.33366     0.15000     -0.23133     -0.24000     0.66218
 47     2.35450     0.14400     -0.23579     -0.28800     0.65103

VALUES OF OTHER INPUT PARAMETERS:

NUM=  57   KDROP=  0   TDELT=  2.0833D-02   TSTART=  1.29200 00

CATIN=  2.2400D-08   ASTART=  0.497   T1=  1.2500   T2=  1.7503
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MN(II)--PERIODATE SYSTEM:  35.03      INDUCTION PERIOD CONSIDERED          6/7/72

    X          Y(OBS)      Y(CALC)      DEV(Y)       % DEV(Y)     WEIGHT(Y)

2.033D 00  -4.938D-08  -3.679D-08  -1.258D-08   34.19744     0.8223
2.041D 00  -4.064D-08  -3.714D-08  -3.502D-09    9.43084     0.8222
2.049D 00  -3.659D-08  -3.749D-08   8.932D-10   -2.38291     0.8221
2.066D 00  -3.418D-08  -3.819D-08   4.011D-09  -10.50395     0.8219
2.083D 00  -3.582D-08  -3.890D-08   3.076D-09   -7.90625     0.8217
2.114D 00  -3.709D-08  -4.018D-08   3.084D-09   -7.67681     0.8213
2.137D 00  -3.867D-08  -4.111D-08   2.448D-09   -5.95492     0.8210
2.165D 00  -4.134D-08  -4.226D-08   9.267D-10   -2.19267     0.8205
2.193D 00  -4.285D-08  -4.344D-08   5.928D-10   -1.36440     0.8201
2.242D 00  -4.316D-08  -4.548D-08   2.323D-09   -5.10826     0.8192
2.283D 00  -4.408D-08  -4.718D-08   3.097D-09   -6.56399     0.8184
2.331D 00  -4.627D-08  -4.916D-08   2.890D-09   -5.87808     0.8175
2.392D 00  -5.092D-08  -5.171D-08   7.849D-10   -1.51793     0.8161
2.457D 00  -5.377D-08  -5.439D-08   6.174D-10   -1.13524     0.8147
2.513D 00  -5.649D-08  -5.669D-08   1.991D-10   -0.35120     0.8133
2.591D 00  -6.038D-08  -5.993D-08  -4.512D-10    0.75285     0.8114
2.660D 00  -6.540D-08  -6.278D-08  -2.617D-09    4.16894     0.8095
2.770D 00  -7.057D-08  -6.736D-08  -3.203D-09    4.75547     0.8065
2.841D 00  -7.241D-08  -7.030D-08  -2.112D-09    3.00392     0.8044
2.941D 00  -7.585D-08  -7.445D-08  -1.395D-09    1.87301     0.8014
3.030D 00  -7.974D-08  -7.815D-08  -1.590D-09    2.03493     0.7987
3.135D 00  -8.584D-08  -8.248D-08  -3.366D-09    4.08066     0.7954
3.236D 00  -8.768D-08  -8.668D-08  -9.976D-10    1.15086     0.7921
3.344D 00  -9.378D-08  -9.117D-08  -2.617D-09    2.87028     0.7885
3.436D 00  -9.806D-08  -9.498D-08  -3.086D-09    3.24879     0.7854
3.546D 00  -9.859D-08  -9.952D-08   9.340D-10   -0.93850     0.7817
3.676D 00  -1.004D-07  -1.049D-07   4.485D-09   -4.27459     0.7771
3.788D 00  -1.046D-07  -1.095D-07   4.914D-09   -4.48600     0.7732
3.922D 00  -1.103D-07  -1.151D-07   4.793D-09   -4.16449     0.7684
4.082D 00  -1.159D-07  -1.217D-07   5.853D-09   -4.80889     0.7626
4.167D 00  -1.220D-07  -1.252D-07   3.274D-09   -2.61452     0.7594
4.310D 00  -1.285D-07  -1.312D-07   2.698D-09   -2.05628     0.7541
4.464D 00  -1.363D-07  -1.376D-07   1.306D-09   -0.94929     0.7483
4.630D 00  -1.506D-07  -1.444D-07  -6.162D-09    4.26654     0.7421
4.739D 00  -1.571D-07  -1.490D-07  -8.082D-09    5.42517     0.7379
4.878D 00  -1.747D-07  -1.547D-07  -1.999D-08   12.91685     0.7326
5.025D 00  -1.722D-07  -1.608D-07  -1.134D-08    7.04997     0.7270
5.128D 00  -1.614D-07  -1.651D-07   3.656D-09   -2.21426     0.7230
5.376D 00  -1.577D-07  -1.754D-07   1.765D-08  -10.06417     0.7133
5.525D 00  -1.605D-07  -1.815D-07   2.107D-08  -11.60454     0.7075
5.780D 00  -1.726D-07  -1.921D-07   1.953D-08  -10.16530     0.6974
5.952D 00  -1.969D-07  -1.992D-07   2.338D-09   -1.17325     0.6906
6.098D 00  -2.240D-07  -2.053D-07  -1.877D-08    9.14587     0.6849
6.329D 00  -2.304D-07  -2.149D-07  -1.553D-08    7.22641     0.6757
6.452D 00  -2.395D-07  -2.199D-07  -1.960D-08    8.91156     0.6708
6.667D 00  -2.260D-07  -2.289D-07   2.878D-09   -1.25776     0.6622
6.944D 00  -2.237D-07  -2.404D-07   1.668D-08   -6.94064     0.6510

   GOODNESS OF FIT:       GAUSS CRITERION,  OMEGA=  5.466D-17

  CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

      CONSTANT     VALUE        STD DEV    REL STD DEV(PPH)

        C(1)     4.7441D-08   3.3117D-09      6.9808

        C(2)    -4.1444D-08   8.5068D-10     -2.0526
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MN(III)--PERIODATE SYSTEM:  35.04      INDUCTION PERIOD CONSIDERED           6/7/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.      TIME      ABSORBANCE   DERIVATIVE      SLOPE        WEIGHT

  1    1.31217      0.66000     -0.09883     -0.09600      0.81931
  2    1.33300      0.65800     -0.14971     -0.09600      0.81945
  3    1.35383      0.65500     -0.20658     -0.14400      0.81966
  4    1.37467      0.64800     -0.27149     -0.33600      0.82014
  5    1.39550      0.64400     -0.32360     -0.19200      0.82039
  6    1.41633      0.63500     -0.37882     -0.43200      0.82094
  7    1.43717      0.62700     -0.42108     -0.38400      0.82138
  8    1.45800      0.61800     -0.44228     -0.43200      0.82183
  9    1.47883      0.60900     -0.48877     -0.43200      0.82223
 10    1.49967      0.59700     -0.52084     -0.57600      0.82269
 11    1.52050      0.58700     -0.57105     -0.48000      0.82300
 12    1.54133      0.57600     -0.61219     -0.52800      0.82326
 13    1.56217      0.56000     -0.63291     -0.76800      0.82350
 14    1.58300      0.54800     -0.63539     -0.57600      0.82355
 15    1.60383      0.53400     -0.63119     -0.67200      0.82348
 16    1.62467      0.52100     -0.64928     -0.62400      0.82328
 17    1.64550      0.50900     -0.66165     -0.57600      0.82297
 18    1.66633      0.49500     -0.69021     -0.67200      0.82246
 19    1.68717      0.48000     -0.69135     -0.72000      0.82171
 20    1.70800      0.46200     -0.68040     -0.86400      0.82053
 21    1.72883      0.45200     -0.65097     -0.48000      0.81973
 22    1.74967      0.43800     -0.60244     -0.67200      0.81842
 23    1.77050      0.42600     -0.57169     -0.57600      0.81711
 24    1.79133      0.41400     -0.58123     -0.57600      0.81562
 25    1.81217      0.40200     -0.57906     -0.57600      0.81394
 26    1.83300      0.39100     -0.55217     -0.52800      0.81221
 27    1.85383      0.37800     -0.52701     -0.62400      0.80992
 28    1.87467      0.36600     -0.48706     -0.57600      0.80755
 29    1.89550      0.36000     -0.47263     -0.28800      0.80626
 30    1.91633      0.34800     -0.46684     -0.57600      0.80348
 31    1.93717      0.34000     -0.45100     -0.38400      0.80145
 32    1.95800      0.33000     -0.45765     -0.48000      0.79871
 33    1.97883      0.31800     -0.44875     -0.57600      0.79509
 34    1.99967      0.31100     -0.40013     -0.33600      0.79280
 35    2.02050      0.30400     -0.38766     -0.33600      0.79037
 36    2.04133      0.29400     -0.38401     -0.48000      0.78662
 37    2.06217      0.28600     -0.35667     -0.28800      0.78421
 38    2.08300      0.28100     -0.37618     -0.33600      0.78124
 39    2.10383      0.27100     -0.38349     -0.48000      0.77665
 40    2.12467      0.26500     -0.37090     -0.28800      0.77369
 41    2.14550      0.25700     -0.35108     -0.38400      0.76948
 42    2.16633      0.24800     -0.33517     -0.43200      0.76436
 43    2.18717      0.24200     -0.31237     -0.28800      0.76070
 44    2.20800      0.23800     -0.30146     -0.19200      0.75814
 45    2.22883      0.23100     -0.29133     -0.33600      0.75341
 46    2.24966      0.22200     -0.29954     -0.43200      0.74683
 47    2.27050      0.21900     -0.29910     -0.14400      0.74450
 48    2.29133      0.21200     -0.29031     -0.33600      0.73677
 49    2.31216      0.20500     -0.26574     -0.33600      0.73261
 50    2.33300      0.20000     -0.26259     -0.24000      0.72792
 51    2.35383      0.19600     -0.25742     -0.19200      0.72398
 52    2.37466      0.18900     -0.24443     -0.33600      0.71664
 53    2.39550      0.18500     -0.24896     -0.19200      0.71218

VALUES OF OTHER INPUT PARAMETERS:

NUM=  63   KDROP=  0   TDELT=  2.0833D-02   TSTART=  1.2080D 00

CATIN=  2.2400D-08   ASTART=  0.665   T1=  1.1670   T2=  1.6872
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MN(II)--PERIODATE SYSTEM:  35.04      INDUCTION PERIOD CONSIDERED          6/7/72

     X           Y(OBS)       Y(CALC)       DEV(Y)      % DEV(Y)    WEIGHT(Y)

1.515D 00   -2.978D-08   -2.332D-08   -6.465D-09    27.72590       0.8193
1.520D 00   -2.571D-08   -2.355D-08   -2.162D-09     9.18331       0.8195
1.527D 00   -2.360D-08   -2.390D-08    2.945D-10    -1.23244       0.8197
1.543D 00   -2.219D-08   -2.472D-08    2.534D-09   -10.25084       0.8201
1.553D 00   -2.254D-08   -2.520D-08    2.665D-09   -10.57448       0.8204
1.575D 00   -2.292D-08   -2.630D-08    3.381D-09   -12.85474       0.8209
1.595D 00   -2.421D-08   -2.731D-08    3.098D-09   -11.34399       0.8214
1.618D 00   -2.674D-08   -2.847D-08    1.729D-09    -6.07218       0.8218
1.642D 00   -2.779D-08   -2.967D-08    1.881D-09    -6.33926       0.8222
1.675D 00   -2.968D-08   -3.132D-08    1.644D-09    -5.24808       0.8227
1.704D 00   -3.057D-08   -3.275D-08    2.185D-09    -6.67293       0.8230
1.736D 00   -3.197D-08   -3.438D-08    2.409D-09    -7.00582       0.8233
1.786D 00   -3.446D-08   -3.686D-08    2.401D-09    -6.51236       0.8235
1.825D 00   -3.804D-08   -3.882D-08    7.780D-10    -2.00403       0.8236
1.873D 00   -4.223D-08   -4.122D-08   -1.011D-09     2.45385       0.8235
1.919D 00   -4.506D-08   -4.356D-08   -1.504D-09     3.45409       0.8233
1.965D 00   -4.833D-08   -4.582D-08   -2.513D-09     5.48546       0.8230
2.020D 00   -5.046D-08   -4.860D-08   -1.854D-09     3.81472       0.8225
2.083D 00   -5.466D-08   -5.176D-08   -2.901D-09     5.60508       0.8217
2.165D 00   -5.623D-08   -5.583D-08   -4.029D-10     0.72164       0.8205
2.212D 00   -5.949D-08   -5.822D-08   -1.265D-09     2.17240       0.8197
2.283D 00   -6.506D-08   -6.177D-08   -3.290D-09     5.32735       0.8184
2.347D 00   -6.937D-08   -6.499D-08   -4.386D-09     6.74937       0.8171
2.415D 00   -6.904D-08   -6.839D-08   -6.440D-10     0.94160       0.8156
2.488D 00   -7.010D-08   -7.200D-08    1.901D-09    -2.64031       0.8139
2.558D 00   -7.436D-08   -7.551D-08    1.146D-09    -1.51752       0.8122
2.646D 00   -7.879D-08   -7.991D-08    1.115D-09    -1.39482       0.8099
2.732D 00   -8.622D-08   -8.425D-08   -1.964D-09     2.33159       0.8075
2.778D 00   -8.984D-08   -8.653D-08   -3.303D-09     3.81722       0.8063
2.874D 00   -9.195D-08   -9.133D-08   -6.231D-10     0.68232       0.8035
2.941D 00   -9.621D-08   -9.471D-08   -1.501D-09     1.58436       0.8014
3.030D 00   -9.584D-08   -9.917D-08    3.340D-09    -3.36738       0.7987
3.145D 00   -9.878D-08   -1.049D-07    6.123D-09    -5.83714       0.7951
3.215D 00   -1.119D-07   -1.084D-07   -3.501D-09     3.22811       0.7928
3.289D 00   -1.168D-07   -1.122D-07   -4.600D-09     4.10180       0.7904
3.401D 00   -1.256D-07   -1.178D-07   -7.864D-09     6.67881       0.7866
3.472D 00   -1.295D-07   -1.213D-07   -8.209D-09     6.76787       0.7842
3.559D 00   -1.240D-07   -1.256D-07    1.596D-09    -1.27041       0.7812
3.690D 00   -1.229D-07   -1.322D-07    9.318D-09    -7.04820       0.7766
3.774D 00   -1.283D-07   -1.364D-07    8.072D-09    -5.91867       0.7737
3.891D 00   -1.369D-07   -1.423D-07    5.379D-09    -3.78094       0.7695
4.032D 00   -1.448D-07   -1.493D-07    4.560D-09    -3.05339       0.7644
4.132D 00   -1.568D-07   -1.543D-07   -2.495D-09     1.61639       0.7607
4.202D 00   -1.641D-07   -1.578D-07   -6.241D-09     3.95464       0.7581
4.329D 00   -1.714D-07   -1.642D-07   -7.176D-09     4.37048       0.7534
4.505D 00   -1.682D-07   -1.730D-07    4.752D-09    -2.74719       0.7468
4.566D 00   -1.700D-07   -1.761D-07    6.030D-09    -3.42448       0.7445
4.717D 00   -1.766D-07   -1.836D-07    6.826D-09    -3.71752       0.7388
4.878D 00   -1.949D-07   -1.917D-07   -3.211D-09     1.67516       0.7326
5.000D 00   -1.990D-07   -1.978D-07   -1.222D-09     0.61761       0.7279
5.102D 00   -2.048D-07   -2.029D-07   -1.926D-09     0.94940       0.7240
5.291D 00   -2.176D-07   -2.124D-07   -5.259D-09     2.47631       0.7166
5.405D 00   -2.155D-07   -2.181D-07    2.555D-09    -1.17176       0.7122


   GOODNESS OF FIT:       GAUSS CRITERION,  OMEGA=  1.300D-17


  CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :


      CONSTANT     VALUE        STD DEV    REL STD DEV(PPH)

        C(1)     5.2542D-08   1.4770D-09       2.8112

        C(2)    -5.0066D-08   4.7978D-10      -0.9583
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MN(II)--PERIODATE SYSTEM:  35.05      INDUCTION PERIOD CONSIDERED        6/7/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.       TIME      ABSORBANCE   DERIVATIVE      SLOPE        WEIGHT

  1     1.43717      0.82700     -0.36052     -0.36400      0.79952
  2     1.45800      0.82200     -0.41272     -0.24000      0.80033
  3     1.47883      0.81200     -0.45698     -0.48000      0.80191
  4     1.49967      0.79900     -0.49639     -0.62400      0.80388
  5     1.52050      0.79200     -0.54587     -0.33600      0.80491
  6     1.54133      0.78000     -0.59933     -0.57600      0.80661
  7     1.56217      0.76500     -0.60560     -0.72000      0.80862
  8     1.58300      0.75300     -0.64412     -0.57600      0.81015
  9     1.60383      0.73900     -0.68870     -0.67200      0.81183
 10     1.62467      0.72400     -0.71973     -0.72000      0.81351
 11     1.64550      0.71200     -0.75589     -0.57600      0.81477
 12     1.66633      0.69200     -0.79961     -0.96000      0.81670
 13     1.68717      0.67600     -0.82293     -0.76800      0.81807
 14     1.70800      0.65800     -0.82230     -0.86400      0.81945
 15     1.72883      0.64300     -0.80070     -0.72000      0.82046
 16     1.74967      0.62500     -0.76534     -0.86400      0.82149
 17     1.77050      0.60900     -0.77710     -0.76800      0.82223
 18     1.79133      0.59500     -0.74025     -0.67200      0.82276
 19     1.81217      0.57900     -0.71871     -0.76800      0.82320
 20     1.83300      0.56300     -0.68940     -0.76800      0.82347
 21     1.85383      0.54800     -0.66787     -0.72000      0.82355
 22     1.87467      0.53900     -0.64603     -0.43200      0.82352
 23     1.89550      0.52200     -0.62284     -0.81600      0.82330
 24     1.91633      0.51000     -0.60270     -0.57600      0.82300
 25     1.93717      0.49800     -0.58245     -0.57600      0.82258
 26     1.95800      0.48500     -0.57326     -0.62400      0.82198
 27     1.97883      0.47400     -0.54521     -0.52800      0.82135
 28     1.99967      0.46400     -0.54439     -0.48000      0.82068
 29     2.02050      0.45200     -0.53126     -0.57600      0.81973
 30     2.04133      0.43900     -0.52315     -0.62400      0.81852
 31     2.06217      0.43000     -0.51309     -0.43200      0.81757
 32     2.08300      0.42000     -0.49525     -0.48000      0.81639
 33     2.10383      0.40900     -0.47774     -0.52800      0.81494
 34     2.12467      0.39900     -0.46411     -0.48000      0.81348
 35     2.14550      0.39000     -0.46434     -0.43200      0.81204
 36     2.16633      0.38000     -0.44737     -0.48000      0.81029
 37     2.18717      0.37100     -0.42349     -0.43200      0.80857
 38     2.20800      0.36300     -0.41350     -0.38400      0.80691
 39     2.22883      0.35300     -0.39097     -0.48000      0.80467
 40     2.24967      0.34600     -0.37256     -0.33600      0.80298
 41     2.27050      0.33900     -0.36993     -0.33600      0.80119
 42     2.29133      0.33000     -0.36948     -0.43200      0.79871
 43     2.31217      0.32400     -0.36035     -0.28800      0.79695
 44     2.33300      0.31500     -0.37870     -0.43200      0.79413
 45     2.35383      0.30700     -0.37456     -0.38400      0.79143
 46     2.37466      0.30000     -0.36878     -0.33600      0.78891
 47     2.39550      0.29300     -0.37196     -0.33600      0.78623
 48     2.41633      0.28300     -0.35241     -0.48000      0.78211
 49     2.43716      0.27800     -0.33703     -0.24000      0.77990
 50     2.45800      0.27000     -0.33303     -0.38400      0.77617
 51     2.47883      0.26300     -0.31878     -0.33600      0.77267
 52     2.49966      0.25800     -0.31125     -0.24000      0.77003
 53     2.52050      0.25100     -0.30956     -0.33600      0.76612
 54     2.54133      0.24300     -0.27175     -0.38400      0.76133
 55     2.56216      0.23900     -0.25553     -0.19200      0.75879

VALUES OF OTHER INPUT PARAMETERS:

NUM=  65   KUROP=  0   TOELT=  2.0833D-02   TSTART=  1.3330D 00

CATIN=  2.2400D-08   ASTART=  0.846   T1=  1.1910   T2=  1.6872
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MN(II)--PERIODATE SYSTEM:  35.05      INDUCTION PERIOD CONSIDERED        6/7/72

      X          Y(OBS)      Y(CALC)       DEV(Y)     % DEV(Y)    WEIGHT(Y)

1.209D 00  -2.580D-08  -2.759D-08   1.784D-09   -6.46722      0.7995
1.217D 00  -2.652D-08  -2.802D-08   1.500D-09   -5.35250      0.8003
1.232D 00  -2.783D-08  -2.889D-08   1.058D-09   -3.66254      0.8019
1.252D 00  -2.946D-08  -3.006D-08   5.926D-10   -1.97155      0.8039
1.263D 00  -3.053D-08  -3.070D-08   1.694D-10   -0.55165      0.8049
1.282D 00  -3.144D-08  -3.183D-08   3.971D-10   -1.24727      0.8066
1.307D 00  -3.492D-08  -3.330D-08  -1.622D-09    4.87145      0.8086
1.328D 00  -3.662D-08  -3.451D-08  -2.109D-09    6.11041      0.8101
1.353D 00  -3.799D-08  -3.598D-08  -2.009D-09    5.58489      0.8118
1.381D 00  -4.011D-08  -3.761D-08  -2.499D-09    6.64357      0.8135
1.404D 00  -4.195D-08  -3.897D-08  -2.981D-09    7.64939      0.8148
1.445D 00  -4.338D-08  -4.134D-08  -2.040D-09    4.93554      0.8167
1.479D 00  -4.592D-08  -4.333D-08  -2.593D-09    5.98411      0.8181
1.520D 00  -4.653D-08  -4.569D-08  -8.372D-10    1.83224      0.8195
1.555D 00  -4.836D-08  -4.776D-08  -6.083D-10    1.27367      0.8205
1.600D 00  -5.121D-08  -5.037D-08  -8.416D-10    1.67086      0.8215
1.642D 00  -5.103D-08  -5.282D-08   1.783D-09   -3.37566      0.8222
1.681D 00  -5.421D-08  -5.507D-08   8.642D-10   -1.56922      0.8228
1.727D 00  -5.648D-08  -5.778D-08   1.297D-09   -2.24455      0.8232
1.776D 00  -5.956D-08  -6.064D-08   1.080D-09   -1.78112      0.8235
1.825D 00  -6.218D-08  -6.347D-08   1.295D-09   -2.04082      0.8236
1.855D 00  -6.500D-08  -6.525D-08   2.474D-10   -0.37917      0.8235
1.916D 00  -6.817D-08  -6.877D-08   6.000D-10   -0.87253      0.8233
1.961D 00  -7.122D-08  -7.140D-08   1.752D-10   -0.24540      0.8230
2.008D 00  -7.450D-08  -7.415D-08  -3.484D-10    0.46979      0.8226
2.062D 00  -7.651D-08  -7.729D-08   7.801D-10   -1.00939      0.8220
2.110D 00  -8.130D-08  -8.008D-08  -1.222D-09    1.52657      0.8214
2.155D 00  -8.228D-08  -8.273D-08   4.481D-10   -0.54161      0.8207
2.212D 00  -8.519D-08  -8.606D-08   8.715D-10   -1.01267      0.8197
2.278D 00  -8.740D-08  -8.988D-08   2.477D-09   -2.75622      0.8185
2.326D 00  -9.003D-08  -9.266D-08   2.633D-09   -2.84161      0.8176
2.381D 00  -9.421D-08  -9.589D-08   1.676D-09   -1.74777      0.8164
2.445D 00  -9.864D-08  -9.962D-08   9.785D-10   -0.98225      0.8149
2.506D 00  -1.025D-07  -1.032D-07   6.476D-10   -0.62753      0.8135
2.564D 00  -1.035D-07  -1.066D-07   3.063D-09   -2.87454      0.8120
2.632D 00  -1.085D-07  -1.105D-07   2.027D-09   -1.83459      0.8103
2.695D 00  -1.157D-07  -1.142D-07  -1.470D-09    1.28691      0.8086
2.755D 00  -1.196D-07  -1.177D-07  -1.930D-09    1.63983      0.8069
2.833D 00  -1.277D-07  -1.222D-07  -5.466D-09    4.47198      0.8047
2.899D 00  -1.353D-07  -1.256D-07  -9.690D-09    7.71661      0.8030
2.950D 00  -1.375D-07  -1.290D-07  -8.434D-09    6.53553      0.8012
3.030D 00  -1.389D-07  -1.337D-07  -5.174D-09    3.86891      0.7987
3.086D 00  -1.437D-07  -1.370D-07  -6.717D-09    4.90263      0.7969
3.175D 00  -1.380D-07  -1.421D-07   4.155D-09   -2.92289      0.7941
3.257D 00  -1.408D-07  -1.470D-07   6.202D-09   -4.22007      0.7914
3.333D 00  -1.442D-07  -1.514D-07   7.164D-09   -4.73180      0.7889
3.413D 00  -1.443D-07  -1.560D-07   1.178D-08   -7.55189      0.7862
3.534D 00  -1.536D-07  -1.631D-07   9.486D-09   -5.81693      0.7821
3.597D 00  -1.620D-07  -1.668D-07   4.795D-09   -2.87489      0.7799
3.704D 00  -1.653D-07  -1.730D-07   7.660D-09   -4.42817      0.7762
3.802D 00  -1.742D-07  -1.787D-07   4.553D-09   -2.54752      0.7727
3.876D 00  -1.799D-07  -1.830D-07   3.133D-09   -1.71173      0.7700
3.984D 00  -1.824D-07  -1.893D-07   6.956D-09   -3.67419      0.7661
4.115D 00  -2.095D-07  -1.970D-07  -1.250D-08    6.34708      0.7613
4.184D 00  -2.246D-07  -2.010D-07  -2.361D-08   11.74481      0.7588


     GOODNESS OF FIT:        GAUSS CRITERION,  OMEGA=  2.304D-17


    CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :


        CONSTANT      VALUE       STD DEV    REL STD DEV(PPH)

          C(1)     4.2895D-08   2.0396D-09       4.7548

          C(2     -5.8289D-08   8.2444D-10      -1.4144
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MN(III)--PERIODATE SYSTEM:  35.06        INDUCTION PERIOD CONSIDERED          6/7/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.        TIME      ABSORBANCE   DERIVATIVE       SLOPE           WEIGHT

  1      1.22917      0.41000     -0.15220       -0.09600        0.81508
  2      1.25000      0.40400     -0.22187       -0.28800        0.81423
  3      1.27083      0.40000     -0.27403       -0.19200        0.81364
  4      1.29167      0.39300     -0.31399       -0.33600        0.81254
  5      1.31250      0.38800     -0.35649       -0.24000        0.81170
  6      1.33333      0.37700     -0.40438       -0.52800        0.80973
  7      1.35417      0.37100     -0.44626       -0.28800        0.80857
  8      1.37500      0.36100     -0.46091       -0.48000        0.80648
  9      1.39583      0.34900     -0.49616       -0.57600        0.80372
 10      1.41667      0.33930     -0.52232       -0.48000        0.80119
 11      1.43750      0.33000     -0.55773       -0.43200        0.79871
 12      1.45833      0.31800     -0.57601       -0.57600        0.79509
 13      1.47917      0.30300     -0.59672       -0.72000        0.79001
 14      1.50000      0.29200     -0.60648       -0.52800        0.78583
 15      1.52083      0.28000     -0.57863       -0.57600        0.78080
 16      1.54167      0.26700     -0.54157       -0.62400        0.77469
 17      1.56250      0.25700     -0.49518       -0.48000        0.76948
 18      1.58333      0.24700     -0.46263       -0.48000        0.76377
 19      1.60417      0.23800     -0.43755       -0.43200        0.75814
 20      1.62500      0.22800     -0.40797       -0.48000        0.75128
 21      1.64583      0.22200     -0.39716       -0.28800        0.74683
 22      1.66667      0.21200     -0.38986       -0.48000        0.73877
 23      1.68750      0.20300     -0.39340       -0.43200        0.73077
 24      1.70833      0.19800     -0.38642       -0.24000        0.72597
 25      1.72917      0.18800     -0.36332       -0.48000        0.71554
 26      1.75000      0.18000     -0.34581       -0.38400        0.70629
 27      1.77083      0.17300     -0.33056       -0.33600        0.69745
 28      1.79167      0.16800     -0.31443       -0.24000        0.69065
 29      1.81250      0.16200     -0.28525       -0.28800        0.68190
 30      1.83333      0.15300     -0.28773       -0.43200        0.66741
 31      1.85417      0.15000     -0.27705       -0.14400        0.66218
 32      1.87500      0.14300     -0.27525       -0.33600        0.64907
 33      1.89583      0.13800     -0.26184       -0.24000        0.63886
 34      1.91667      0.13200     -0.25097       -0.28800        0.62555
 35      1.93750      0.12800     -0.24060       -0.19200        0.61595


VALUES OF OTHER INPUT PARAMETERS:

NUM=  45    KORGP=  0    TDELT=  2.0833D-02    TSTART=  1.1250D 00

CATIN=  2.2400D-08    ASTART=  0.415    T1=  1.0830    T2=  1.5000
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MN(III)--PERIODATE SYSTEM:  35.06        INDUCTION PERIOD CONSIDERED          6/7/72

     X           Y(OBS)       Y(CALC)       DEV(Y)      % DEV(Y)    WEIGHT(Y)

2.439D 00   -2.712D-08   -2.632D-08   -8.013D-10     3.04394         0.8151
2.475D 00   -2.429D-08   -2.737D-08    3.078D-09   -11.24698         0.8142
2.500D 00   -2.488D-08   -2.808D-08    3.203D-09   -11.40548         0.8136
2.545D 00   -2.680D-08   -2.936D-08    2.568D-09    -8.74578         0.8125
2.577D 00   -2.855D-08   -3.031D-08    1.760D-09    -5.80551         0.8117
2.653D 00   -2.994D-08   -3.248D-08    2.532D-09    -7.79522         0.8097
2.695D 00   -3.184D-08   -3.371D-08    1.873D-09    -5.55669         0.8086
2.770D 00   -3.575D-08   -3.586D-08    1.181D-10    -0.32937         0.8065
2.865D 00   -3.811D-08   -3.861D-08    4.955D-10    -1.28346         0.8037
2.950D 00   -4.119D-08   -4.104D-08   -1.422D-10     0.34648         0.8012
3.030D 00   -4.354D-08   -4.336D-08   -1.764D-10     0.40682         0.7987
3.145D 00   -4.726D-08   -4.666D-08   -5.995D-10     1.28498         0.7951
3.300D 00   -5.082D-08   -5.114D-08    3.221D-10    -0.62979         0.7900
3.425D 00   -5.540D-08   -5.473D-08   -6.744D-10     1.23232         0.7858
3.571D 00   -5.887D-08   -5.896D-08    8.212D-11    -0.13929         0.7808
3.745D 00   -6.377D-08   -6.397D-08    2.024D-10    -0.31641         0.7747
3.891D 00   -7.068D-08   -6.817D-08   -2.514D-09     3.68748         0.7695
4.049D 00   -7.666D-08   -7.271D-08   -3.956D-09     5.44056         0.7638
4.202D 00   -8.212D-08   -7.712D-08   -5.005D-09     6.48973         0.7581
4.386D 00   -8.922D-08   -8.243D-08   -6.792D-09     8.23918         0.7513
4.505D 00   -9.283D-08   -8.585D-08   -6.980D-09     8.13117         0.7468
4.717D 00   -9.576D-08   -9.197D-08   -3.793D-09     4.12366         0.7388
4.926D 00   -9.609D-08   -9.800D-08    1.910D-09    -1.94942         0.7308
5.051D 00   -9.903D-08   -1.016D-07    2.553D-09    -2.51364         0.7260
5.319D 00   -1.066D-07   -1.093D-07    2.713D-09    -2.48179         0.7155
5.556D 00   -1.134D-07   -1.161D-07    2.778D-09    -2.39214         0.7063
5.780D 00   -1.200D-07   -1.226D-07    2.613D-09    -2.13134         0.6974
5.952D 00   -1.276D-07   -1.276D-07   -6.564D-11     0.05146         0.6906
6.173D 00   -1.423D-07   -1.339D-07   -8.407D-09     6.27750         0.6819
6.536D 00   -1.427D-07   -1.444D-07    1.662D-09    -1.15102         0.6674
6.667D 00   -1.499D-07   -1.482D-07   -1.755D-09     1.18471         0.6622
6.993D 00   -1.526D-07   -1.576D-07    4.974D-09    -3.15676         0.6491
7.246D 00   -1.622D-07   -1.649D-07    2.674D-09    -1.62208         0.6389
7.576D 00   -1.711D-07   -1.744D-07    3.281D-09    -1.88173         0.6255
7.813D 00   -1.804D-07   -1.812D-07    7.915D-10    -0.43685         0.6160


     GOODNESS OF FIT:         GAUSS CRITERION,  OMEGA=  7.687D-18


    CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

          CONSTANT       VALUE        STD DEV    REL STD DEV(PPH)

             C(1)     4.3965D-08   1.5429D-09       3.5094

             C(2)    -2.8818D-08   3.3860D-10      -1.1750
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MN(III)--PERIODATE SYSTEM:  35.07       INDUCTION PERIOD CONSIDERED          6/7/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.      TIME     ABSORBANCE   DERIVATIVE      SLOPE         WEIGHT

  1     1.43717     0.56800     -0.33929     -0.28800       0.82340
  2     1.45800     0.55900     -0.40022     -0.43200       0.82350
  3     1.47883     0.55100     -0.43399     -0.36400       0.82355
  4     1.49967     0.54200     -0.47309     -0.43200       0.82354
  5     1.52050     0.53100     -0.52142     -0.52800       0.82345
  6     1.54133     0.52000     -0.56753     -0.52800       0.82326
  7     1.56217     0.50900     -0.62282     -0.52800       0.82297
  8     1.58300     0.49300     -0.67990     -0.76800       0.82237
  9     1.60383     0.48000     -0.71135     -0.62400       0.82171
 10     1.62467     0.46500     -0.73276     -0.72000       0.82075
 11     1.64550     0.44900     -0.71182     -0.76800       0.81946
 12     1.66633     0.43300     -0.70136     -0.76800       0.81789
 13     1.68717     0.42100     -0.68434     -0.57600       0.81651
 14     1.70800     0.40600     -0.67325     -0.72000       0.81452
 15     1.72883     0.39400     -0.65649     -0.57600       0.81270
 16     1.74967     0.37700     -0.63705     -0.81600       0.80973
 17     1.77050     0.36700     -0.58540     -0.48000       0.80775
 18     1.79133     0.35200     -0.52173     -0.72000       0.80444
 19     1.81217     0.34400     -0.49549     -0.38400       0.80246
 20     1.83300     0.33400     -0.49088     -0.48000       0.79983
 21     1.85383     0.32600     -0.49398     -0.38400       0.79755
 22     1.87467     0.31300     -0.48504     -0.62400       0.79347
 23     1.89550     0.30100     -0.48916     -0.57600       0.78928
 24     1.91633     0.29200     -0.45494     -0.43200       0.78583
 25     1.93717     0.28600     -0.42243     -0.28800       0.78338
 26     1.95800     0.27500     -0.40861     -0.52800       0.77853
 27     1.97883     0.26700     -0.40366     -0.38400       0.77469
 28     1.99967     0.25900     -0.40670     -0.38400       0.77056
 29     2.02050     0.25000     -0.37803     -0.43200       0.76554
 30     2.04133     0.24100     -0.35136     -0.43200       0.76007
 31     2.06217     0.23700     -0.34052     -0.19200       0.75748
 32     2.08300     0.22800     -0.32909     -0.43200       0.75128
 33     2.10383     0.22300     -0.31290     -0.24000       0.74759
 34     2.12467     0.21400     -0.31133     -0.43200       0.74045
 35     2.14550     0.20900     -0.32306     -0.24000       0.73619
 36     2.16633     0.20200     -0.30619     -0.33600       0.72983
 37     2.18717     0.19700     -0.31020     -0.24000       0.72498
 38     2.20800     0.18900     -0.30340     -0.38400       0.71664
 39     2.22883     0.18200     -0.29468     -0.33600       0.70869
 40     2.24967     0.17800     -0.27565     -0.19200       0.70384
 41     2.27050     0.17100     -0.26777     -0.33600       0.69478


VALUES OF OTHER INPUT PARAMETERS:

NUM=  51   KDROP=  0   TDELT=  2.0833D-02   TSTART=  1.3330D 00

CATIN=  2.2400D-08   ASTART=  0.586   T1=  1.2300   T2=  1.6247
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MN(III)--PERIODATE SYSTEM:  35.07       INDUCTION PERIOD CONSIDERED          6/7/72

     X          Y(OBS)      Y(CALC)       DEV(Y)      % DEV(Y)    WEIGHT(Y)

1.7610 00  -2.955D-08  -3.218D-08   2.625D-09    -8.15768       0.8234
1.7890 00  -3.035D-08  -3.329D-08   2.942D-09    -8.83708       0.8235
1.8150 00  -3.333D-08  -3.431D-08   9.714D-10    -2.83156       0.8235
1.8450 00  -3.591D-08  -3.549D-08  -4.282D-10     1.20656       0.8235
1.8830 00  -3.781D-08  -3.698D-08  -8.325D-10     2.25112       0.8234
1.9230 00  -3.990D-08  -3.854D-08  -1.363D-09     3.53518       0.8233
1.9650 00  -4.139D-08  -4.017D-08  -1.222D-09     3.04244       0.8230
2.0280 00  -4.282D-08  -4.266D-08  -1.561D-10     0.36593       0.8224
2.0830 00  -4.590D-08  -4.482D-08  -1.086D-09     2.42261       0.8217
2.1510 00  -4.967D-08  -4.745D-08  -2.219D-09     4.67601       0.8207
2.2270 00  -5.178D-08  -5.045D-08  -1.334D-09     2.64533       0.8195
2.3090 00  -5.322D-08  -5.367D-08   4.497D-10    -0.83792       0.8179
2.3750 00  -5.523D-08  -5.625D-08   1.021D-09    -1.81506       0.8165
2.4630 00  -5.683D-08  -5.968D-08   2.854D-09    -4.78213       0.8145
2.5380 00  -5.899D-08  -6.262D-08   3.629D-09    -5.79526       0.8127
2.6530 00  -6.152D-08  -6.710D-08   5.578D-09    -8.31268       0.8097
2.7250 00  -6.775D-08  -6.993D-08   2.182D-09    -3.11969       0.8078
2.8410 00  -7.691D-08  -7.447D-08  -2.435D-09     3.26991       0.8044
2.9070 00  -8.192D-08  -7.706D-08  -4.863D-09     6.31081       0.8025
2.9940 00  -8.364D-08  -8.047D-08  -3.175D-09     3.94582       0.7998
3.0670 00  -8.406D-08  -8.335D-08  -7.192D-10     0.86297       0.7975
3.1950 00  -8.658D-08  -8.833D-08   1.757D-09    -1.98875       0.7935
3.3220 00  -8.680D-08  -9.332D-08   6.519D-09    -6.98534       0.7893
3.4250 00  -9.436D-08  -9.733D-08   2.973D-09    -3.05447       0.7858
3.4970 00  -1.027D-07  -1.001D-07  -2.579D-09     2.57548       0.7834
3.6360 00  -1.073D-07  -1.056D-07  -1.722D-09     1.63025       0.7785
3.7450 00  -1.098D-07  -1.099D-07   7.109D-11    -0.06470       0.7747
3.8610 00  -1.101D-07  -1.144D-07   4.273D-09    -3.73515       0.7706
4.0000 00  -1.197D-07  -1.199D-07   1.301D-10    -0.10858       0.7655
4.1490 00  -1.301D-07  -1.257D-07  -4.440D-09     3.53188       0.7601
4.2190 00  -1.357D-07  -1.284D-07  -7.209D-09     5.61265       0.7575
4.3860 00  -1.418D-07  -1.350D-07  -6.818D-09     5.05206       0.7513
4.4840 00  -1.506D-07  -1.388D-07  -1.180D-08     8.49965       0.7476
4.6730 00  -1.529D-07  -1.462D-07  -6.672D-09     4.56373       0.7405
4.7850 00  -1.488D-07  -1.506D-07   1.810D-09    -1.20237       0.7362
4.9500 00  -1.585D-07  -1.571D-07  -1.417D-09     0.90234       0.7298
5.0760 00  -1.579D-07  -1.620D-07   4.046D-09    -2.49765       0.7250
5.2910 00  -1.630D-07  -1.704D-07   7.381D-09    -4.33182       0.7166
5.4950 00  -1.694D-07  -1.784D-07   8.937D-09    -5.01040       0.7087
5.6180 00  -1.828D-07  -1.832D-07   3.806D-10    -0.20776       0.7038
5.8480 00  -1.899D-07  -1.922D-07   2.262D-09    -1.17697       0.6948


   GOODNESS OF FIT:        GAUSS CRITERION,  OMEGA=  1.305D-17


  CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

        CONSTANT      VALUE        STD DEV    REL STD DEV(PPH)

          C(1)     3.6747D-08   1.8479D-09       5.0288

          C(2)    -3.9150D-08   5.3256D-10      -1.3603
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MN(II)--PERIODATE SYSTEM:  35.08       INDUCTION PERIOD CONSIDERED          6/7/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NC.      TIME     ABSORBANCE   DERIVATIVE      SLOPE        WEIGHT

  1     1.31217     0.75500     -0.33051     -0.24000     0.80990
  2     1.33300     0.74300     -0.42120     -0.57600     0.81136
  3     1.35383     0.73600     -0.50474     -0.33600     0.81218
  4     1.37467     0.72400     -0.57368     -0.57600     0.81351
  5     1.39550     0.71400     -0.59916     -0.48000     0.81457
  6     1.41633     0.69600     -0.62308     -0.86400     0.81633
  7     1.43717     0.68600     -0.67480     -0.48000     0.81723
  8     1.45800     0.67100     -0.71409     -0.72000     0.81846
  9     1.47883     0.65800     -0.75465     -0.62400     0.81945
 10     1.49967     0.64000     -0.78311     -0.86400     0.82064
 11     1.52050     0.62200     -0.82449     -0.86400     0.82164
 12     1.54133     0.60500     -0.80682     -0.81600     0.82240
 13     1.56217     0.59000     -0.79912     -0.72000     0.82291
 14     1.58300     0.57300     -0.77383     -0.81600     0.82332
 15     1.60383     0.55700     -0.74694     -0.76800     0.82352
 16     1.62467     0.54200     -0.74340     -0.72000     0.82354
 17     1.64550     0.52500     -0.72688     -0.81600     0.82336
 18     1.66633     0.51200     -0.68461     -0.62400     0.82306
 19     1.68717     0.49900     -0.65153     -0.62400     0.82262
 20     1.70800     0.48200     -0.60866     -0.81600     0.82182
 21     1.72883     0.47200     -0.58235     -0.48000     0.82123
 22     1.74967     0.46100     -0.58709     -0.52800     0.82045
 23     1.77050     0.44800     -0.57567     -0.62400     0.81938
 24     1.79133     0.43700     -0.57291     -0.52800     0.81831
 25     1.81217     0.42300     -0.57374     -0.67200     0.81676
 26     1.83300     0.41100     -0.54296     -0.57600     0.81522
 27     1.85383     0.40200     -0.49808     -0.43200     0.81394
 28     1.87467     0.39100     -0.47292     -0.52800     0.81221
 29     1.89550     0.38200     -0.45525     -0.43200     0.81065
 30     1.91633     0.37200     -0.44502     -0.48000     0.80876
 31     1.93717     0.36400     -0.43718     -0.38400     0.80713
 32     1.95800     0.35300     -0.41704     -0.52800     0.80467
 33     1.97883     0.34500     -0.41100     -0.38400     0.80273
 34     1.99967     0.33800     -0.42077     -0.33600     0.80092
 35     2.02050     0.32800     -0.43365     -0.48000     0.79813
 36     2.04133     0.32000     -0.42689     -0.38400     0.79572
 37     2.06217     0.31000     -0.41994     -0.48000     0.79246
 38     2.08300     0.30000     -0.38189     -0.48000     0.78891
 39     2.10383     0.29400     -0.33858     -0.28800     0.78662
 40     2.12467     0.28600     -0.31546     -0.28800     0.78421
 41     2.14550     0.28100     -0.31777     -0.33600     0.78124
 42     2.16633     0.27500     -0.34781     -0.28800     0.77853
 43     2.18717     0.26700     -0.36836     -0.38400     0.77469
 44     2.20800     0.25900     -0.36394     -0.38400     0.77056
 45     2.22883     0.25000     -0.34937     -0.43200     0.76554
 46     2.24966     0.24400     -0.32657     -0.28800     0.76194
 47     2.27050     0.23900     -0.28936     -0.24000     0.75879
 48     2.29133     0.23200     -0.27324     -0.33600     0.75411
 49     2.31216     0.22600     -0.26731     -0.28800     0.74983


VALUES OF OTHER INPUT PARAMETERS:

NUM=  59   KDROP=  0   TDELT=  2.0833D-02   TSTART=  1.2080D 00

CATIN=  2.2400D-08   ASTART=  0.772   T1=  1.1320   T2=  1.5205
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MN(II)--PERIODATE SYSTEM:  35.08       INDUCTION PERIOD CONSIDERED          6/7/72

    X            Y(OBS)       Y(CALC)        DEV(Y)       % DEV(Y)     WEIGHT(Y)

1.325D 00   -2.216D-08   -2.346D-08    1.298D-09    -5.53243        0.8099
1.346D 00   -2.164D-08   -2.455D-08    2.905D-09   -11.83418        0.8114
1.359D 00   -2.200D-08   -2.520D-08    3.201D-09   -12.70202        0.8122
1.381D 00   -2.316D-08   -2.635D-08    3.186D-09   -12.09036        0.8135
1.401D 00   -2.615D-08   -2.733D-08    1.185D-09    -4.33397        0.8146
1.437D 00   -2.928D-08   -2.918D-08   -1.001D-10     0.34296        0.8163
1.458D 00   -3.114D-08   -3.025D-08   -8.960D-10     2.96246        0.8172
1.490D 00   -3.358D-08   -3.191D-08   -1.678D-09     5.25882        0.8185
1.520D 00   -3.597D-08   -3.341D-08   -2.565D-09     7.67712        0.8195
1.563D 00   -3.895D-08   -3.558D-08   -3.370D-09     9.46976        0.8206
1.608D 00   -4.131D-08   -3.789D-08   -3.423D-09     9.03511        0.8216
1.653D 00   -4.279D-08   -4.019D-08   -2.605D-09     6.48221        0.8224
1.695D 00   -4.379D-08   -4.233D-08   -1.461D-09     3.45145        0.8229
1.745D 00   -4.582D-08   -4.489D-08   -9.335D-10     2.07959        0.8233
1.795D 00   -4.810D-08   -4.744D-08   -6.544D-10     1.37936        0.8235
1.845D 00   -4.895D-08   -4.997D-08    1.019D-09    -2.04001        0.8235
1.905D 00   -5.071D-08   -5.302D-08    2.309D-09    -4.35427        0.8234
1.953D 00   -5.452D-08   -5.548D-08    9.590D-10    -1.72858        0.8231
2.004D 00   -5.801D-08   -5.807D-08    6.705D-11    -0.11546        0.8226
2.075D 00   -6.286D-08   -6.167D-08   -1.185D-09     1.92152        0.8218
2.119D 00   -6.650D-08   -6.391D-08   -2.588D-09     4.04864        0.8212
2.169D 00   -6.676D-08   -6.649D-08   -2.709D-10     0.40743        0.8205
2.232D 00   -6.889D-08   -6.969D-08    8.013D-10    -1.14973        0.8194
2.288D 00   -7.004D-08   -7.255D-08    2.516D-09    -3.46731        0.8183
2.364D 00   -7.075D-08   -7.641D-08    5.663D-09    -7.41052        0.8168
2.433D 00   -7.562D-08   -7.993D-08    4.307D-09    -5.38873        0.8152
2.488D 00   -8.337D-08   -8.270D-08   -6.686D-10     0.80839        0.8139
2.558D 00   -8.879D-08   -8.627D-08   -2.525D-09     2.92741        0.8122
2.618D 00   -9.326D-08   -8.934D-08   -3.927D-09     4.39614        0.8107
2.688D 00   -9.646D-08   -9.292D-08   -3.537D-09     3.80657        0.8088
2.747D 00   -9.926D-08   -9.593D-08   -3.325D-09     3.46639        0.8071
2.833D 00   -1.052D-07   -1.003D-07   -4.875D-09     4.86056        0.8047
2.899D 00   -1.078D-07   -1.036D-07   -4.210D-09     4.06237        0.8027
2.959D 00   -1.065D-07   -1.067D-07    2.407D-10    -0.22557        0.8009
3.049D 00   -1.044D-07   -1.113D-07    6.922D-09    -6.22011        0.7981
3.125D 00   -1.071D-07   -1.152D-07    8.059D-09    -6.99725        0.7957
3.226D 00   -1.100D-07   -1.203D-07    1.031D-08    -8.56824        0.7925
3.333D 00   -1.222D-07   -1.258D-07    3.606D-09    -2.86670        0.7889
3.401D 00   -1.392D-07   -1.292D-07   -9.936D-09     7.68735        0.7866
3.472D 00   -1.509D-07   -1.329D-07   -1.801D-08    13.55433        0.7842
3.559D 00   -1.512D-07   -1.373D-07   -1.397D-08    10.17958        0.7812
3.636D 00   -1.395D-07   -1.412D-07    1.703D-09    -1.20612        0.7785
3.745D 00   -1.330D-07   -1.468D-07    1.377D-08    -9.38174        0.7747
3.861D 00   -1.359D-07   -1.527D-07    1.676D-08   -10.98168        0.7706
4.000D 00   -1.429D-07   -1.597D-07    1.684D-08   -10.54227        0.7655
4.098D 00   -1.543D-07   -1.648D-07    1.045D-08    -6.34048        0.7619
4.184D 00   -1.758D-07   -1.691D-07   -6.643D-09     3.92813        0.7588
4.310D 00   -1.878D-07   -1.756D-07   -1.229D-08     7.00122        0.7541
4.425D 00   -1.938D-07   -1.814D-07   -1.237D-08     6.82252        0.7498


   GOODNESS OF FIT:        GAUSS CRITERION,  OMEGA=  3.806D-17


  CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

       CONSTANT      VALUE        STD DEV   REL STD DEV(PPH)

         C(1)     4.4006D-08   2.8710D-09      6.5241

         C(2)    -5.0937D-08   1.0807D-09     -2.1217
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MN(III)--PERIODATE SYSTEM:  35.09      INDUCTION PERIOD CONSIDERED        6/7/72

CETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.     TIME      ABSORBANCE   DERIVATIVE      SLOPE        WEIGHT

 1     1.39617     0.93700     -0.40861     -0.48000      0.77820
 2     1.41700     0.92900     -0.51564     -0.38400      0.77998
 3     1.43783     0.91500     -0.58276     -0.67200      0.78301
 4     1.45867     0.90300     -0.65346     -0.57600      0.78551
 5     1.47950     0.89000     -0.66985     -0.62400      0.78813
 6     1.50033     0.87500     -0.74606     -0.72000      0.79104
 7     1.52117     0.86000     -0.78737     -0.72000      0.79382
 8     1.54200     0.84000     -0.85457     -0.96000      0.79734
 9     1.56283     0.82700     -0.90019     -0.62400      0.79952
10     1.58367     0.80100     -0.94497     -1.24800      0.80359
11     1.60450     0.78700     -0.95364     -0.67200      0.80563
12     1.62533     0.76400     -0.93529     -1.10400      0.80875
13     1.64617     0.74500     -0.92741     -0.91200      0.81112
14     1.66700     0.72500     -0.86988     -0.96000      0.81340
15     1.68783     0.71000     -0.87740     -0.72000      0.81497
16     1.70867     0.69100     -0.86137     -0.91200      0.81679
17     1.72950     0.67200     -0.84852     -0.91200      0.81840
18     1.75033     0.65700     -0.82400     -0.72000      0.81952
19     1.77117     0.63600     -0.78506     -1.00800      0.82088
20     1.79200     0.62100     -0.73731     -0.72000      0.82169
21     1.81283     0.61000     -0.69736     -0.52800      0.82219
22     1.83367     0.59300     -0.67291     -0.81600      0.82282
23     1.85450     0.58000     -0.64901     -0.62400      0.82318
24     1.87533     0.56500     -0.63529     -0.72000      0.82344
25     1.89617     0.55400     -0.60225     -0.52800      0.82354
26     1.91700     0.54000     -0.57279     -0.67200      0.82353
27     1.93783     0.52900     -0.58280     -0.52800      0.82342
28     1.95867     0.51900     -0.58113     -0.48000      0.82324
29     1.97950     0.50500     -0.56192     -0.67200      0.82284
30     2.00033     0.49200     -0.54463     -0.62400      0.82233
31     2.02117     0.48100     -0.52729     -0.52800      0.82177
32     2.04200     0.47200     -0.52387     -0.43200      0.82123
33     2.06283     0.46300     -0.50356     -0.43200      0.82060
34     2.08367     0.44900     -0.50882     -0.67200      0.81946
35     2.10450     0.44000     -0.51047     -0.43200      0.81862
36     2.12533     0.42700     -0.47768     -0.62400      0.81723
37     2.14617     0.42100     -0.42984     -0.28800      0.81651
38     2.16700     0.41000     -0.42284     -0.52800      0.81508
39     2.18783     0.40200     -0.43052     -0.38400      0.81394
40     2.20867     0.39500     -0.43030     -0.33600      0.81286
41     2.22950     0.38400     -0.45288     -0.52800      0.81101
42     2.25033     0.37200     -0.43605     -0.57600      0.80876
43     2.27117     0.36700     -0.42458     -0.24000      0.80775
44     2.29200     0.35700     -0.39534     -0.48000      0.80559
45     2.31283     0.34800     -0.36751     -0.43200      0.80348
46     2.33366     0.34200     -0.36767     -0.28800      0.80197
47     2.35450     0.33400     -0.38079     -0.38400      0.79983
48     2.37533     0.32600     -0.37419     -0.38400      0.79755
49     2.39616     0.31800     -0.37932     -0.38400      0.79509
50     2.41700     0.31000     -0.37864     -0.38400      0.79246
51     2.43783     0.30200     -0.35332     -0.38400      0.78965
52     2.45866     0.29500     -0.31715     -0.33600      0.78701
53     2.47950     0.28900     -0.30144     -0.28800      0.78462
54     2.50033     0.28200     -0.30956     -0.33600      0.78167
55     2.52116     0.27700     -0.32573     -0.24000      0.77945
56     2.54200     0.27100     -0.33747     -0.28800      0.77665
57     2.56283     0.26100     -0.32477     -0.48000      0.77162

VALUES OF OTHER INPUT PARAMETERS:

NUM=  67   KDROP=  0   TDELT=  2.0833D-02   TSTART=  1.2920D 00

CATIN=  2.2400D-06   ASTART=  0.955   T1=  1.1910   T2=  1.6045
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MN(III)--PERIODATE SYSTEM:  35.09      INDUCTION PERIOD CONSIDERED        6/7/72

     X          Y(OBS)      Y(CALC)       DEV(Y)      % DEV(Y)     WEIGHT(Y)

1.067D 00  -2.165D-08  -2.333D-08   1.679D-09   -7.19451       0.7782
1.076D 00  -2.082D-08  -2.389D-08   3.066D-09  -12.83535       0.7800
1.093D 00  -2.198D-08  -2.488D-08   2.905D-09  -11.67401       0.7830
1.107D 00  -2.305D-08  -2.576D-08   2.711D-09  -10.52349       0.7855
1.124D 00  -2.612D-08  -2.673D-08   6.139D-10   -2.29638       0.7881
1.143D 00  -2.696D-08  -2.789D-08   9.355D-10   -3.35357       0.7910
1.163D 00  -2.910D-08  -2.910D-08  -5.303D-12    0.01823       0.7938
1.190D 00  -3.030D-08  -3.077D-08   4.625D-10   -1.50320       0.7973
1.209D 00  -3.228D-08  -3.190D-08  -3.893D-10    1.22043       0.7995
1.248D 00  -3.430D-08  -3.426D-08  -3.458D-11    0.10091       0.8036
1.271D 00  -3.769D-08  -3.560D-08  -2.085D-09    5.85649       0.8056
1.309D 00  -3.893D-08  -3.791D-08  -1.016D-09    2.68015       0.8088
1.342D 00  -3.976D-08  -3.992D-08   1.636D-10   -0.40984       0.8111
1.379D 00  -4.293D-08  -4.216D-08  -7.688D-10    1.82366       0.8134
1.408D 00  -4.309D-08  -4.392D-08   8.247D-10   -1.87802       0.8150
1.447D 00  -4.443D-08  -4.625D-08   1.817D-09   -3.92895       0.8168
1.488D 00  -4.566D-08  -4.872D-08   3.063D-09   -6.28603       0.8184
1.522D 00  -4.758D-08  -5.077D-08   3.187D-09   -6.27707       0.8195
1.572D 00  -5.054D-08  -5.380D-08   3.264D-09   -6.06674       0.8209
1.610D 00  -5.444D-08  -5.609D-08   1.648D-09   -2.93893       0.8217
1.639D 00  -5.823D-08  -5.784D-08  -3.875D-10    0.66997       0.8222
1.686D 00  -6.104D-08  -6.068D-08  -3.618D-10    0.59621       0.8228
1.724D 00  -6.401D-08  -6.296D-08  -1.049D-09    1.66671       0.8232
1.770D 00  -6.612D-08  -6.572D-08  -4.047D-10    0.61581       0.8234
1.805D 00  -7.053D-08  -6.784D-08  -2.688D-09    3.96213       0.8235
1.852D 00  -7.497D-08  -7.066D-08  -4.306D-09    6.09440       0.8235
1.890D 00  -7.448D-08  -7.298D-08  -1.497D-09    2.05169       0.8234
1.927D 00  -7.550D-08  -7.518D-08  -3.173D-10    0.42206       0.8232
1.980D 00  -7.891D-08  -7.840D-08  -5.064D-10    0.64592       0.8228
2.033D 00  -8.227D-08  -8.156D-08  -7.132D-10    0.87444       0.8223
2.079D 00  -8.586D-08  -8.436D-08  -1.499D-09    1.77675       0.8218
2.119D 00  -8.731D-08  -8.675D-08  -5.594D-10    0.64477       0.8212
2.160D 00  -9.176D-08  -8.924D-08  -2.523D-09    2.82739       0.8206
2.227D 00  -9.173D-08  -9.330D-08   1.570D-09   -1.68306       0.8195
2.273D 00  -9.235D-08  -9.605D-08   3.701D-09   -3.85285       0.8186
2.342D 00  -9.966D-08  -1.002D-07   5.577D-10   -0.55649       0.8172
2.375D 00  -1.118D-07  -1.022D-07  -9.607D-09    9.39741       0.8165
2.439D 00  -1.148D-07  -1.061D-07  -8.717D-09    8.21718       0.8151
2.488D 00  -1.138D-07  -1.090D-07  -4.827D-09    4.42791       0.8139
2.532D 00  -1.150D-07  -1.117D-07  -3.309D-09    2.96318       0.8129
2.604D 00  -1.103D-07  -1.160D-07   5.766D-09   -4.96897       0.8110
2.688D 00  -1.156D-07  -1.211D-07   5.507D-09   -4.54702       0.8088
2.725D 00  -1.198D-07  -1.233D-07   3.494D-09   -2.83354       0.8078
2.801D 00  -1.299D-07  -1.279D-07  -1.945D-09    1.52019       0.8056
2.874D 00  -1.410D-07  -1.323D-07  -8.680D-09    6.56114       0.8035
2.924D 00  -1.422D-07  -1.353D-07  -6.844D-09    5.05701       0.8020
2.994D 00  -1.385D-07  -1.396D-07   1.053D-09   -0.75485       0.7998
3.067D 00  -1.422D-07  -1.440D-07   1.795D-09   -1.24645       0.7975
3.145D 00  -1.415D-07  -1.486D-07   7.142D-09   -4.80461       0.7951
3.226D 00  -1.430D-07  -1.535D-07   1.055D-08   -6.87124       0.7925
3.311D 00  -1.546D-07  -1.587D-07   4.135D-09   -2.60558       0.7896
3.390D 00  -1.737D-07  -1.634D-07  -1.022D-08    6.25525       0.7870
3.460D 00  -1.843D-07  -1.677D-07  -1.658D-08    9.88629       0.7846
3.546D 00  -1.809D-07  -1.729D-07  -8.070D-09    4.66839       0.7817
3.610D 00  -1.734D-07  -1.767D-07   3.339D-09   -1.88958       0.7795
3.690D 00  -1.687D-07  -1.815D-07   1.281D-08   -7.05820       0.7766
3.831D 00  -1.768D-07  -1.901D-07   1.331D-08   -7.00122       0.7716

   GODDNESS OF FIT:        GAUSS CRITERION,  OMEGA=  2.180D-17

  CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

      CONSTANT     VALUE        STD DEV    REL STD DEV(PPH)

        C(1)    4.1042D-08   1.9534D-09       4.7594

        C(2)   -6.0320D-08   8.6305D-10      -1.4308
```

```
MN(II)--PERIODATE SYSTEM:  DETN OF K2 FROM PLOT OF SLOPE VS AZERO


    X           Y(OBS)      Y(CALC)       DEV(Y)     % DEV(Y)     WEIGHT(Y)

1.508D-08  -2.418D-08  -2.501D-08   8.280D-10   -3.31133       1.1995
1.980D-08  -2.835D-08  -3.143D-08   3.074D-09   -9.78019       1.6591
3.060D-08  -4.196D-08  -4.614D-08   4.184D-09   -9.06671       1.6502
4.782D-08  -6.865D-08  -6.960D-08   9.466D-10   -1.36019       1.0326
2.031D-08  -3.107D-08  -3.213D-08   1.065D-09   -3.31428       0.9759
2.358D-08  -4.144D-08  -3.658D-08  -4.860D-09   13.30454       0.9669
3.494D-08  -5.007D-08  -5.205D-08   1.987D-09   -3.81748       1.7069
3.629D-08  -5.829D-08  -5.389D-08  -4.398D-09    8.16103       0.9659
1.825D-08  -2.882D-08  -2.931D-08   4.957D-10   -1.69088       2.4092
2.153D-08  -3.915D-08  -3.379D-08  -5.357D-09   15.85364       1.5454
3.397D-08  -5.094D-08  -5.074D-08  -2.014D-10    0.39705       0.7474
3.920D-08  -6.032D-08  -5.785D-08  -2.470D-09    4.26973       0.8969


    GOODNESS OF FIT:        GAUSS CRITERION,  OMEGA=  1.462D-17


   CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

        CONSTANT      VALUE        STD DEV   REL STD DEV(PPH)

           C(1)   -4.4618D-09   2.9519D-09    -66.1583

           C(2)   -1.3621D 00   1.0323D-01     -7.5784




   DETERMINATION OF SYSTEM PARAMETERS--SUMMARY OF RESULTS




   MEAN VALUES OF RATE CONSTANTS:

        CONSTANT        VALUE        STD DEV      REL STD DEV(PPH)

           K1         1.3624D 04   2.7437D 03     20.13963

           K2         2.2412D 08   1.4828D 08     66.15834

           K-2        8.4309D 08   6.3893D 07      7.57842
```

APPENDIX F

ESTIMATION OF K_{Ac}

Relationships between the stability constants of complexes and the characteristic properties of their constituents give information on the nature of the chemical bonding in complexes and may be used to make possible estimation of unknown stability constants.(29) A few linear plots of log K - log K' can be found in the literature. Irving and Rossotti(30) and Freiser et al.(31) found linear relationships between the stability constants of complexes of two metal ions with a series of related ligands. Irving and Rossotti also pointed out that the logarithm of the stability constants of the corresponding metal complexes formed with another but analogous ligand give straight lines.

In a search for an approximate value for the stability constant of the manganese (III)-acetate complex (ML_3), a few correlating plots were tried. The main difficulty is the lack of data for the formation constant of trivalent metal cations. Plotting the log M(II) vs. log M(III) for the chelates of iron and manganese with a series of aminopolycarboxylic acids, (Figure 28) roughly a straight line relationship is obtained. If the value for the manganese (II)-acetate complex, MnA_2, is entered in this plot, log K for MnA_3 would seem to have a value of 13.8. It is of interest to observe that by means of this plot the log K for Mn(III)-NTA complex is equal to 19.5, in reasonable good agreement with a recently reported value of 20.25.(28) In Figure 29 log K of the

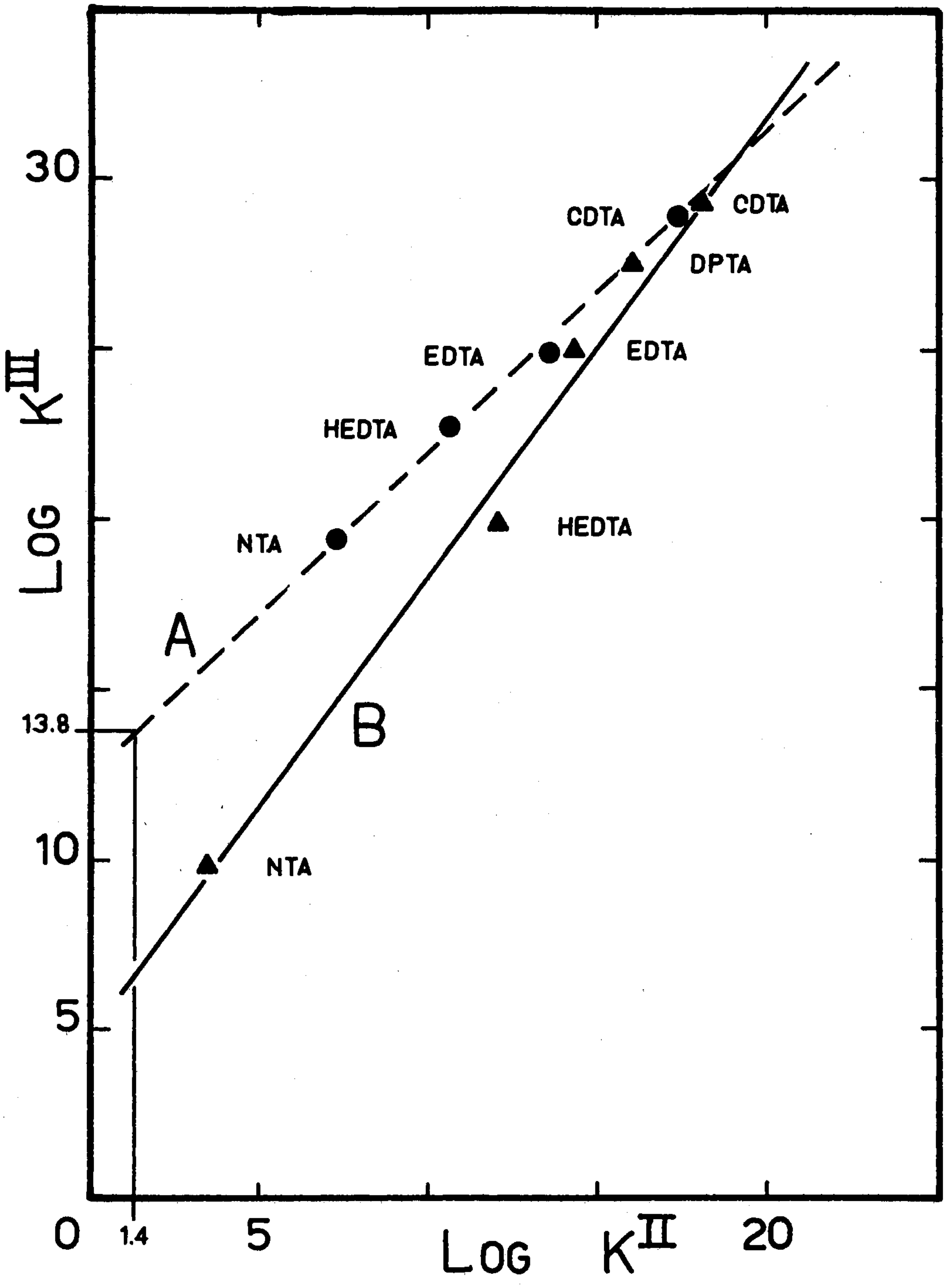

Figure 28. Estimation of Formation Constant of Mn(III)-Acetate Complex. Curve A: Manganese Complexes. Curve B: Iron Complexes. Constants From Ringbom (32) and Hamm (33)

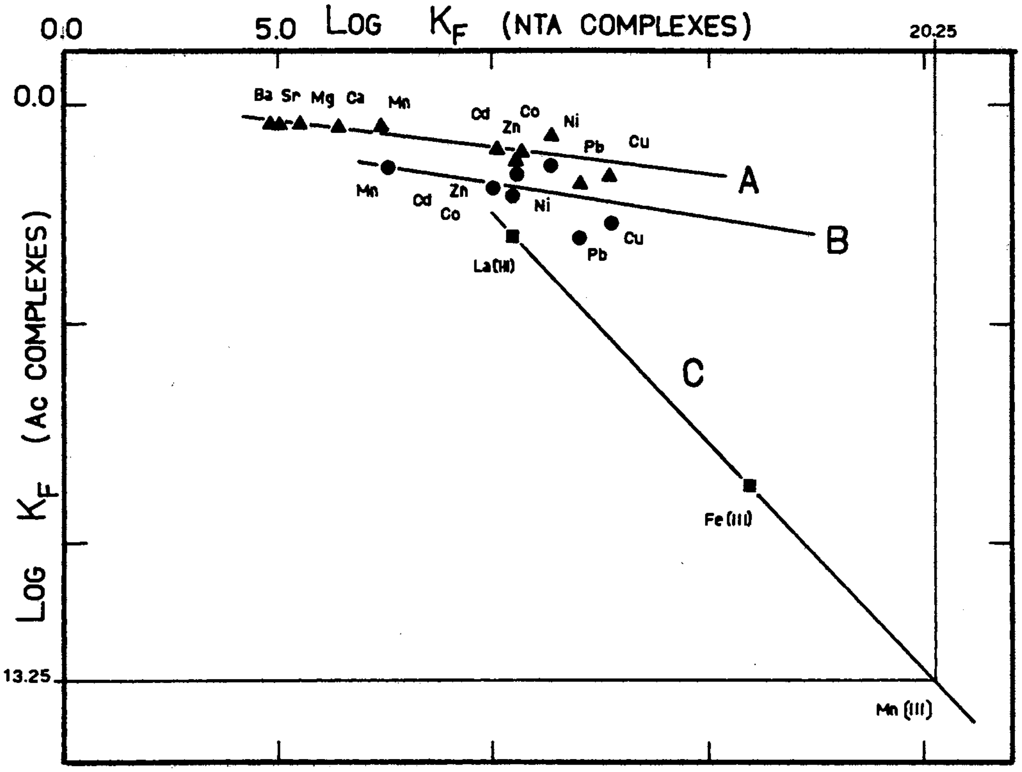

Figure 29. Estimation of Formation Constant of Mn(III)-Acetate Complex. Curve A: Monovalent Metal Complexes. Curve B: Divalent Metal Complexes. Curve C: Trivalent Metal Complexes. Constants From Ringbom (32)

MA complexes for a series of bivalent cations are plotted against the corresponding log K for the NTA complexes. A definite trend which could be roughly fitted by a straight line is observed. The MA_2 complexes seem to follow the same trend with a slightly steeper slope. The only two trivalent cations which could be used to construct a similar plot for the MA_3 complexes are iron (III) and lanthanum (III). Recognizing that is rather brave to fit a straight line through these two points, when this is done though, and the value for Mn(III)-NTA is entered, a value of log K = 13.25 is obtained which coincidentally or surprisingly agrees very well with the value obtained in the plot of aminopolycarboxylate complexes. In light of these observations, a reasonable maximum limit for the value of log K for the Mn(III)-Acetate complex can be set at $K_F^{Ac^-} \leq 10^{14}$.

Having this estimate in hand, the competition of NTA and Acetate for any Mn(III) present in a given system can be represented in the following manner:

$$Cx + 3A \rightleftarrows CxA_3 \quad K_A = \frac{[CxA_3]}{[Cx][A]^3} \tag{F-1}$$

$$Cx + L \rightleftarrows CxL \quad K_L' = \frac{[CxL]}{[Cx][L]'} \tag{F-2}$$

(Note: 3:1 Ac complex is preferred due to large concn. of Ac^-)

where:

$Cx = Mn(III)$,

$A = CH_3COO^-$,

$L = N-(CH_2-COO^-)_3 = NTA^{3-}$

K_A = formation constant for the Mn(III)-acetate complex,

K_L' = conditional formation constant for the Mn(III)-NDA^{3-} complex$^{(32)}$, and

$[L]'$ = all forms of the ligand present not complexed with Mn(III)$^{(32)}$.

From the required mass balance:

$$[C]_o = [Cx] + [CxA_3] + [CxL] \qquad \text{(F-3)}$$

where:

$[C]_o$ = total catalyst added to the system.

From the formation constant expressions:

$$[CxA_3] = K_A\,[Cx][A]^3 \text{ and} \qquad \text{(F-4)}$$

$$[CxL] = K_L'\,[Cx][L]' \qquad \text{(F-5)}$$

Substitution of these expressions into Equation (F-3) and solving for [Cx] gives:

$$[Cx] = \frac{[C]_o}{1 + K_A[A]^3 + K_L'\,[L]'} \qquad \text{(F-6)}$$

Substitution of Equation [F-6] into Equation [F-5] leads to:

$$[CxL] = \frac{K_L'[L]'[C]_o}{1 + K_A[A]^3 + K_L'[L]'} \qquad \text{(F-7)}$$

But, from mass balance:

$$[L]' = C_L - [CxL] \qquad \text{(F-8)}$$

Substitution of this expression into Equation [F-7] yields:

$$[CxL] = \frac{K_L' \, (C_L - [CxL])[C]_o}{1 + K_A[A]^3 + K_L' \, (C_L - [CxL])} \tag{F-9}$$

Letting x = [CxL] to simplify the algebra somewhat and proceeding with the solution:

$$x + K_A[A]^3x + K_LC_{Lx} - K_L'x^2 = K_L' \, C_L[C]_o - K_L'[C]_ox \tag{F-10}$$

$$K_L'x^2 - (1 + K_A[A]^3 + K_L'C_L + K_L'[C]_o)x + K_L'C_L[C]_o = 0 \tag{F-11}$$

$$K_L'x^2 - (1 + K_A[A]^3 + (C_L + [C]_o)K_L')x + K_L'C_L[C]_o = 0 \tag{F-12}$$

Application of the quadratic formula and selection of the negative root since this gives the proper result when $C_L = 0.0$, leads to the final expression for concentration of Mn(III)-complex:

$$[CxL] = \left\{\frac{[1+K_A[A]^3+(C_L+[C]_o)K_L'] - \sqrt{[1+K_A[A]^3+(C_L+[C]_o)K_L']^2-4K_L'^2C_L[C]_o}}{2\,K_L'}\right\} \tag{F-13}$$

According to Ringbom (32), a value for K_L' may be obtained from the expression:

$$K_L' = \frac{K_L}{\alpha_L(H)}$$

where:

K_L = the formation constant for Mn(III)-NTA^{3-} complex and

$\alpha_L(H)$ = the inverse of the fraction of NTA present in the N-$(CH_2\text{-}COO^-)_3$ form.

Since $K_L = 10^{20.25} = 1.8 \times 10^{20}$ and, from Table A.4c in Ringbom's book, $\alpha_L(H)$ for NTA at pH = 4.7 can be interpolated as $\alpha_L(H) = 5.1$, the final value for the conditional formation constant obtained was: $K_L' = 3.5 \times 10^{19}$.

Looking at the term

$$T = 1 + K_A[A]^3 + (C_L + [C]_o)\ K_L'$$

in Equation [F-13] and assigning the following values used in obtaining titration curves:

$$[A] = 0.5,\ C_L = 10^{-5},\ [C]_o = 10^{-8},\ \text{and}\ K_L' = 3.5 \times 10^{19}$$

leads to:

$$\begin{aligned} T &= 1 + K_A(.125) + 10^{-5}(3.5 \times 10^{19}) \\ &\cong (.125)\ K_A + 3.5 \times 10^{14} \end{aligned} \qquad \text{(F-15)}$$

Since a maximum value of 10^{14} has been set for K_A, the above expression becomes:

$$T = (.125 \times 10^{14}) + (3.5 \times 10^{14}) \qquad \text{(F-16)}$$

It can be seen, then, that a value of $K_A = 10^{14}$, under the conditions specified, introduces an "acetate effect" of only $\frac{.125}{3.5} \times 100\%$ or 3.6%. In light of the satisfactory results obtained and considering the magnitude of other errors introduced in estimation, it seems reasonable to assume that, for all practical purposes, all of the Mn(III) present in the system will be complexed by NTA.

APPENDIX G

COMPLETE LISTING OF OUTPUT FROM DETERMINATION OF SYSTEM PARAMETERS--NTA PRESENT

```
MN(II)--PERIODATE SYSTEM: NTA ADDED       34.11                                6/6/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NC.        TIME       ABSORBANCE    DERIVATIVE      SLOPE          WEIGHT

  1      0.47917       0.72800      -0.57482      -0.48000        0.81308
  2      0.50000       0.71600      -0.73657      -0.57600        0.81436
  3      0.52083       0.69700      -0.82820      -0.91200        0.81624
  4      0.54167       0.67900      -0.93649      -0.86400        0.81783
  5      0.56250       0.65600      -0.99540      -1.10400        0.81959
  6      0.58333       0.63800      -1.03721      -0.86400        0.82076
  7      0.60417       0.62000      -1.05320      -0.86400        0.82174
  8      0.62500       0.59000      -1.07595      -1.44000        0.82291
  9      0.64583       0.57100      -1.11265      -0.91200        0.82335
 10      0.66667       0.54700      -1.15308      -1.15200        0.82355
 11      0.68750       0.52500      -1.15620      -1.05600        0.82336
 12      0.70833       0.50000      -1.16133      -1.20000        0.82266
 13      0.72917       0.47300      -1.15072      -1.29600        0.82129
 14      0.75000       0.45100      -1.10904      -1.05600        0.81964
 15      0.77083       0.42800      -1.07223      -1.10400        0.81734
 16      0.79167       0.40600      -1.03406      -1.05600        0.81452
 17      0.81250       0.38900      -1.03013      -0.81600        0.81187
 18      0.83333       0.36200      -1.02480      -1.29600        0.80670
 19      0.85417       0.34300      -0.98444      -0.91200        0.80223
 20      0.87500       0.32200      -0.96306      -1.00800        0.79634
 21      0.89583       0.30200      -0.91846      -0.96000        0.78965
 22      0.91667       0.28600      -0.85958      -0.76800        0.78338
 23      0.93750       0.26800      -0.81961      -0.86400        0.77519
 24      0.95833       0.24800      -0.77291      -0.96000        0.76436
 25      0.97917       0.23500      -0.72593      -0.62400        0.75615
 26      1.00000       0.22000      -0.68727      -0.72000        0.74528
 27      1.02083       0.20800      -0.63895      -0.57600        0.73531
 28      1.04167       0.19200      -0.58809      -0.76800        0.71986
 29      1.06250       0.18200      -0.56464      -0.48000        0.70869
 30      1.08333       0.16900      -0.51922      -0.62400        0.69204
 31      1.10417       0.16000      -0.47883      -0.43200        0.67883
 32      1.12500       0.15200      -0.43340      -0.38400        0.66569
 33      1.14583       0.14000      -0.40845      -0.57600        0.64304
 34      1.16667       0.13300      -0.37758      -0.33600        0.62785
 35      1.18750       0.12600      -0.36617      -0.33600        0.61092

VALUES OF OTHER INPUT PARAMETERS:

NUM=  45   KDROP=  0   TDELT=  2.0833D-02   TSTART=  3.7500D-01

CATIN=  2.2400D-08   ASTART=  0.755   T1=  0.1320   T2=  0.7083
```

```
MN(III)--PERIODATE SYSTEM: NTA ADDED       34.11                                6/6/72

     X          Y(OBS)       Y(CALC)       DEV(Y)      % DEV(Y)     WEIGHT(Y)

1.374D 00   -1.002D-08   -6.751D-09   -3.265D-09    48.36313        0.8131
1.397D 00   -8.782D-09   -6.963D-09   -1.819D-09    26.12642        0.8144
1.435D 00   -8.720D-09   -7.315D-09   -1.406D-09    19.21817        0.8162
1.473D 00   -8.560D-09   -7.666D-09   -8.950D-10    11.67519        0.8178
1.524D 00   -8.894D-09   -8.142D-09   -7.518D-10     9.23342        0.8196
1.567D 00   -9.381D-09   -8.539D-09   -8.425D-10     9.86714        0.8208
1.613D 00   -1.011D-08   -8.959D-09   -1.153D-09    12.86933        0.8217
1.695D 00   -1.079D-08   -9.715D-09   -1.075D-09    11.06584        0.8229
1.751D 00   -1.134D-08   -1.024D-08   -1.099D-09    10.73993        0.8234
1.828D 00   -1.184D-08   -1.094D-08   -8.977D-10     8.20205        0.8236
1.905D 00   -1.275D-08   -1.165D-08   -1.097D-09     9.41723        0.8234
2.000D 00   -1.366D-08   -1.253D-08   -1.132D-09     9.03477        0.8227
2.114D 00   -1.419D-08   -1.358D-08   -6.101D-10     4.49138        0.8213
2.217D 00   -1.515D-08   -1.454D-08   -6.128D-10     4.21617        0.8196
2.336D 00   -1.610D-08   -1.563D-08   -4.687D-10     2.99777        0.8173
2.463D 00   -1.715D-08   -1.680D-08   -3.461D-10     2.05983        0.8145
2.571D 00   -1.767D-08   -1.780D-08    1.286D-10    -0.72241        0.8119
2.762D 00   -1.821D-08   -1.957D-08    1.351D-09    -6.90284        0.8067
2.915D 00   -1.944D-08   -2.098D-08    1.542D-09    -7.34897        0.8022
3.106D 00   -2.035D-08   -2.273D-08    2.380D-09   -10.46990        0.7963
3.311D 00   -2.185D-08   -2.463D-08    2.781D-09   -11.29302        0.7896
3.497D 00   -2.389D-08   -2.634D-08    2.451D-09    -9.30641        0.7834
3.731D 00   -2.562D-08   -2.851D-08    2.884D-09   -10.11627        0.7752
4.032D 00   -2.777D-08   -3.128D-08    3.508D-09   -11.21480        0.7644
4.255D 00   -3.021D-08   -3.334D-08    3.126D-09    -9.37707        0.7562
4.545D 00   -3.259D-08   -3.602D-08    3.425D-09    -9.50919        0.7453
4.808D 00   -3.579D-08   -3.844D-08    2.649D-09    -6.89221        0.7353
5.208D 00   -3.968D-08   -4.213D-08    2.458D-09    -5.83320        0.7199
5.495D 00   -4.215D-08   -4.477D-08    2.624D-09    -5.86056        0.7087
5.917D 00   -4.674D-08   -4.867D-08    1.937D-09    -3.98021        0.6920
6.250D 00   -5.165D-08   -5.175D-08    9.134D-11    -0.17652        0.6788
6.579D 00   -5.814D-08   -5.478D-08   -3.364D-09     6.14142        0.6657
7.143D 00   -6.284D-08   -5.998D-08   -2.856D-09     4.76053        0.6430
7.519D 00   -6.921D-08   -6.345D-08   -5.761D-09     9.07863        0.6279
7.937D 00   -7.264D-08   -6.731D-08   -5.336D-09     7.92825        0.6109


   GOODNESS OF FIT:         GAUSS CRITERION,  OMEGA=  4.243D-18


  CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

       CONSTANT      VALUE        STD DEV    REL STD DEV(PPH)

           C(1)     5.9237D-09   8.0226D-10     13.5433

           C(2)    -9.2271D-09   2.1270D-10     -2.3052
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MN(III)--PERIODATE SYSTEM:  34.12   DETN OF CONSTANT FOR NTA EFFECT        6/8/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.      TIME       ABSORBANCE   DERIVATIVE      SLOPE        WEIGHT

  1     0.43717      0.71400     -0.76689      -0.76800      0.81457
  2     0.45800      0.69200     -0.91215      -1.05600      0.81670
  3     0.47883      0.67500     -1.00113      -0.81600      0.81816
  4     0.49967      0.65200     -1.08644      -1.10400      0.81987
  5     0.52050      0.63300     -1.08827      -0.91200      0.82105
  6     0.54133      0.60500     -1.11681      -1.34400      0.82240
  7     0.56217      0.58400     -1.15438      -1.00800      0.82308
  8     0.58300      0.55800     -1.16238      -1.24800      0.82351
  9     0.60383      0.53800     -1.16470      -0.96000      0.82352
 10     0.62467      0.51000     -1.17639      -1.34400      0.82300
 11     0.64550      0.48600     -1.18524      -1.15200      0.82204
 12     0.66633      0.46200     -1.15844      -1.15200      0.82053
 13     0.68717      0.43900     -1.11273      -1.10400      0.81852
 14     0.70800      0.41300     -1.03019      -1.24800      0.81549
 15     0.72883      0.39600     -0.97768      -0.81600      0.81302
 16     0.74967      0.37400     -0.93648      -1.05600      0.80916
 17     0.77050      0.35700     -0.90610      -0.81600      0.80559
 18     0.79133      0.33800     -0.88824      -0.91200      0.80092
 19     0.81217      0.31900     -0.85281      -0.91200      0.79541
 20     0.83300      0.30000     -0.80403      -0.91200      0.78891
 21     0.85383      0.28500     -0.76113      -0.72000      0.78296
 22     0.87467      0.27000     -0.71435      -0.72000      0.77617
 23     0.89550      0.25600     -0.67118      -0.57600      0.77003
 24     0.91633      0.24000     -0.64486      -0.86400      0.75943
 25     0.93717      0.22900     -0.63153      -0.52800      0.75200
 26     0.95800      0.21500     -0.60069      -0.67200      0.74128

VALUES OF OTHER INPUT PARAMETERS:

NUM=  36   KDROP=  0   TDELT=  2.0833D-02   TSTART=  3.3300D-01

CATIN=  2.2400D-08   ASTART=  0.757   T1=  0.2460   T2=  0.6455
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MN(III)--PERIODATE SYSTEM:  34.12   DETN OF CONSTANT FOR NTA EFFECT        6/8/72

     X          Y(OBS)      Y(CALC)       DEV(Y)     % DEV(Y)     WEIGHT(Y)

1.401D 00  -4.317D-09  -4.904D-09   5.870D-10  -11.97001      0.8146
1.445D 00  -4.464D-09  -5.338D-09   8.742D-10  -16.37676      0.8167
1.481D 00  -4.906D-09  -5.693D-09   7.870D-10  -13.82412      0.8182
1.534D 00  -5.366D-09  -6.202D-09   8.363D-10  -13.48447      0.8199
1.580D 00  -6.273D-09  -6.651D-09   3.779D-10   -5.68252      0.8211
1.653D 00  -7.075D-09  -7.363D-09   2.877D-10   -3.90708      0.8224
1.712D 00  -7.845D-09  -7.942D-09   9.732D-11   -1.22536      0.8231
1.792D 00  -8.852D-09  -8.720D-09  -1.318D-10    1.51117      0.8235
1.859D 00  -9.960D-09  -9.369D-09  -5.909D-10    6.30702      0.8235
1.961D 00  -1.104D-08  -1.036D-08  -6.791D-10    6.55308      0.8230
2.058D 00  -1.220D-08  -1.131D-08  -8.923D-10    7.89146      0.8220
2.165D 00  -1.288D-08  -1.235D-08  -5.357D-10    4.33825      0.8205
2.278D 00  -1.383D-08  -1.345D-08  -3.794D-10    2.81982      0.8185
2.421D 00  -1.539D-08  -1.485D-08  -5.432D-10    3.65762      0.8155
2.525D 00  -1.670D-08  -1.586D-08  -8.345D-10    5.26004      0.8130
2.674D 00  -1.793D-08  -1.731D-08  -6.199D-10    3.58109      0.8092
2.801D 00  -1.905D-08  -1.855D-08  -4.954D-10    2.67029      0.8056
2.959D 00  -1.996D-08  -2.009D-08   1.307D-10   -0.65081      0.8009
3.135D 00  -2.133D-08  -2.180D-08   4.716D-10   -2.16294      0.7954
3.333D 00  -2.321D-08  -2.374D-08   5.316D-10   -2.23933      0.7889
3.509D 00  -2.513D-08  -2.545D-08   3.200D-10   -1.25763      0.7830
3.704D 00  -2.743D-08  -2.735D-08  -7.916D-11    0.28946      0.7762
3.876D 00  -2.989D-08  -2.903D-08  -8.599D-10    2.96234      0.7700
4.167D 00  -3.183D-08  -3.186D-08   2.935D-11   -0.09213      0.7594
4.367D 00  -3.324D-08  -3.381D-08   5.688D-10   -1.68222      0.7520
4.651D 00  -3.572D-08  -3.658D-08   8.565D-10   -2.34137      0.7413


   GOODNESS OF FIT:        GAUSS CRITERION,  OMEGA=  2.933D-19


  CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

       CONSTANT      VALUE        STD DEV   REL STD DEV(PPH)

          C(1)     8.7439D-09   3.3668D-10      3.8504

          C(2)    -9.7448D-09   1.2354D-10     -1.2678
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MN(III)--PERIODATE SYSTEM:  34.13   DETN OF CONSTANT FOR NTA EFFECT       6/8/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.       TIME      ABSORBANCE   DERIVATIVE      SLOPE         WEIGHT

  1     0.18747     0.74700     -0.32179     -0.14400       0.81088
  2     0.20830     0.74000     -0.46345     -0.33600       0.81171
  3     0.22913     0.72700     -0.60542     -0.62400       0.81319
  4     0.24997     0.71100     -0.71838     -0.76800       0.81487
  5     0.27080     0.69600     -0.79328     -0.72000       0.81633
  6     0.29163     0.68000     -0.83750     -0.76800       0.81774
  7     0.31247     0.66200     -0.85045     -0.86400       0.81916
  8     0.33330     0.64500     -0.86919     -0.81600       0.82033
  9     0.35413     0.62500     -0.89054     -0.96000       0.82149
 10     0.37497     0.60600     -0.88723     -0.91200       0.82236
 11     0.39580     0.59000     -0.88450     -0.76800       0.82291
 12     0.41663     0.57000     -0.89842     -0.96000       0.82337
 13     0.43747     0.55100     -0.92347     -0.91200       0.82355
 14     0.45830     0.53300     -0.94239     -0.86400       0.82347
 15     0.47913     0.51200     -0.96742     -1.00800       0.82306
 16     0.49997     0.49100     -0.97063     -1.00800       0.82228
 17     0.52080     0.47100     -0.96893     -0.96000       0.82116
 18     0.54163     0.45300     -0.96424     -0.86400       0.81981
 19     0.56247     0.43000     -0.96252     -1.10400       0.81757
 20     0.58330     0.41200     -0.94203     -0.86400       0.81535
 21     0.60413     0.39300     -0.91827     -0.91200       0.81254
 22     0.62497     0.37200     -0.88541     -1.00800       0.80876
 23     0.64580     0.35400     -0.83144     -0.86400       0.80490
 24     0.66663     0.34000     -0.82162     -0.67200       0.80145
 25     0.68747     0.32100     -0.79290     -0.91200       0.79603
 26     0.70830     0.30500     -0.78578     -0.76800       0.79075
 27     0.72913     0.29000     -0.77898     -0.72000       0.78503
 28     0.74997     0.27100     -0.74992     -0.91200       0.77665
 29     0.77080     0.25800     -0.70674     -0.62400       0.77003
 30     0.79163     0.24200     -0.68973     -0.76800       0.76070
 31     0.81247     0.23000     -0.66495     -0.57600       0.75271
 32     0.83330     0.21600     -0.63300     -0.67200       0.74209
 33     0.85413     0.20200     -0.61548     -0.67200       0.72983
 34     0.87497     0.18900     -0.57542     -0.62400       0.71664

VALUES OF OTHER INPUT PARAMETERS:

NUM=  44   KORDP=  0   TDELT=  2.0833D-02   TSTART=  8.3300D-02

CATIN=  2.2400D-08   ASTART=  0.760   T1=  0.0280   T2=  0.5000
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MN(III)--PERIODATE SYSTEM:  34.13   DETN OF CONSTANT FOR NTA EFFECT       6/8/72

     X          Y(OBS)      Y(CALC)       DEV(Y)     % DEV(Y)     WEIGHT(Y)

1.339D 00  -3.973D-09  -4.620D-09   6.468D-10  -13.99999        0.8109
1.351D 00  -3.527D-09  -4.718D-09   1.191D-09  -25.25238        0.8117
1.376D 00  -3.360D-09  -4.905D-09   1.546D-09  -31.50987        0.8132
1.406D 00  -3.448D-09  -5.145D-09   1.697D-09  -32.97842        0.8149
1.437D 00  -3.736D-09  -5.380D-09   1.643D-09  -30.54769        0.8163
1.471D 00  -4.172D-09  -5.641D-09   1.469D-09  -26.04097        0.8177
1.511D 00  -4.784D-09  -5.951D-09   1.167D-09  -19.61399        0.8192
1.550D 00  -5.391D-09  -6.259D-09   8.680D-10  -13.86669        0.8203
1.600D 00  -6.005D-09  -6.644D-09   6.388D-10   -9.61515        0.8215
1.650D 00  -6.822D-09  -7.032D-09   2.103D-10   -2.99008        0.8224
1.695D 00  -7.689D-09  -7.379D-09  -3.107D-10    4.21025        0.8229
1.754D 00  -8.452D-09  -7.839D-09  -6.128D-10    7.81745        0.8234
1.815D 00  -9.128D-09  -8.308D-09  -8.202D-10    9.87308        0.8235
1.876D 00  -9.878D-09  -8.783D-09  -1.096D-09   12.47581        0.8235
1.953D 00  -1.058D-08  -9.378D-09  -1.198D-09   12.77842        0.8231
2.037D 00  -1.154D-08  -1.003D-08  -1.513D-09   15.08825        0.8223
2.123D 00  -1.204D-08  -1.070D-08  -1.345D-09   12.57316        0.8212
2.208D 00  -1.258D-08  -1.135D-08  -1.234D-09   10.87271        0.8198
2.326D 00  -1.309D-08  -1.226D-08  -8.268D-10    6.74248        0.8176
2.427D 00  -1.387D-08  -1.305D-08  -8.200D-10    6.28342        0.8154
2.545D 00  -1.474D-08  -1.396D-08  -7.784D-10    5.57630        0.8125
2.688D 00  -1.581D-08  -1.507D-08  -7.399D-10    4.90925        0.8088
2.825D 00  -1.740D-08  -1.613D-08  -1.269D-09    7.86643        0.8049
2.941D 00  -1.817D-08  -1.703D-08  -1.144D-09    6.71666        0.8014
3.115D 00  -1.944D-08  -1.838D-08  -1.057D-09    5.75283        0.7960
3.279D 00  -2.019D-08  -1.964D-08  -5.467D-10    2.78319        0.7907
3.448D 0C  -2.097D-08  -2.096D-08  -8.858D-12    0.04227        0.7850
3.690D 00  -2.240D-08  -2.283D-08   4.289D-10   -1.87867        0.7766
3.876D 00  -2.443D-08  -2.427D-08  -1.601D-10    0.65954        0.7700
4.132D 00  -2.571D-08  -2.625D-08   5.453D-10   -2.07681        0.7607
4.348D 00  -2.737D-08  -2.792D-08   5.553D-10   -1.98859        0.7527
4.630D 00  -2.949D-08  -3.011D-08   6.189D-10   -2.05583        0.7421
4.950D 00  -3.109D-08  -3.259D-08   1.506D-09   -4.62177        0.7298
5.291D 00  -3.406D-08  -3.523D-08   1.169D-09   -3.31695        0.7166


   GOODNESS OF FIT:        GAUSS CRITERION,  OMEGA=  8.949D-19


   CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

        CONSTANT      VALUE        STD DEV    REL STD DEV(PPH)

          C(1)     5.7477D-09   4.4950D-10       7.8206

          C(2)    -7.7446D-09   1.6384D-10      -2.1156
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MN(III)--PERIODATE SYSTEM:  34.14   DETN OF CONSTANT FOR NTA EFFECT        6/8/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.       TIME     ABSORBANCE   DERIVATIVE     SLOPE        WEIGHT

  1     0.56217     0.74200     -0.21585     -0.24000     0.81146
  2     0.58300     0.73600     -0.30090     -0.28800     0.81218
  3     0.60383     0.73100     -0.42270     -0.24000     0.81274
  4     0.62467     0.71900     -0.54277     -0.57600     0.81405
  5     0.64550     0.70900     -0.66540     -0.48000     0.81508
  6     0.66633     0.69200     -0.77708     -0.81600     0.81670
  7     0.68717     0.67300     -0.86070     -0.91200     0.81832
  8     0.70800     0.65700     -0.92485     -0.76800     0.81952
  9     0.72883     0.63700     -0.89454     -0.96000     0.82082
 10     0.74967     0.61800     -0.88767     -0.91200     0.82183
 11     0.77050     0.59800     -0.89970     -0.96000     0.82266
 12     0.79133     0.57900     -0.93940     -0.91200     0.82320
 13     0.81217     0.56800     -0.99269     -0.52800     0.82340
 14     0.83300     0.53600     -1.05218     -1.53600     0.82350
 15     0.85383     0.51800     -1.09399     -0.86400     0.82321
 16     0.87467     0.49300     -1.11715     -1.20000     0.82237
 17     0.89550     0.47000     -1.08114     -1.10400     0.82109
 18     0.91633     0.45000     -1.00709     -0.96000     0.81955
 19     0.93717     0.42800     -1.00846     -1.05600     0.81734
 20     0.95800     0.40700     -0.96308     -1.00800     0.81466
 21     0.97883     0.38900     -0.94496     -0.86400     0.81187
 22     0.99967     0.36800     -0.93630     -1.00800     0.80796
 23     1.02050     0.34900     -0.90245     -0.91200     0.80372
 24     1.04133     0.33100     -0.85836     -0.86400     0.79899
 25     1.06217     0.31300     -0.82289     -0.86400     0.79347
 26     1.08300     0.29500     -0.76882     -0.86400     0.78701
 27     1.10383     0.28200     -0.74310     -0.62400     0.78167
 28     1.12467     0.26700     -0.71151     -0.72000     0.77469
 29     1.14550     0.25000     -0.68102     -0.81600     0.76554
 30     1.16633     0.23800     -0.66056     -0.57600     0.75814
 31     1.18717     0.22300     -0.62318     -0.72000     0.74759
 32     1.20800     0.21200     -0.56305     -0.52800     0.73877
 33     1.22883     0.20000     -0.52634     -0.57600     0.72792
 34     1.24967     0.18900     -0.48124     -0.52800     0.71664
 35     1.27050     0.18100     -0.43773     -0.38400     0.70750
 36     1.29133     0.17100     -0.40830     -0.48000     0.69478
 37     1.31217     0.16200     -0.37930     -0.43200     0.68190
 38     1.33300     0.15700     -0.36912     -0.24000     0.67407


VALUES OF OTHER INPUT PARAMETERS:

NUM=  48   KORDP=  0   TDELT=  2.0833D-02   TSTART=  4.5800D-01

CATIN=  2.2400D-08   ASTART=  0.760   T1=  0.4170   T2=  0.8747
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MN(III)--PERIODATE SYSTEM:  34.14   DETN OF CONSTANT FOR NTA EFFECT        6/8/72

     X          Y(OBS)      Y(CALC)       DEV(Y)      % DEV(Y)    WEIGHT(Y)

1.348D 00   -9.132D-09   -6.966D-09   -2.166D-09    31.09213       0.8115
1.359D 00   -8.566D-09   -7.111D-09   -1.455D-09    20.45328       0.8122
1.368D 00   -7.724D-09   -7.234D-09   -4.900D-10     6.77305       0.8127
1.391D 00   -7.432D-09   -7.536D-09    1.043D-10    -1.38365       0.8140
1.410D 00   -7.340D-09   -7.796D-09    4.560D-10    -5.84958       0.8151
1.445D 00   -7.483D-09   -8.254D-09    7.709D-10    -9.33921       0.8167
1.486D 00   -7.932D-09   -8.794D-09    8.612D-10    -9.79355       0.8183
1.522D 00   -8.565D-09   -9.272D-09    7.076D-10    -7.63098       0.8195
1.570D 00   -1.017D-08   -9.904D-09   -2.639D-10     2.66458       0.8208
1.618D 00   -1.166D-08   -1.054D-08   -1.119D-09    10.61620       0.8218
1.672D 00   -1.299D-08   -1.126D-08   -1.734D-09    15.39927       0.8227
1.727D 00   -1.395D-08   -1.198D-08   -1.969D-09    16.42910       0.8232
1.761D 00   -1.471D-08   -1.243D-08   -2.288D-09    18.41243       0.8234
1.866D 00   -1.538D-08   -1.382D-08   -1.568D-09    11.35138       0.8235
1.931D 00   -1.632D-08   -1.467D-08   -1.642D-09    11.19108       0.8232
2.028D 00   -1.754D-08   -1.597D-08   -1.570D-09     9.82901       0.8224
2.128D 00   -1.855D-08   -1.728D-08   -1.273D-09     7.36382       0.8211
2.222D 00   -2.038D-08   -1.853D-08   -1.850D-09     9.98061       0.8196
2.336D 00   -2.082D-08   -2.004D-08   -7.740D-10     3.86165       0.8173
2.457D 00   -2.228D-08   -2.164D-08   -6.450D-10     2.98122       0.8147
2.571D 00   -2.320D-08   -2.314D-08   -6.248D-11     0.26998       0.8119
2.717D 00   -2.392D-08   -2.508D-08    1.165D-09    -4.64326       0.8080
2.865D 00   -2.533D-08   -2.704D-08    1.707D-09    -6.31356       0.8037
3.021D 00   -2.717D-08   -2.910D-08    1.923D-09    -6.60833       0.7990
3.195D 00   -2.891D-08   -3.140D-08    2.482D-09    -7.90629       0.7935
3.390D 00   -3.155D-08   -3.397D-08    2.420D-09    -7.12304       0.7870
3.546D 00   -3.327D-08   -3.604D-08    2.766D-09    -7.67556       0.7817
3.745D 00   -3.541D-08   -3.868D-08    3.268D-09    -8.44940       0.7747
4.000D 00   -3.768D-08   -4.204D-08    4.366D-09   -10.38353       0.7655
4.202D 00   -3.955D-08   -4.471D-08    5.160D-09   -11.53986       0.7581
4.484D 00   -4.267D-08   -4.845D-08    5.776D-09   -11.92215       0.7476
4.717D 00   -4.806D-08   -5.153D-08    3.467D-09    -6.72927       0.7388
5.000D 00   -5.230D-08   -5.527D-08    2.972D-09    -5.37725       0.7279
5.291D 00   -5.817D-08   -5.912D-08    9.498D-10    -1.60656       0.7166
5.525D 00   -6.502D-08   -6.221D-08   -2.806D-09     4.51069       0.7075
5.848D 00   -7.084D-08   -6.648D-08   -4.362D-09     6.56091       0.6948
6.173D 00   -7.749D-08   -7.078D-08   -6.712D-09     9.48244       0.6819
6.369D 00   -8.089D-08   -7.338D-08   -7.514D-09    10.23926       0.6741


   GOODNESS OF FIT:       GAUSS CRITERION,  OMEGA=  6.196D-18


  CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

      CONSTANT      VALUE        STD DEV    REL STD DEV(PPH)

         C(1)     1.0858D-08   9.8645D-10       9.0854

         C(2)    -1.3225D-08   3.0751D-10      -2.3252
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MN(II)--PERIODATE SYSTEM:  35.13   DETN OF CONSTANT FOR NTA EFFECT        6/8/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.        TIME      ABSORBANCE   DERIVATIVE      SLOPE        WEIGHT

  1      0.64617      0.59000      -0.50564      -0.24000      0.82291
  2      0.66700      0.57600      -0.69909      -0.67200      0.82326
  3      0.68783      0.55700      -0.83443      -0.91200      0.82352
  4      0.70867      0.54000      -0.93276      -0.81600      0.82353
  5      0.72950      0.51800      -0.95431      -1.05600      0.82321
  6      0.75033      0.50000      -0.97471      -0.86400      0.82266
  7      0.77117      0.48100      -0.96180      -0.91200      0.82177
  8      0.79200      0.45800      -0.99735      -1.10400      0.82022
  9      0.81283      0.44100      -1.02369      -0.81600      0.81872
 10      0.83367      0.41400      -1.02415      -1.29600      0.81562
 11      0.85450      0.40000      -0.97694      -0.67200      0.81364
 12      0.87533      0.37200      -0.94746      -1.34400      0.80876
 13      0.89617      0.35600      -0.91457      -0.76800      0.80536
 14      0.91700      0.34100      -0.83424      -0.72000      0.80171
 15      0.93783      0.32200      -0.81059      -0.91200      0.79634
 16      0.95867      0.30200      -0.75081      -0.96000      0.78965
 17      0.97950      0.29000      -0.74634      -0.57600      0.78503
 18      1.00033      0.27700      -0.68065      -0.62400      0.77945
 19      1.02117      0.25900      -0.62307      -0.86400      0.77056
 20      1.04200      0.24800      -0.58957      -0.52800      0.76436
 21      1.06283      0.23600      -0.57645      -0.57600      0.75682
 22      1.08367      0.22600      -0.55052      -0.48000      0.74983
 23      1.10450      0.21300      -0.52659      -0.62400      0.73962
 24      1.12533      0.20300      -0.52432      -0.48000      0.73077
 25      1.14617      0.19100      -0.48870      -0.57600      0.71880
 26      1.16700      0.18100      -0.44901      -0.48000      0.70750
 27      1.18783      0.17400      -0.39153      -0.33600      0.69876
 28      1.20867      0.16500      -0.36173      -0.43200      0.68636
 29      1.22950      0.15800      -0.34405      -0.33600      0.67567
 30      1.25033      0.15100      -0.34711      -0.33600      0.66395
 31      1.27117      0.14500      -0.35179      -0.28800      0.65295
 32      1.29200      0.13600      -0.33678      -0.43200      0.63456
 33      1.31283      0.12900      -0.31653      -0.33600      0.61841

VALUES OF OTHER INPUT PARAMETERS:

NUM=  43   KDROP=  0   TDELT=  2.0833D-02   TSTART=  5.4200D-01

CATIN=  2.2400D-08   ASTART=  0.610   T1=  0.4580   T2=  0.8337
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MN(II)--PERIODATE SYSTEM:  35.13   DETN OF CONSTANT FOR NTA EFFECT        6/6/72

     X          Y(OBS)      Y(CALC)       DEV(Y)      % DEV(Y)    WEIGHT(Y)

1.695D 00   -9.266D-09   -6.790D-09   -2.476D-09     36.46654        0.8229
1.736D 00   -8.268D-09   -7.378D-09   -8.902D-10     12.06602        0.8233
1.795D 00   -8.377D-09   -8.223D-09   -1.537D-10      1.86910        0.8235
1.852D 00   -8.914D-09   -9.030D-09    1.160D-10     -1.28477        0.8235
1.931D 00   -1.022D-08   -1.015D-08   -6.840D-11      0.67378        0.8232
2.000D 00   -1.160D-08   -1.114D-08   -4.572D-10      4.10213        0.8227
2.079D 00   -1.349D-08   -1.227D-08   -1.221D-09      9.94769        0.8218
2.183D 00   -1.480D-08   -1.376D-08   -1.038D-09      7.54522        0.8202
2.268D 00   -1.627D-08   -1.496D-08   -1.311D-09      8.76238        0.8187
2.415D 00   -1.823D-08   -1.707D-08   -1.159D-09      6.79006        0.8156
2.500D 00   -1.959D-08   -1.828D-08   -1.311D-09      7.17370        0.8136
2.688D 00   -2.069D-08   -2.097D-08    2.722D-10     -1.29838        0.8088
2.809D 00   -2.195D-08   -2.269D-08    7.423D-10     -3.27139        0.8054
2.933D 00   -2.462D-08   -2.446D-08   -1.671D-10      0.68312        0.8017
3.106D 00   -2.592D-08   -2.692D-08    1.009D-09     -3.74690        0.7963
3.311D 00   -2.860D-08   -2.986D-08    1.259D-09     -4.21708        0.7896
3.448D 00   -2.940D-08   -3.182D-08    2.419D-09     -7.60158        0.7850
3.610D 00   -3.292D-08   -3.413D-08    1.206D-09     -3.53323        0.7795
3.861D 00   -3.671D-08   -3.771D-08    9.954D-10     -2.63971        0.7706
4.032D 00   -3.959D-08   -4.015D-08    5.621D-10     -1.39999        0.7644
4.237D 00   -4.130D-08   -4.308D-08    1.778D-09     -4.12755        0.7568
4.425D 00   -4.409D-08   -4.575D-08    1.661D-09     -3.63080        0.7498
4.695D 00   -4.698D-08   -4.961D-08    2.626D-09     -5.29412        0.7396
4.926D 00   -4.808D-08   -5.291D-08    4.834D-09     -9.13535        0.7308
5.236D 00   -5.254D-08   -5.733D-08    4.792D-09     -8.35935        0.7188
5.525D 00   -5.822D-08   -6.146D-08    3.237D-09     -5.26795        0.7075
5.747D 00   -6.796D-08   -6.463D-08   -3.329D-09      5.15167        0.6988
6.061D 00   -7.485D-08   -6.910D-08   -5.742D-09      8.30890        0.6864
6.329D 00   -8.005D-08   -7.294D-08   -7.113D-09      9.75297        0.6757
6.623D 00   -8.069D-08   -7.712D-08   -3.565D-09      4.62203        0.6639
6.897D 00   -8.094D-08   -8.104D-08    9.379D-11     -0.11574        0.6530
7.353D 00   -8.593D-08   -8.755D-08    1.617D-09     -1.84672        0.6346
7.752D 00   -9.291D-08   -9.324D-08    3.396D-10     -0.36418        0.6184

    GOODNESS OF FIT:        GAUSS CRITERION,  OMEGA=  4.727D-18

   CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

         CONSTANT      VALUE        STD DEV   REL STD DEV(PPH)

           C(1)     1.7403D-08   1.0225D-09       5.8754

           C(2)    -1.4274D-08   2.4803D-10      -1.7377
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MN(II)--PERIODATE SYSTEM:  35.14   DETN OF CONSTANT FOR NTA EFFECT        6/8/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.       TIME      ABSORBANCE   DERIVATIVE      SLOPE        WEIGHT

 1       0.60417     0.58300     -0.55578      -0.48000      0.82310
 2       0.62500     0.56800     -0.73645      -0.72000      0.82340
 3       0.64583     0.55000     -0.87354      -0.86400      0.82355
 4       0.66667     0.53300     -0.93797      -0.81600      0.82347
 5       0.68750     0.51000     -0.98179      -1.10400      0.82300
 6       0.70833     0.49100     -0.99600      -0.91200      0.82228
 7       0.72917     0.47100     -1.02882      -0.96000      0.82116
 8       0.75000     0.45000     -1.05243      -1.00800      0.81955
 9       0.77083     0.42500     -1.06214      -1.20000      0.81699
10       0.79167     0.40600     -1.04727      -0.91200      0.81452
11       0.81250     0.38100     -1.02340      -1.20000      0.81047
12       0.83333     0.36200     -0.98224      -0.91200      0.80670
13       0.85417     0.34200     -0.93396      -0.96000      0.80197
14       0.87500     0.32500     -0.91182      -0.81600      0.79725
15       0.89583     0.30200     -0.87390      -1.10400      0.78965
16       0.91667     0.28700     -0.85219      -0.72000      0.78380
17       0.93750     0.27000     -0.79327      -0.81600      0.77617
18       0.95833     0.25200     -0.73526      -0.86400      0.76669
19       0.97917     0.23800     -0.67197      -0.67200      0.75814
20       1.00000     0.22500     -0.64423      -0.62400      0.74909
21       1.02083     0.21300     -0.58476      -0.57600      0.73962
22       1.04167     0.20000     -0.54610      -0.62400      0.72792
23       1.06250     0.18900     -0.51287      -0.52800      0.71664
24       1.08333     0.17800     -0.48763      -0.52800      0.70384
25       1.10417     0.17000     -0.44792      -0.38400      0.69342
26       1.12500     0.16000     -0.41369      -0.48000      0.67883
27       1.14583     0.15200     -0.39546      -0.38400      0.66569
28       1.16667     0.14200     -0.39664      -0.48000      0.64709
29       1.18750     0.13700     -0.37865      -0.24000      0.63672
30       1.20833     0.12800     -0.36405      -0.43200      0.61595


VALUES OF OTHER INPUT PARAMETERS:

NUM=  40   KDROP=  0   TDELT=  2.0833D-02   TSTART=  5.0000D-01

CATIN=  2.2400D-08   ASTART=  0.610   T1=  0.4580   T2=  0.7708
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MN(II)--PERIODATE SYSTEM:  35.14   DETN OF CONSTANT FOR NTA EFFECT        6/8/72


    X           Y(OBS)      Y(CALC)       DEV(Y)      % DEV(Y)    WEIGHT(Y)

1.715D 00  -6.782D-09  -6.638D-09  -1.444D-10     2.17511        0.8231
1.761D 00  -6.681D-09  -7.147D-09   4.654D-10    -6.51145        0.8234
1.818D 00  -7.126D-09  -7.794D-09   6.682D-10    -8.57289        0.8235
1.876D 00  -8.190D-09  -8.446D-09   2.554D-10    -3.02376        0.8235
1.961D 00  -9.465D-09  -9.396D-09  -6.890D-11     0.73323        0.8230
2.037D 00  -1.110D-08  -1.025D-08  -8.522D-10     8.31544        0.8223
2.123D 00  -1.261D-08  -1.122D-08  -1.390D-09    12.38529        0.8212
2.222D 00  -1.429D-08  -1.233D-08  -1.961D-09    15.89638        0.8196
2.353D 00  -1.626D-08  -1.380D-08  -2.454D-09    17.78350        0.8170
2.463D 00  -1.693D-08  -1.504D-08  -1.894D-09    12.59184        0.8145
2.625D 00  -1.778D-08  -1.685D-08  -9.291D-10     5.51215        0.8105
2.762D 00  -1.900D-08  -1.840D-08  -6.016D-10     3.26933        0.8067
2.924D 00  -2.049D-08  -2.022D-08  -2.688D-10     1.32944        0.8020
3.077D 00  -2.150D-08  -2.194D-08   4.404D-10    -2.00776        0.7972
3.311D 00  -2.296D-08  -2.457D-08   1.606D-09    -6.53834        0.7896
3.484D 00  -2.409D-08  -2.651D-08   2.418D-09    -9.11991        0.7838
3.704D 00  -2.647D-08  -2.898D-08   2.505D-09    -8.64386        0.7762
3.968D 00  -2.920D-08  -3.195D-08   2.753D-09    -8.61805        0.7667
4.202D 00  -3.264D-08  -3.457D-08   1.932D-09    -5.58813        0.7581
4.444D 00  -3.477D-08  -3.730D-08   2.530D-09    -6.78172        0.7491
4.695D 00  -3.910D-08  -4.011D-08   1.008D-09    -2.51287        0.7396
5.000D 00  -4.273D-08  -4.354D-08   8.137D-10    -1.86886        0.7279
5.291D 00  -4.641D-08  -4.681D-08   4.047D-10    -0.86453        0.7166
5.618D 00  -4.976D-08  -5.048D-08   7.191D-10    -1.42444        0.7038
5.882D 00  -5.522D-08  -5.345D-08  -1.765D-09     3.30108        0.6934
6.250D 00  -6.092D-08  -5.758D-08  -3.331D-09     5.78452        0.6788
6.579D 00  -6.490D-08  -6.128D-08  -3.623D-09     5.91264        0.6657
7.042D 00  -6.589D-08  -6.649D-08   5.991D-10    -0.90107        0.6471
7.299D 00  -7.025D-08  -6.937D-08  -8.771D-10     1.26436        0.6367
7.813D 00  -7.435D-08  -7.514D-08   7.894D-10    -1.05055        0.6160


   GOODNESS OF FIT:        GAUSS CRITERION,  OMEGA=  2.185D-18


  CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

      CONSTANT      VALUE         STD DEV   REL STD DEV(PPH)

         C(1)     1.2633D-08   7.1834D-10       5.6864

         C(2)    -1.1235D-08   1.7413D-10      -1.5499
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MN(III)--PERIODATE SYSTEM:  35.15   DETN OF CONSTANT FOR NTA EFFECT        6/8/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.       TIME      ABSORBANCE   DERIVATIVE      SLOPE         WEIGHT

  1     0.60417      0.58500     -0.61001      -0.48000      0.82305
  2     0.62500      0.56900     -0.84418      -0.76800      0.82339
  3     0.64583      0.54800     -1.04086      -1.00800      0.82355
  4     0.66667      0.52500     -1.16972      -1.10400      0.82336
  5     0.68750      0.50100     -1.24427      -1.15200      0.82270
  6     0.70833      0.47100     -1.27656      -1.44000      0.82116
  7     0.72917      0.44800     -1.25727      -1.10400      0.81938
  8     0.75000      0.42200     -1.19606      -1.24800      0.81664
  9     0.77083      0.39500     -1.16394      -1.29600      0.81286
 10     0.79167      0.37200     -1.13924      -1.10400      0.80876
 11     0.81250      0.35200     -1.11571      -0.96000      0.80444
 12     0.83333      0.32900     -1.08117      -1.10400      0.79842
 13     0.85417      0.30100     -1.03481      -1.34400      0.78928
 14     0.87500      0.28300     -0.99352      -0.86400      0.78211
 15     0.89583      0.26500     -0.92572      -0.86400      0.77369
 16     0.91667      0.24400     -0.82416      -1.00800      0.76194
 17     0.93750      0.23000     -0.74730      -0.67200      0.75271
 18     0.95833      0.21200     -0.70885      -0.86400      0.73877
 19     0.97917      0.19900     -0.66137      -0.62400      0.72695
 20     1.00000      0.18800     -0.62310      -0.52800      0.71554
 21     1.02083      0.17400     -0.59704      -0.67200      0.69876
 22     1.04167      0.16100     -0.53368      -0.62400      0.68037
 23     1.06250      0.14900     -0.49444      -0.57600      0.66038
 24     1.08333      0.14100     -0.44124      -0.38400      0.64508
 25     1.10417      0.13300     -0.39414      -0.38400      0.62785


VALUES OF OTHER INPUT PARAMETERS:

NUM=  35   KDROP=  0   TDELT=  2.0833D-02   TSTART=  5.0000D-01

CATIN=  2.2400D-08   ASTART=  0.610   T1=  0.4760   T2=  0.7083
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MN(III)--PERIODATE SYSTEM:  35.15   DETN OF CONSTANT FOR NTA EFFECT        6/8/72


    X           Y(OBS)      Y(CALC)       DEV(Y)     % DEV(Y)     WEIGHT(Y)

1.709D 00  -7.915D-09  -6.933D-09  -9.825D-10    14.17113        0.8231
1.757D 00  -7.730D-09  -7.336D-09  -3.946D-10     5.37947        0.8234
1.825D 00  -8.145D-09  -7.900D-09  -2.453D-10     3.10493        0.8236
1.905D 00  -9.135D-09  -8.570D-09  -5.653D-10     6.59625        0.8234
1.996D 00  -1.057D-08  -9.335D-09  -1.233D-09    13.20344        0.8227
2.123D 00  -1.243D-08  -1.040D-08  -2.029D-09    19.50784        0.8212
2.232D 00  -1.299D-08  -1.131D-08  -1.677D-09    14.82495        0.8194
2.370D 00  -1.405D-08  -1.247D-08  -1.580D-09    12.67207        0.8166
2.532D 00  -1.483D-08  -1.382D-08  -1.011D-09     7.31230        0.8129
2.688D 00  -1.557D-08  -1.514D-08  -4.303D-10     2.84297        0.8088
2.841D 00  -1.631D-08  -1.642D-08   1.033D-10    -0.62906        0.8044
3.040D 00  -1.727D-08  -1.808D-08   8.149D-10    -4.50691        0.7984
3.322D 00  -1.849D-08  -2.045D-08   1.960D-09    -9.58449        0.7893
3.534D 00  -1.973D-08  -2.222D-08   2.493D-09   -11.21862        0.7821
3.774D 00  -2.168D-08  -2.423D-08   2.555D-09   -10.54494        0.7737
4.098D 00  -2.491D-08  -2.695D-08   2.040D-09    -7.56746        0.7619
4.348D 00  -2.810D-08  -2.904D-08   9.436D-10    -3.24874        0.7527
4.717D 00  -3.028D-08  -3.214D-08   1.855D-09    -5.77078        0.7388
5.025D 00  -3.316D-08  -3.472D-08   1.558D-09    -4.48579        0.7270
5.319D 00  -3.595D-08  -3.718D-08   1.236D-09    -3.32266        0.7155
5.747D 00  -3.830D-08  -4.077D-08   2.471D-09    -6.06164        0.6988
6.211D 00  -4.372D-08  -4.466D-08   9.392D-10    -2.10293        0.6804
6.711D 00  -4.813D-08  -4.885D-08   7.182D-10    -1.47010        0.6604
7.092D 00  -5.500D-08  -5.204D-08  -2.952D-09     5.67221        0.6451
7.519D 00  -6.275D-08  -5.562D-08  -7.134D-09    12.82603        0.6279


   GOODNESS OF FIT:        GAUSS CRITERION,  OMEGA=  3.334D-18


  CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

      CONSTANT      VALUE         STD DEV    REL STD DEV(PPH)

        C(1)      7.3930D-09    9.7592D-10       13.2005

        C(2)     -8.3807D-09    2.4263D-10       -2.8952
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MN(III)--PERIODATE SYSTEM:  35.16   DETN OF CONSTANT FOR NTA EFFECT          6/8/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.       TIME      ABSORBANCE   DERIVATIVE      SLOPE        WEIGHT

  1     0.43717      0.59200     -0.42946      -0.33600      0.82285
  2     0.45800      0.57900     -0.56348      -0.62400      0.82320
  3     0.47883      0.56600     -0.70198      -0.62400      0.82343
  4     0.49967      0.54800     -0.81660      -0.86400      0.82355
  5     0.52050      0.53500     -0.87611      -0.62400      0.82349
  6     0.54133      0.51500     -0.92139      -0.96000      0.82314
  7     0.56217      0.49300     -0.94146      -1.05600      0.82237
  8     0.58300      0.47300     -0.93340      -0.96000      0.82129
  9     0.60383      0.45600     -0.92354      -0.81600      0.82006
 10     0.62467      0.43600     -0.90244      -0.96000      0.81821
 11     0.64550      0.41900     -0.91119      -0.81600      0.81627
 12     0.66633      0.39900     -0.92523      -0.96000      0.81348
 13     0.68717      0.37900     -0.92154      -0.96000      0.81010
 14     0.70800      0.35900     -0.89102      -0.96000      0.80604
 15     0.72883      0.34200     -0.86008      -0.81600      0.80197
 16     0.74967      0.32500     -0.81616      -0.81600      0.79725
 17     0.77050      0.30800     -0.79264      -0.81600      0.79178
 18     0.79133      0.29200     -0.75213      -0.76800      0.78583
 19     0.81217      0.27600     -0.73077      -0.76800      0.77899
 20     0.83300      0.26100     -0.69164      -0.72000      0.77162
 21     0.85383      0.24700     -0.65391      -0.67200      0.76377
 22     0.87467      0.23600     -0.61922      -0.52800      0.75682
 23     0.89550      0.22000     -0.59591      -0.76800      0.74528
 24     0.91633      0.21000     -0.57318      -0.48000      0.73706
 25     0.93717      0.19800     -0.53794      -0.57600      0.72597
 26     0.95800      0.18700     -0.50022      -0.52800      0.71443
 27     0.97883      0.17600     -0.45473      -0.52800      0.70133
 28     0.99967      0.16800     -0.42642      -0.38400      0.69065
 29     1.02050      0.16000     -0.38521      -0.38400      0.67883
 30     1.04133      0.15100     -0.37144      -0.43200      0.66395
 31     1.06217      0.14400     -0.36900      -0.33600      0.65103
 32     1.08300      0.13700     -0.36291      -0.33600      0.63672
 33     1.10383      0.12900     -0.34684      -0.38400      0.61841

VALUES OF OTHER INPUT PARAMETERS:

NUM=  43   KDRUP=  0   TDELT=  2.0833D-02   TSTART=  3.3300D-01

CATIN=  2.2400D-08   ASTART=  0.610   T1=  0.3040   T2=  0.5622
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MN(III)--PERIODATE SYSTEM:  35.16   DETN OF CONSTANT FOR NTA EFFECT         6/8/72

     X           Y(OBS)      Y(CALC)       DEV(Y)     % DEV(Y)     WEIGHT(Y)

1.689D 00   -7.802D-09  -7.246D-09  -5.558D-10    7.67132        0.8229
1.727D 00   -7.952D-09  -7.640D-09  -3.121D-10    4.08527        0.8232
1.767D 00   -8.227D-09  -8.052D-09  -1.748D-10    2.17124        0.8234
1.825D 00   -8.458D-09  -8.655D-09  -2.029D-10    2.34446        0.8236
1.869D 00   -1.011D-08  -9.116D-09  -9.922D-10   10.88404        0.8235
1.942D 00   -1.155D-08  -9.870D-09  -1.680D-09   17.02036        0.8231
2.028D 00   -1.338D-08  -1.077D-08  -2.605D-09   24.18644        0.8224
2.114D 00   -1.399D-08  -1.166D-08  -2.329D-09   19.97290        0.8213
2.193D 00   -1.465D-08  -1.248D-08  -2.165D-09   17.34498        0.8201
2.294D 00   -1.551D-08  -1.353D-08  -1.979D-09   14.63238        0.8182
2.387D 00   -1.587D-08  -1.449D-08  -1.375D-09    9.48995        0.8163
2.506D 00   -1.613D-08  -1.574D-08  -3.958D-10    2.51538        0.8135
2.639D 00   -1.670D-08  -1.711D-08   4.074D-10   -2.38126        0.8101
2.786D 00   -1.780D-08  -1.864D-08   8.391D-10   -4.50187        0.8060
2.924D 00   -1.898D-08  -2.008D-08   1.095D-09   -5.45320        0.8020
3.077D 00   -2.058D-08  -2.167D-08   1.091D-09   -5.03533        0.7972
3.247D 00   -2.177D-08  -2.343D-08   1.656D-09   -7.06890        0.7918
3.425D 00   -2.357D-08  -2.528D-08   1.712D-09   -6.77186        0.7858
3.623D 00   -2.489D-08  -2.734D-08   2.447D-09   -8.95078        0.7790
3.831D 00   -2.698D-08  -2.951D-08   2.528D-09   -8.56709        0.7716
4.049D 00   -2.925D-08  -3.176D-08   2.514D-09   -7.91607        0.7638
4.237D 00   -3.164D-08  -3.372D-08   2.083D-09   -6.17613        0.7568
4.545D 00   -3.366D-08  -3.693D-08   3.264D-09   -8.83995        0.7453
4.762D 00   -3.581D-08  -3.917D-08   3.364D-09   -8.58766        0.7371
5.051D 00   -3.902D-08  -4.217D-08   3.150D-09   -7.46902        0.7260
5.348D 00   -4.290D-08  -4.526D-08   2.361D-09   -5.21655        0.7144
5.682D 00   -4.822D-08  -4.873D-08   5.169D-10   -1.06074        0.7013
5.952D 00   -5.251D-08  -5.155D-08  -9.668D-10    1.87561        0.6906
6.250D 00   -5.934D-08  -5.464D-08  -4.704D-09    8.60879        0.6788
6.623D 00   -6.280D-08  -5.851D-08  -4.289D-09    7.33103        0.6639
6.944D 00   -6.448D-08  -6.185D-08  -2.625D-09    4.24308        0.6510
7.299D 00   -6.685D-08  -6.554D-08  -1.305D-09    1.99132        0.6367
7.752D 00   -7.129D-08  -7.024D-08  -1.043D-09    1.48488        0.6184

    GOODNESS OF FIT:        GAUSS CRITERION,  OMEGA=  3.511D-18

   CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

        CONSTANT      VALUE        STD DEV   REL STD DEV(PPH)

          C(1)     1.0307D-08   8.5769D-10      8.3215

          C(2)    -1.0391D-08   2.1324D-10     -2.0521
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MN(II)--PERIODATE SYSTEM:  NTA ADDED      35.17                        6/6/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.       TIME     ABSORBANCE   DERIVATIVE       SLOPE           WEIGHT

  1      0.60417     0.58200     -0.76233      -0.62400         0.82313
  2      0.62500     0.56200     -0.99640      -0.96000         0.82348
  3      0.64583     0.53800     -1.17809      -1.15200         0.82352
  4      0.66667     0.51300     -1.27927      -1.20000         0.82309
  5      0.68750     0.48400     -1.33958      -1.39200         0.82193
  6      0.70833     0.45800     -1.34196      -1.24800         0.82022
  7      0.72917     0.43000     -1.32615      -1.34400         0.81757
  8      0.75000     0.40200     -1.32929      -1.34400         0.81394
  9      0.77083     0.37300     -1.29514      -1.39200         0.80896
 10      0.79167     0.35000     -1.28062      -1.10400         0.80396
 11      0.81250     0.32200     -1.24769      -1.34400         0.79634
 12      0.83333     0.29400     -1.20309      -1.34400         0.78662
 13      0.85417     0.27400     -1.13029      -0.96000         0.77807
 14      0.87500     0.24700     -1.05142      -1.29600         0.76377
 15      0.89583     0.22700     -0.96569      -0.96000         0.75056
 16      0.91667     0.20900     -0.91144      -0.86400         0.73619
 17      0.93750     0.19200     -0.85357      -0.81600         0.71986
 18      0.95833     0.17300     -0.77238      -0.91200         0.69745
 19      0.97917     0.15600     -0.71875      -0.81600         0.67244
 20      1.00000     0.14300     -0.62840      -0.62400         0.64907
 21      1.02083     0.13200     -0.52634      -0.52800         0.62555
 22      1.04167     0.12100     -0.45419      -0.52800         0.59759
 23      1.06250     0.11200     -0.41551      -0.43200         0.57050
 24      1.08333     0.10500     -0.37965      -0.33600         0.54615
 25      1.10417     0.09700     -0.34526      -0.38400         0.51392
 26      1.12500     0.08800     -0.32355      -0.43200         0.47054


VALUES OF OTHER INPUT PARAMETERS:

NUM=  26   KDROP=  0   TDELT=  2.0833D-02   TSTART=  5.0000D-01

CATIN=  2.2400D-08   ASTART=  0.610   T1=  0.5140   T2=  0.7083
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MN(II)--PERIODATE SYSTEM:  NTA ADDED      35.17                        6/6/72

    X           Y(OBS)      Y(CALC)       DEV(Y)      % DEV(Y)      WEIGHT(Y)

1.718D 00  -4.481D-09  -4.648D-09   1.672D-10    -3.59651        0.8231
1.779D 00  -5.195D-09  -5.076D-09  -1.194D-10     2.35312        0.8235
1.859D 00  -6.198D-09  -5.631D-09  -5.668D-10    10.06563        0.8235
1.949D 00  -7.654D-09  -6.265D-09  -1.389D-09    22.17199        0.8231
2.066D 00  -9.441D-09  -7.083D-09  -2.358D-09    33.29510        0.8219
2.183D 00  -1.182D-08  -7.904D-09  -3.920D-09    49.59334        0.8202
2.326D 00  -1.232D-08  -8.899D-09  -3.418D-09    38.40386        0.8176
2.488D 00  -1.264D-08  -1.003D-08  -2.606D-09    25.97258        0.8139
2.681D 00  -1.333D-08  -1.139D-08  -1.946D-09    17.08700        0.8090
2.857D 00  -1.385D-08  -1.262D-08  -1.228D-09     9.73193        0.8040
3.106D 00  -1.459D-08  -1.436D-08  -2.286D-10     1.59210        0.7963
3.401D 00  -1.552D-08  -1.643D-08   9.128D-10    -5.55644        0.7866
3.650D 00  -1.693D-08  -1.817D-08   1.238D-09    -6.81662        0.7781
4.049D 00  -1.864D-08  -2.096D-08   2.317D-09   -11.05570        0.7638
4.405D 00  -2.078D-08  -2.346D-08   2.676D-09   -11.40691        0.7506
4.785D 00  -2.253D-08  -2.611D-08   3.582D-09   -13.71950        0.7362
5.208D 00  -2.460D-08  -2.908D-08   4.473D-09   -15.38463        0.7199
5.780D 00  -2.779D-08  -3.308D-08   5.287D-09   -15.98183        0.6974
6.410D 00  -3.052D-08  -3.749D-08   6.972D-09   -18.59900        0.6724
6.993D 00  -3.565D-08  -4.157D-08   5.921D-09   -14.24475        0.6491
7.576D 00  -4.344D-08  -4.565D-08   2.201D-09    -4.82261        0.6255
8.264D 00  -5.137D-08  -5.047D-08  -9.070D-10     1.79727        0.5976
8.929D 00  -5.728D-08  -5.511D-08  -2.165D-09     3.92815        0.5705
9.524D 00  -6.392D-08  -5.928D-08  -4.638D-09     7.82455        0.5462
1.031D 01  -7.164D-08  -6.478D-08  -6.859D-09    10.58784        0.5139
1.136D 01  -7.789D-08  -7.216D-08  -5.727D-09     7.93707        0.4705


   GOODNESS OF FIT:        GAUSS CRITERION,  OMEGA=  8.588D-18


  CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

       CONSTANT      VALUE        STD DEV   REL STD DEV(PPH)

         C(1)     7.3783D-09   1.3006D-09       17.6276

         C(2)    -6.9992D-09   2.5240D-10       -3.6061
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MN(III)--PERIODATE SYSTEM:  35.18   DETN OF CONSTANT FOR NTA EFFECT        6/8/72

DETERMINATION OF DERIVATIVE USING 11-POINT CUBIC SMOOTH

NO.       TIME      ABSORBANCE   DERIVATIVE      SLOPE         WEIGHT

  1     0.52117      0.59200      -0.63415     -0.46000       0.82285
  2     0.54200      0.57100      -0.84591     -1.00800       0.82335
  3     0.56283      0.55200      -1.03574     -0.91200       0.82354
  4     0.58367      0.53000      -1.15533     -1.05600       0.82343
  5     0.60450      0.50700      -1.18782     -1.10400       0.82291
  6     0.62533      0.48000      -1.21123     -1.29600       0.82171
  7     0.64617      0.45300      -1.22672     -1.29600       0.81981
  8     0.66700      0.43000      -1.21051     -1.10400       0.81757
  9     0.68783      0.40600      -1.19098     -1.15200       0.81452
 10     0.70867      0.37900      -1.16414     -1.29600       0.81010
 11     0.72950      0.35700      -1.15554     -1.05600       0.80559
 12     0.75033      0.33200      -1.12400     -1.20000       0.79928
 13     0.77117      0.30900      -1.05900     -1.10400       0.79212
 14     0.79200      0.26800      -0.99389     -1.00800       0.78421
 15     0.81283      0.26700      -0.93968     -1.00800       0.77469
 16     0.83367      0.25000      -0.86804     -0.81600       0.76554
 17     0.85450      0.23200      -0.80083     -0.86400       0.75411
 18     0.87533      0.21500      -0.74912     -0.81600       0.74128
 19     0.89617      0.20000      -0.69293     -0.72000       0.72792
 20     0.91700      0.18700      -0.64312     -0.62400       0.71443
 21     0.93783      0.17500      -0.58637     -0.57600       0.70005
 22     0.95867      0.16100      -0.51593     -0.67200       0.68037
 23     0.97950      0.15200      -0.46836     -0.43200       0.66569
 24     1.00033      0.14200      -0.44234     -0.48000       0.64709
 25     1.02117      0.13400      -0.41600     -0.38400       0.63012

VALUES OF OTHER INPUT PARAMETERS:

NUM=  35   KDROP=  0   TDELT=  2.0833D-02   TSTART=  4.1700D-01

CATIN=  2.2400D-08   ASTART=  0.615   T1=  0.3850   T2=  0.6462
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MN(II)--PERIODATE SYSTEM:  35.18   DETN OF CONSTANT FOR NTA EFFECT        6/8/72

    X           Y(OBS)       Y(CALC)       DEV(Y)      % DEV(Y)   WEIGHT(Y)

1.689D 00   -6.204D-09   -5.434D-09   -7.701D-10    14.17012       0.8229
1.751D 00   -6.183D-09   -5.925D-09   -2.584D-10     4.36097       0.8234
1.812D 00   -6.479D-09   -6.401D-09   -7.820D-11     1.22163       0.8235
1.887D 00   -7.249D-09   -6.995D-09   -2.543D-10     3.63520       0.8234
1.972D 00   -8.607D-09   -7.671D-09   -9.364D-10    12.20645       0.8229
2.083D 00   -1.012D-08   -8.547D-09   -1.572D-09    18.39269       0.8217
2.208D 00   -1.180D-08   -9.528D-09   -2.271D-09    23.83426       0.8198
2.326D 00   -1.234D-08   -1.046D-08   -1.882D-09    17.98965       0.8176
2.463D 00   -1.294D-08   -1.155D-08   -1.390D-09    12.04120       0.8145
2.639D 00   -1.364D-08   -1.293D-08   -7.035D-10     5.44010       0.8101
2.801D 00   -1.414D-08   -1.422D-08    7.528D-11    -0.52953       0.8056
3.012D 00   -1.495D-08   -1.588D-08    9.293D-10    -5.85111       0.7993
3.236D 00   -1.631D-08   -1.765D-08    1.342D-09    -7.59980       0.7921
3.472D 00   -1.785D-08   -1.952D-08    1.667D-09    -8.54185       0.7842
3.745D 00   -1.938D-08   -2.167D-08    2.298D-09   -10.60199       0.7747
4.000D 00   -2.151D-08   -2.369D-08    2.173D-09    -9.17237       0.7655
4.310D 00   -2.390D-08   -2.614D-08    2.236D-09    -8.55322       0.7541
4.651D 00   -2.617D-08   -2.883D-08    2.655D-09    -9.20801       0.7413
5.000D 00   -2.897D-08   -3.158D-08    2.614D-09    -8.27617       0.7279
5.348D 00   -3.194D-08   -3.433D-08    2.390D-09    -6.96064       0.7144
5.714D 00   -3.583D-08   -3.723D-08    1.399D-09    -3.75794       0.7001
6.211D 00   -4.162D-08   -4.115D-08   -4.727D-10     1.14870       0.6804
6.579D 00   -4.685D-08   -4.405D-08   -2.792D-09     6.33766       0.6657
7.042D 00   -5.066D-08   -4.771D-08   -2.943D-09     6.16759       0.6471
7.463D 00   -5.499D-08   -5.103D-08   -3.951D-09     7.74264       0.6301


     GOODNESS OF FIT:        GAUSS CRITERION,  OMEGA=  2.811D-18


    CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

        CONSTANT     VALUE         STD DEV   REL STD DEV(PPH)

           C(1)     7.9071D-09   8.9059D-10      11.2632

           C(2)    -7.8982D-09   2.2353D-10      -2.8302
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MN(II)--PERIODATE SYSTEM:  NTA ADDED, DETN OF RATE CONSTANT FOR NTA EFFECT  6/13


    X          Y(OBS)      Y(CALC)       DEV(Y)     % DEV(Y)     WEIGHT(Y)

4.472D-09  -9.227D-09  -7.993D-09  -1.234D-09   15.43959       3.8078
6.619D-09  -9.745D-09  -1.027D-08   5.229D-10   -5.09222       6.5535
4.366D-09  -7.745D-09  -7.883D-09   1.380D-10   -1.75126       4.9392
8.252D-09  -1.323D-08  -1.200D-08  -1.228D-09   10.23339       2.6317
1.062D-08  -1.427D-08  -1.450D-08   2.287D-10   -1.57669       3.3149
7.706D-09  -1.123D-08  -1.142D-08   1.844D-10   -1.61457       4.7217
4.510D-09  -8.381D-09  -8.033D-09  -3.481D-10    4.33364       3.3886
6.267D-09  -1.039D-08  -9.916D-09  -4.753D-10    4.79310       3.8557
4.501D-09  -6.999D-09  -8.023D-09   1.024D-09  -12.76169       3.2576
4.863D-09  -7.898D-09  -8.407D-09   5.086D-10   -6.04953       3.6772


   GOODNESS OF FIT:        GAUSS CRITERION,  OMEGA=  2.204D-18


  CONSTANTS FOUND FOR POLYNOMIAL CURVE FIT OF DEGREE 1 :

      CONSTANT      VALUE        STD DEV   REL STD DEV(PPH)

         C(1)   -3.2542D-09   8.0476D-10    -24.7299

         C(2)   -1.0596D 00   1.2497D-01    -11.7943




  DETERMINATION OF SYSTEM PARAMETERS--SUMMARY OF RESULTS




  MEAN VALUES OF RATE CONSTANTS:

     CONSTANT        VALUE         STD DEV      REL STD DEV(PPH)

        K1         4.1965D 05    1.5814D 05     37.68275

        K2         3.0729D 06    7.5994D 07     24.72994

        K-2        5.4662D 09    6.4470D 08     11.79426
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VITA

Benny Edward Simpson

Candidate for the Degree of

Master of Science

Thesis: SOME STUDIES OF SIMULATION AND ANALYSIS OF INDICATOR REACTIONS FOR CATALYTIC DETERMINATIONS

Major Field: Chemistry

Biographical:

Personal Data: Born in Miami, Oklahoma, September 25, 1947, the son of Mr. and Mrs. Jake W. Simpson.

Education: Graduated from Wyandotte High School, Wyandotte, Oklahoma, in May, 1965; received Associate of Arts degree from Northeastern Oklahoma A & M College in 1967; received Bachelor of Science degree in Chemistry from Oklahoma State University in 1970; completed requirements for the Master of Science degree in Chemistry at Oklahoma State University in May, 1973.

Professional Experience: Research and Development Assistant, Phillips Petroleum Company, 1967-68; graduate research assistant, Department of Chemistry, Oklahoma State University, 1970-71; graduate teaching assistant, Department of Chemistry, Oklahoma State University, 1971-72; Chemist, Dowell Division of the Dow Chemical Company, 1972.