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TRANSIENT RESPONSE OF A TUBULAR REACTOR

BY

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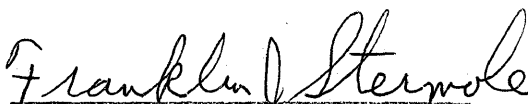
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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Science in Chemical and Petroleum Refining Engineering.

Signed: 
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Date: May 8, 1968

To
My Parents

ABSTRACT

This study concerns the transient response of tubular reactors in which a second-order reaction takes place under isothermal conditions. The reaction studied was the saponification of methyl acetate with sodium hydroxide. Experimental data were obtained in a tubular reactor for single concentration upsets, single flow upsets, and simultaneous concentration and flow upsets.

Theoretical models using partial differential equations and residence time distribution techniques have been developed. The study was conducted at 36° C. The reactor was a 13-ft-long, $\frac{1}{4}$ -in.-diam copper tube in the form of a spiral with a volume of 110 cc. The range of flow rates studied was from 40 to 160 cc/min and the concentration range studied was from 0 to 0.25 moles/liter.

The agreement obtained between the experimental data and the theoretical predictions was very good and the deviations observed were within $\pm 5\%$. Back mixing was observed in the reactor. This non-ideality was easily accounted for in the residence time distribution (RTD) model, since back mixing was observed to be mainly a function of flow rate.

The RTD model, extended to non-isothermal cases and tubular reactors with recycle, shows the versatility of the model.

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INTRODUCTION

Chemical reactors have drawn a lot of attention in the past few years, and many workers such as Aris, Amundson, Koppel, just to name a few, have contributed greatly to the literature existing on chemical reactors. However, much of the work that has been done is highly theoretical. Considerable work has been done on the stability of reactors, but very little experimentally verified research has been done on the dynamics of chemical reactors. The CFSTR (continuous flow stirred tank reactor) has obtained most of the attention, and very little work has been done with tubular reactors.

The main purpose of this project was to conduct transient response studies on a tubular reactor that was not packed and to develop a theoretical model to predict the response. The basic mathematical equations were obtained by writing mass balances for each component; this will be discussed in detail in the theoretical development. The system that was studied was a tubular reactor under isothermal conditions for a second-order reaction. This system can be represented by a set of non-linear differential equations which can be solved simultaneously.

One of the reasons why distributed parameter problems of this nature have been studied very little in the past

may be the complexity of the theoretical modeling. Almost all conventional techniques to get an analytical solution for the equations describing the system fail even in the simple cases.

Most of the regular techniques used for developing transfer functions cannot be used here because of the non-linear nature of the describing equations. This leads to the development of the "lumped parameter model," which is one of the techniques used for simplifying models of distributed parameter systems. The lumped parameter model is the only model that can be conveniently used in an analog computer. A solution with reasonable accuracy may be obtained by using an analog computer. However, large numbers of amplifiers are required if the distributed system is broken into a number of finite cells. The lumped parameter model lends itself to straightforward programming for a digital computer. This has been done in the present study on a CDC 8090 computer. However, it was found that the computer time needed was large to get an accuracy within ± 5 percent.

These simulation problems lead to the development of the "Residence Time Distribution (RTD) model" in this study, which the author believes is a highly versatile model. This model gives the best agreement with experimental data and the method can be extended to non-isothermal systems and for

tubular reactors with recycle. It may be noted at this point that the accuracy with which this model predicts the response curves is very good, and the error bounds are within ± 5 percent. The details of this model will be discussed in the theoretical section.

The reaction used in the present study was the saponification of methyl acetate by sodium hydroxide, given by



This reaction was used mainly because it is an irreversible second-order reaction with a relatively high reaction rate constant between 35 and 40° C. The kinetics of this reaction were obtained from a previous study (1) and are listed in Appendix III of this dissertation.

LITERATURE SURVEY

Over the years, quite a lot of literature about chemical reactors and their behavior has accumulated. Among reactors, as mentioned before, the CFSTR seems to have drawn more attention than tubular reactors. This is understandable since the mathematics involved in the tubular case are much more complex than that in the corresponding CFSTR case. Basically, the literature reviewed can be divided into three broad categories:

- i) Theoretical development
- ii) Non-ideality in reactors
- iii) Frequency response studies

It should be noted at this point that the division which has been made is not hard and fast. There is always a certain amount of intermingling, which is essential for the understanding of the broader concept. The amount of literature available on transient response data is quite small.

i) Theoretical Development

One of the most recent solutions has been provided by Crider and Foss (2). In this study, locally linearized dynamic equations have been solved, the system studied being an adiabatic chemical reactor with chemically inert packing and a homogeneous first-order reaction. Transfer functions have been developed which include the various

effects.

Douglas and Eagleton (3) in their work give analytical solution for the dynamics of adiabatic unpacked reactors. The analytical solutions describing the adiabatic reactor operation for simple reaction mechanisms are presented in the form of exponential integral functions.

Many different methods have been adopted to obtain the dynamics of distributed parameter systems. One of the methods is to lump a parameter, e.g. the space coordinate, and reduce the describing equation to a form where it can be solved. An approach similar to this is presented by Batke et al. (4). These authors have solved the simplified dynamic equations in an analog computer.

Yet another method to solve the dynamic equations is to finite difference the partial differential equations with respect to all independent variables, to form simple equations which can be solved with the help of a high-speed digital computer. Deans and Lapidus (5) in their article describe the best procedure for differencing the partial differential equations for the case of fixed bed reactors.

Wang and Perlmutter (6) discuss models to describe a plug-flow tubular reactor and proceed to derive phase plane plots with a numerical example.

Koppel (7, 8, 9) in his various publications discusses the analytical solution for the case of an isothermal

plug-flow tubular reactor parametrically forced by throughput and the various linearization techniques employed.

Schisser (10) presents a method of simulating linear distributed systems by the use of finite integral transforms. The method is well developed and discussed in detail, principally through example applications.

In an earlier work Williams (11) discusses in a qualitative manner the dynamics of chemical reactors in general and has extended the discussion to include control of reactors.

Bilous and Amundson (12) in their paper discuss in detail the complexity involved in the analysis of stability of tubular cases. These authors have developed transfer functions, using Laplace technique for the first-order irreversible reaction taking place in an isothermal reactor. The mathematical equation describing the case turns out to be a first-order linear partial-differential equation. The treatment is extended to a complicated system using the method of matrices. The analog computer has been used extensively by these authors.

Denbigh (13) in his discussion of tubular reactors brings out many salient features. According to Denbigh, even though plug flow cannot be ideally achieved, one could approach plug flow by the use of baffles or the construction of the tubular reactor in the form of a spiral instead

of a straight tube. According to Kramers and Westerterp (14), the secondary flow, which is induced by spiralling, has beneficial effects both by flattening the velocity profile and by increasing radial diffusion.

ii) Non-ideality in Reactors

In the region of non-ideality a great deal of work has been done. One of the pioneers in this field is Danckwartz (15), who in his article discusses non-ideality in terms of the distribution of residence time occurring in flow systems. Mathematically he defines a function $F(\theta)$ as

$$F(\theta) = 1.0 - \exp(-v\theta/V)$$

where $F(\theta)$: Fraction of material in outflow which has been in system for less than
 θ : Average residence time
 v : Volumetric flow rate
 V : Volume of reactor

The application of this method of describing non-ideality has been extended to different systems like blenders, reactors, etc.

In a later article in 1957 Levenspiel and Smith (16) discuss longitudinal mixing of fluids in flow. Here the non-ideality is explained by the definition of a dimensionless parameter, the Peclet number as compared with the "longitudinal dispersion coefficient" used by some of the previous workers.

Croockewit et al. (17) in their work simulated non-ideality by letting fluid flow through the space between a

stationary outer cylinder and a rotating cylinder core; thus they have determined the diffusion coefficient, using frequency response analysis.

Wehner and William (18) have presented theoretical methods for obtaining boundary conditions to be applied in a steady state flow reactor with axial diffusion and first-order reaction.

One of the earlier theoretical approaches to dispersion is that of Taylor (19, 20). The effect of molecular diffusion in dispersion is discussed, and experimental data have also been presented.

Vincent and co-workers (21) have successfully used the pulse technique to determine the mixing parameters and average residence time for shell and tube heat exchangers. The standard diffusion equation,

$$\frac{\partial T(x,t)}{\partial t} = D \frac{\partial^2 T(x,t)}{\partial x^2} - u \frac{\partial T(x,t)}{\partial x}$$

where D : Dispersion coefficient
 u : Velocity
 x : Length variable
 t : Time
 T(x,t) : Temperature

has been used for the theoretical development.

Roemer and Durbin (22) have derived equations for determining the overall impulse and step response of the back-flow cell model. This model consists of N perfectly mixed cells of equal volume ($V_n = V/N$) with constant net or bulk

flow rate \underline{q} , at any cross section and with equal recirculation or back-flow rate \underline{f} , from each cell back to the preceding cell of the train. This paper includes a good bibliography on the diffusion model in general. The limitation of the model is in the assumption that diffusion is taking place just in one direction.

In a recent publication Wolf and Resnick (23) discuss residence time distributions in real systems. The residence time distribution has been presented by an \underline{F} function of the form

$$F(t) = 1 - \exp \left\{ -\eta \left(\frac{t-\epsilon}{\theta} \right) \right\} \text{ for } t \geq \epsilon$$

$$F(t) = 0 \text{ for } 0 \leq t < \epsilon$$

where $F(t)$: Residence time function
 η : Coefficient of exponent
 ϵ : System phase shift
 θ : Average residence time
 t : Time

Various models have been discussed in a most clear manner and transfer functions have also been developed.

Levenspiel (24) in his book gives a detailed discussion of non-ideality in reactors.

As can be seen from the above references, dispersion has drawn a lot of attention, but the complete understanding of non-ideality is still in the infantile stages. In the present study dispersion was observed and was found to be a distinct function of throughput through the reactor. A

detailed discussion of this aspect will be done in the later chapters.

iii) Frequency Response Studies

There has been some notable activity in the field of frequency response of chemical reactors. Liang-Tseng Fan and Yong-Kee Ahn (25) present a generalized approach to the frequency response of tubular systems, using the dispersion model, with dimensionless bode plots.

Kramers and Alberda (26) deal with frequency response analysis of continuous systems. The discussion is limited to systems for which the describing mathematical equations can be solved analytically.

The most general approach in this direction is the one taken by Schisser (27). This author, discussing various cases, has a very good mathematical treatment covering simple and partial linear differential equations with constant and variable coefficients.

Hougen and Walsch (28) discuss pulse techniques for obtaining frequency response data. The literature cited at the end of the paper has an excellent bibliography on the dynamic studies performed in heat exchangers before 1961.

Tinkler (29) obtained frequency response data by following effluent temperature in an adiabatic system.

Sinai and Foss (30) have studied the frequency response for a liquid-phase packed bed reactor.

Simpkins (31), studying the reaction between acetyl chloride and water acetone solution, obtained frequency response data in a packed tubular reactor. Analytical methods are presented for a first-order system in a packed tubular reactor under adiabatic conditions.

As can be seen from all the literature cited, there has been very little work done on the transient response of tubular chemical reactors. It is the hope of the author that the gap will be filled to a certain extent by this dissertation.

EXPERIMENTAL SECTION

Equipment

The tubular reactor system used in this study is shown schematically in Figure 1. All flow lines used were $\frac{1}{4}$ -in. Imperial-Eastman polyflow tubing. The use of polyflow tubing facilitated easy dismantling of the equipment. The reactants as shown in Figure 1 were stored in tanks 10, 11, 12, and 13. The reactants were pumped to the reactor with the help of air controlled by the pressure regulators 18 and 19. The pressures at the outlet of the regulators were measured by manometers 16 and 17. A safety relief valve was introduced in the air line before the regulators, so any excess back pressure over 5 lb/sq in. could be released.

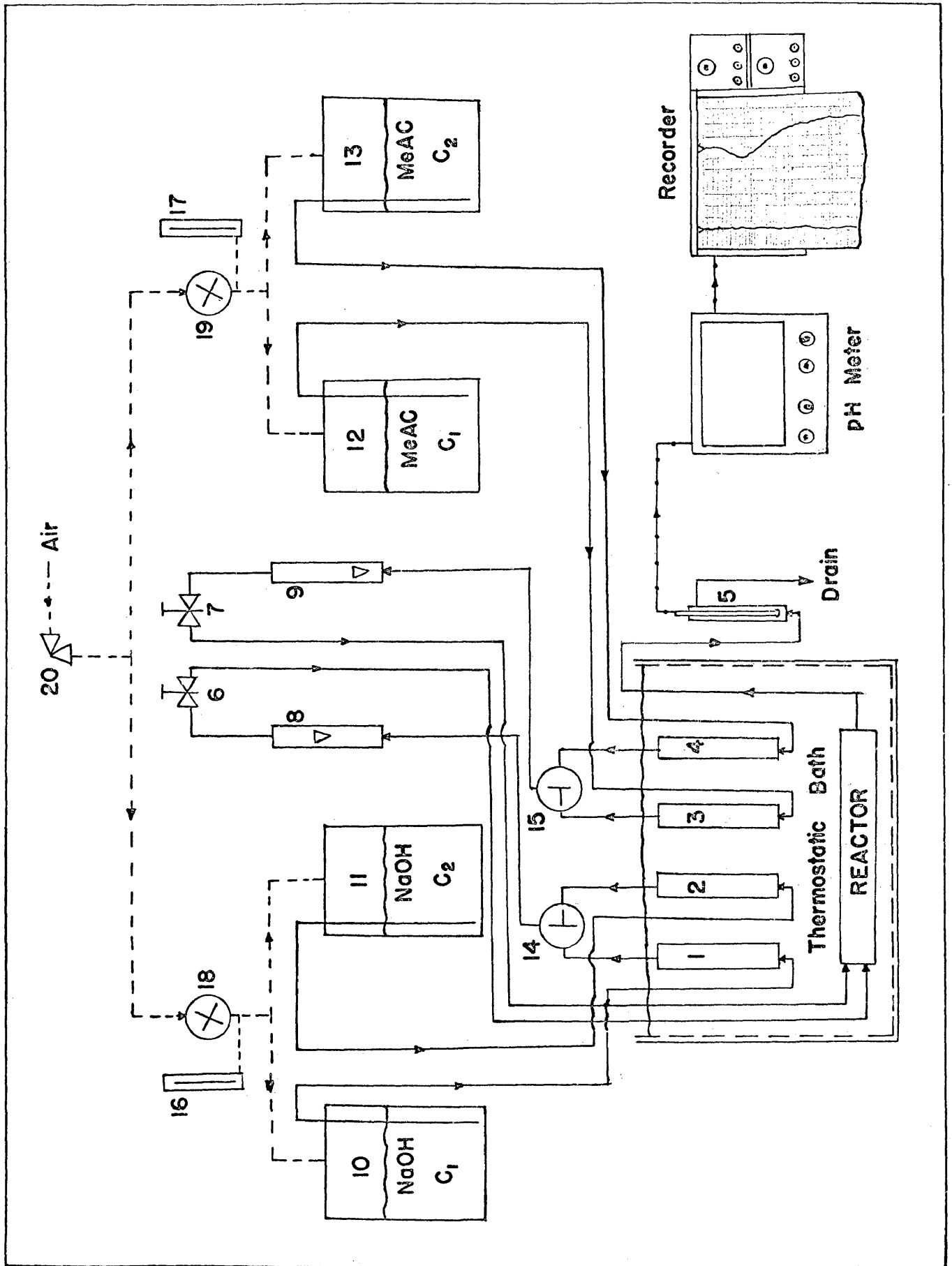
The air from the regulators proceeded to the feed tanks. The feed tanks, 20-liter pyrex-glass containers, had to be periodically filled. Tanks 10 and 11 contained sodium hydroxide; tanks 12 and 13 were used for methyl acetate.

Reactants displaced from the feed tanks by air pressure were pre-heated by pre-heaters 1, 2, 3, and 4. The pre-heaters were immersed in a thermostatic bath which was maintained around 37°C. The pre-heaters were made out of $\frac{1}{4}$ -in.-diam copper tube.

The pre-heated reactants then passed through the three-way Teflon valves 14 and 15. The amount of reactants

Figure 1. Flow diagram of tubular reactor system

1, 2, 3, 4	Pre - heaters
5	Flow cell with combination electrode
6, 7	Needle valves
8, 9	Rotameters
10, 11, 12, 13	Feed tanks
14, 15	Three - way valves
16, 17	Manometers
18, 19	Pressure regulators
20	Safety relief valve



flowing was metered with rotameters 8 and 9. Good control of flow rates was obtained with the needle valves 6 and 7.

The metered streams of reactants then entered the reactor, which was kept at the same temperature as the preheaters by immersing it in the same thermostatic bath. Thus essentially isothermal operation was assured. The reactor was a 13-ft-long $\frac{1}{4}$ -in.-diam copper tube in the form of a spiral.

The effluent from the reactor passed through a flow cell, where the concentration was monitored with a Sargent combination electrode (range 0 to 14 pH). The pH was recorded on a Moseley strip-chart recorder.

The concentration of solutions in tanks 10 and 12 was approximately double the concentration in tanks 11 and 13. The three-way valves 14 and 15 were used to make step changes in concentration of either sodium hydroxide or methyl acetate, or both. Flow upsets, either single or multiple, were made with pressure regulators 18 and 19. Fine control was obtained with needle valves 14 and 15.

The reactants used in this study were sodium hydroxide and methyl acetate. The concentrations used were approximately 0.25 and 0.125 N. The solutions of desired normality were prepared in an Alsop mixer by using reagent grade chemicals. The exact concentrations of the solutions prepared were obtained through standard titration techniques.

Procedure

Before starting a run the pH electrode used was soaked in a 2 N solution of sodium hydroxide for at least 6 hours. The system was started by closing all the valves except the air valve. Then, the air in the feed lines was purged by opening valves 6 and 7. The position of the three-way valves 14 and 15 determined what concentration was being fed to the reactor.

The concentration at the outlet of the reactor was monitored with a pH meter which was standardized with a buffer.

When the concentration reached steady state, a sample was drawn at the outlet and titrated to obtain the sodium hydroxide concentration of the reactor effluent. The sample drawn was quenched with excess hydrochloric acid in order to stop the saponification reaction. Then the concentration of sodium hydroxide which was present was obtained through back titration.

The upsets were then made by manipulating the respective valves. The temperature at the outlet of the reactor was also monitored to make sure isothermal conditions prevailed during the run.

When the new steady state was reached, the concentration of sodium hydroxide in the exit stream was determined as mentioned before. The results were interpreted through a

calibration curve of pH readings versus concentration obtained on a semi-log plot. Data for both single and simultaneous upsets in concentration and flow rate were obtained.

THEORY

Lumped Parameter Model

The basic equations that describe the concentration history in a tubular reactor can be easily obtained by writing a mass balance over a differential element of the reactor. For a second order isothermal plug-flow system, the mass balance equations are as follows:

$$\frac{\partial C_a}{\partial t} + v \frac{\partial C_a}{\partial x} = k C_a C_b \quad (4-1)$$

$$\frac{\partial C_b}{\partial t} + v \frac{\partial C_b}{\partial x} = k C_a C_b \quad (4-2)$$

where C_a : Concentration of A, mole/liter
 (function of x and t)
 C_b : Concentration of B, mole/liter
 (function of x and t)
 v : Velocity of fluid front, cm/min
 x : Length variable, cm
 t : Time, min

Equations 4-1 and 4-2 are non-linear partial-differential equations and have to be solved simultaneously. These equations cannot be easily solved by analytical methods.

However, with the application of various simplifying assumptions the equations could be solved. One of the methods is to lump the parameters with respect to one of the independent variables. In this particular case since the variable of interest is time, the spatial parameter, viz. x , will be lumped. This merely means that one would

use an approximation for $\frac{\partial C_a}{\partial x}$, $\frac{\partial C_b}{\partial x}$

$$\text{e.g., } \frac{\partial C_a}{\partial x} = \frac{C_{a1} - C_{a0}}{L} \quad (4-3)$$

$$\frac{\partial C_b}{\partial x} = \frac{C_{b1} - C_{b0}}{L} \quad (4-4)$$

where C_{a1} : Concentration of A @ $x = L$
 C_{a0} : Concentration of A @ $x = 0$
 C_{b1} : Concentration of B @ $x = L$
 C_{b0} : Concentration of B @ $x = 0$
 L : Length of reactor

Substituting 4-3 and 4-4 in equations 4-1 and 4-2

$$\frac{dC_a}{dt} + v \frac{C_{a1} - C_{a0}}{L} = kC_a C_b \quad (4-5)$$

$$\frac{dC_b}{dt} + v \frac{C_{b1} - C_{b0}}{L} = kC_a C_b \quad (4-6)$$

The term on the right hand side of equations 4-5 and 4-6 is the generation term. Hence, another approximation that will bring the model close to reality would come from the use of an average value for the generation term. With this approximation equations 4-5 and 4-6 become

$$\frac{dC_a}{dt} + v \frac{C_{a1} - C_{a0}}{L} = k \frac{C_{a0} + C_{a1}}{2} \frac{C_{b0} + C_{b1}}{2} \quad (4-7)$$

$$\frac{dC_b}{dt} + v \frac{C_{b1} - C_{b0}}{L} = k \frac{C_{a0} + C_{a1}}{2} \frac{C_{b0} + C_{b1}}{2} \quad (4-8)$$

The concentration of interest is at the outlet of the reactor, so evaluating equations 4-7 and 4-8, which are now ordinary differential equations, at the outlet of the reactor, one could obtain equations 4-9 and 4-10.

$$\frac{dC_{a1}}{dt} + v \frac{C_{a1} - C_{a0}}{L} = k \frac{C_{a0} + C_{a1}}{2} \frac{C_{b0} + C_{b1}}{2} \quad (4-9)$$

$$\frac{dC_{b1}}{dt} + v \frac{C_{b1} - C_{b0}}{L} = k \frac{C_{a0} + C_{a1}}{2} \frac{C_{b0} + C_{b1}}{2} \quad (4-10)$$

The accuracy of this method can be increased by dividing the reactor into more than one section as in Figure 2. Then concentration at different points in the reactor can be described by the following equations:

Point 1 ($x = L/N$)

$$\frac{dC_{a1}}{dt} + \frac{C_{a1} - C_{a0}}{L/N} = k \frac{C_{a1} + C_{a0}}{2} \frac{C_{b1} + C_{b0}}{2}$$

$$\frac{dC_{b1}}{dt} + \frac{C_{b1} - C_{b0}}{L/N} = k \frac{C_{a1} + C_{a0}}{2} \frac{C_{b1} + C_{b0}}{2}$$

Point 2 ($x = 2L/N$)

$$\frac{dC_{a2}}{dt} + \frac{C_{a2} - C_{a1}}{L/N} = k \frac{C_{a1} + C_{a2}}{2} \frac{C_{b1} + C_{b2}}{2}$$

$$\frac{dC_{b2}}{dt} + \frac{C_{b2} - C_{b1}}{L/N} = k \frac{C_{a1} + C_{a2}}{2} \frac{C_{b1} + C_{b2}}{2}$$

..

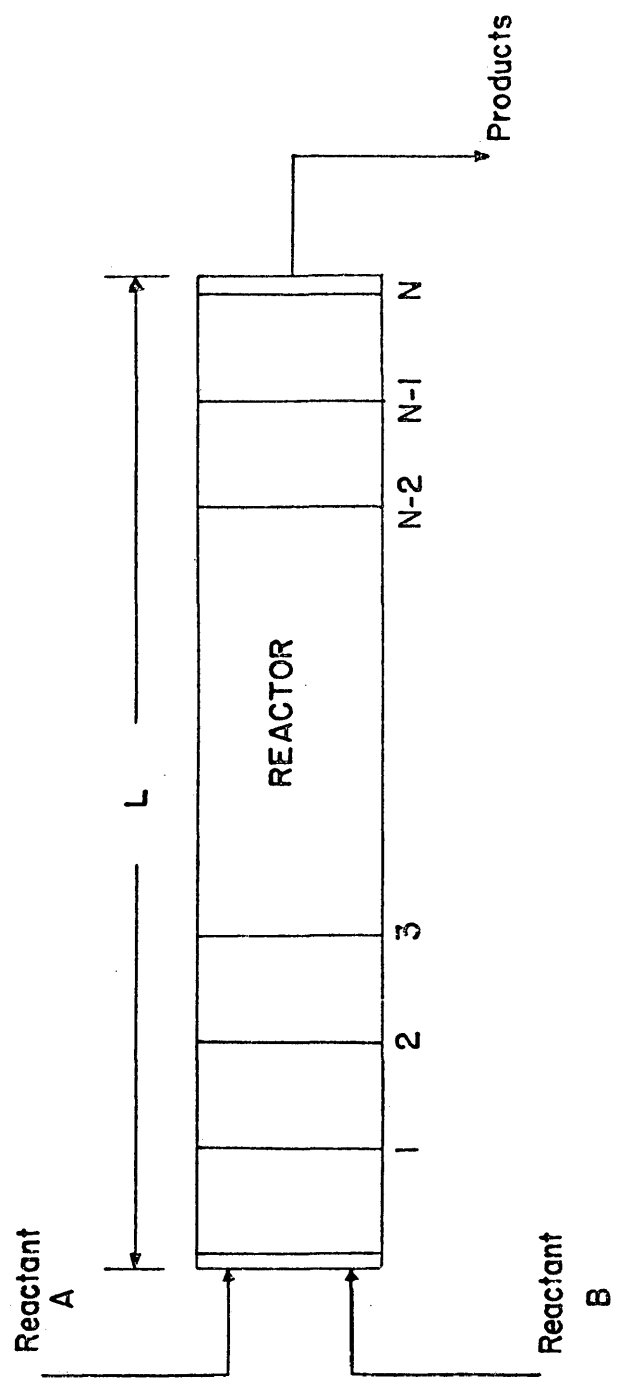
Point N ($x = NL/N = L$)

$$\frac{dC_{aN}}{dt} + \frac{C_{aN} - C_{a(N-1)}}{L/N} = k \frac{C_{aN} + C_{a(N-1)}}{2} \frac{C_{bN} + C_{b(N-1)}}{2}$$

$$\frac{dC_{bN}}{dt} + \frac{C_{bN} - C_{b(N-1)}}{L/N} = k \frac{C_{aN} + C_{a(N-1)}}{2} \frac{C_{bN} + C_{b(N-1)}}{2}$$

where N is the number of times the reactor is divided. In this study it was found that even when the reactor was

Figure 2. Lumped parameter model.



divided 8 times, the results obtained showed significant variation between experimental and theoretical results as shown in Figure 6. Theoretically, when N tends to infinity, the solution would approach the exact solution, which gives a step change in concentration when time after the upset equals the residence time.

The equations were programmed for a digital computer for $N=8$. The program as listed for a CDC 8090 computer is given in Appendix IV. The language used was Fortran II and the Runge-Kutta method was used to conserve memory space. It should be mentioned here that this lumped parameter method has not been used extensively in this study as the accuracy obtained was not sufficiently good; and also, the computer time needed was large.

Residence Time Distribution (RTD) Model

As Levenspiel (23) says in his book, a plug-flow reactor can be visualized as a flow of small batch reactors passing through the reactor in succession. If one takes a close look at the design equations for a plug-flow tubular reactor (PFTR) and a batch reactor, he can easily see that length in a PFTR corresponds to time in a batch reactor. The longer the PFTR the more the conversion and the longer the time in the batch reactor the more the conversion.

The appropriate reactor equations for constant volume

conditions are:

$$\text{Batch reactor, } t = C_{A0} \int \frac{dx_A}{-r_A} \quad (4-11)$$

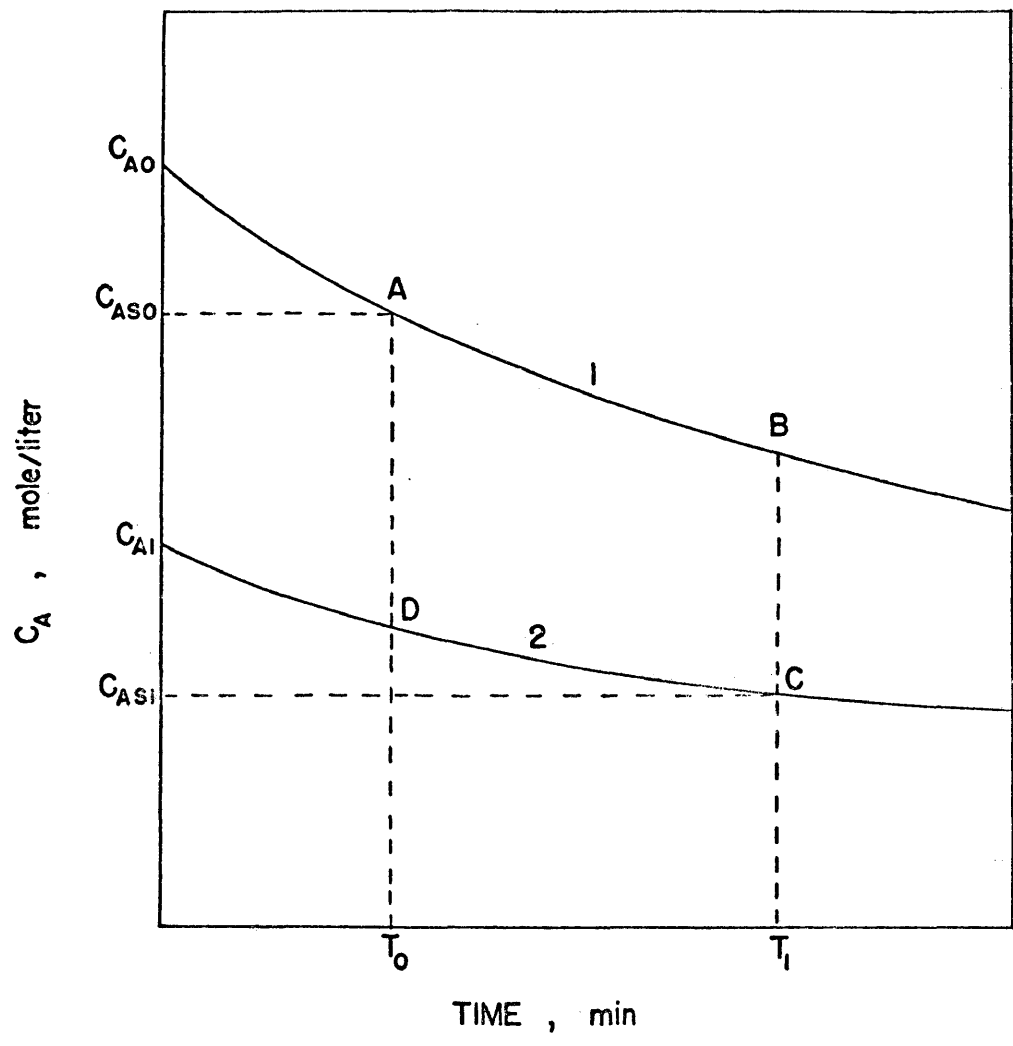
$$\text{Plug-flow reactor, } \tau = C_{A0} \int \frac{dx_A}{-r_A} \quad (4-12)$$

where the nomenclature has been taken from Levenspiel (24).

- t : Amount of time in the batch reactor
- τ : Space time
- C_{A0} : Initial concentration of component A
- X_A : Conversion of A
- $-r_A$: Reaction rate

This analogy that exists between the batch and the tubular reactor can be used conveniently for predicting the response of a plug-flow tubular reactor. The steady state concentration of component A at the outlet of a tubular reactor of residence time T_0 , is the same as the concentration of A in a batch reactor at $t = T_0$, with the following conditions: the conditions in the batch reactor at $t = 0$ must be the same as those in the plug-flow tubular reactor at $X = 0$. Figure 3 shows concentration of A plotted versus time for a batch reactor with different initial conditions. Curve 1 in Figure 3 corresponds to initial conditions of C_{A0} , C_{B0} , and curve 2 corresponds to C_{A1} , C_{B1} . For a tubular reactor with inlet conditions of C_{A0} , C_{B0} , and residence time of T_0 , the concentration of A at the outlet of the reactor will be C_{AS0} shown in Figure 3. The concentration can be schematically represented by point A in Figure 3. By a similar

Figure 3. Determination of response path using batch curves.



argument, the outlet concentration of a tubular reactor with inlet conditions of C_{A1} , C_{B1} , and residence time T_1 , would be C_{AS1} (Point C in Figure 3). If the inlet conditions in the tubular reactor were changed from C_{A0} , C_{B0} , T_0 to C_{A1} , C_{B1} , T_0 , the concentration of A at the outlet of the reactor will stay at Point A in Figure 3 until $t = T_0$ and at $t = T_0$ jump to Point D. Thus the response path followed will be A - D. The concentration of A at the outlet of the reactor stays at C_{AS0} until $t = T_0$ because the reactor has some fluid elements with the old concentration history which must be displaced before the upset is seen. The fluid elements with the old concentration history are completely displaced from the reactor at $t = T_0$, and the fluid elements with the new concentration history start showing up at the outlet of the reactor. Hence at $t = T_0$ the concentration of A at the outlet goes to the new value corresponding to point D.

In the case where the residence time is also changed, from T_0 to T_1 , the response path followed will be A - B - C. The details of obtaining the responses for different kinds of upsets will be discussed in the sections to follow.

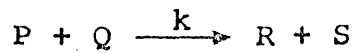
Basically, the concentration in a batch reactor depends upon the initial conditions and the amount of time the components have had to react. Of course, other variables

which affect the concentration history could be listed as the reaction-rate constant, temperature, rate of cooling, etc. In the case of a PFTR, the amount of time which each fluid element has to react is the residence time.

From the above discussion, it is apparent that the concentration history of a PFTR can be obtained easily by knowing the initial concentration of the fluid elements which enter the reactor and the residence time each of these elements have, before leaving the reactor. This is the fundamental basis for the RTD model. One of the assumptions made in this model is that the reactants are incompressible.

The basic model follows batch reactor theory, utilizing the relationship between steady state tubular reactor equations and the unsteady state batch reactor theory. The starting point for this model is the batch equations. Since the system was isothermal in the present study, the rate constant does not change as a function of time. Hence, the only variables which affect the outlet concentration are the initial concentrations of the reactants and their respective flow rates. The flow rates of the reactants determine the actual concentration in the reactor and also the residence time.

The equations that give the concentration history in a constant volume batch reactor with a second order isothermal reaction



are:

Case (i) Initial concentrations of both the reactants are equal.

$$C_{PI} = C_{QI}$$

$$C_P = \frac{1}{\frac{1}{C_{PI}} - kt}$$

$$C_Q = C_P$$

Case (ii) Initial concentrations of both the reactants are not equal.

$$C_{PI} \neq C_{QI}$$

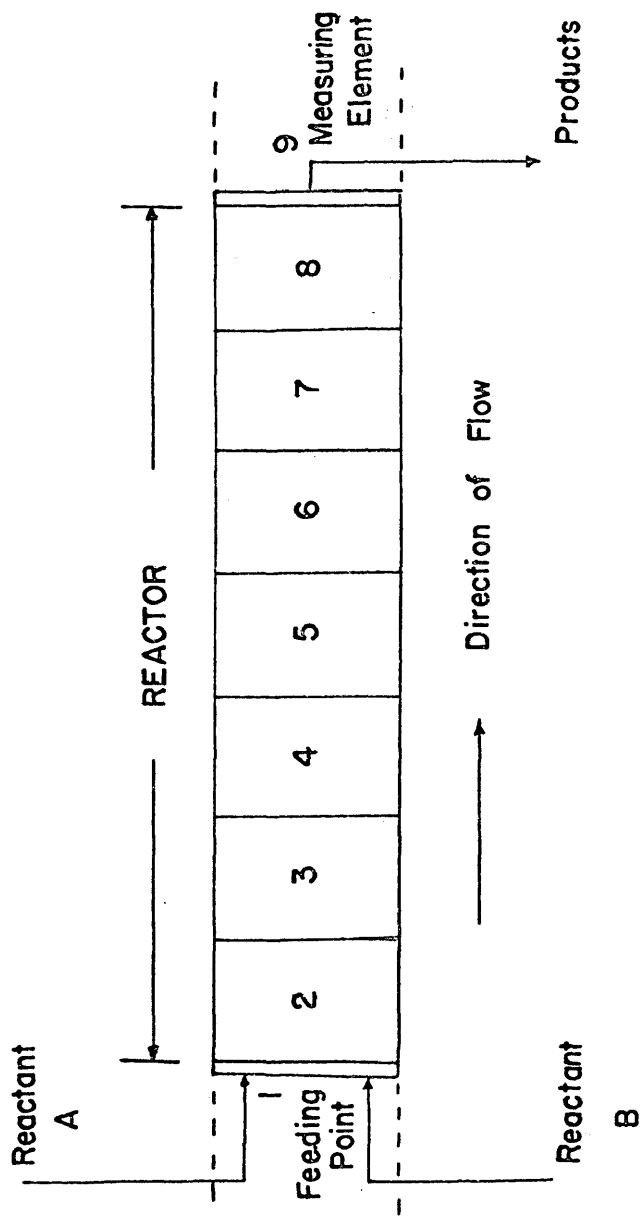
$$C_P = \frac{C_{QI} - C_{PI}}{\frac{C_{QI}}{C_{PI}} \exp\{(C_{QI} - C_{PI}) kt\}}$$

$$C_Q = C_{QI} - C_{PI} + C_P$$

where C_{PI} : Initial concentration of component P,
mole/liter
 C_{QI} : Initial concentration of component Q,
mole/liter
 C_P : Concentration of P @ any time t,
mole/liter
 C_Q : Concentration of Q @ any time t,
mole/liter
k : Reaction rate constant, liter/(mole)(min)
t : Time, min

In the tubular reactor shown schematically in Figure 4, Block 1 is the feeding point, or the imaginary block where the feeds just mix and enter the reactor. Blocks 2 to 8 constitute the reactor, and Block 9 is the measuring chamber

Figure 4. Residence time distribution model.



where the outlet of the reactor is monitored.

The residence time of each block of fluid as it moves through the reactor will depend upon the rate of feed. Hence, if the rate of feed is known as a function of time, the residence time of each block of fluid as it moves through the reactor can be calculated. It should be noted that it has been assumed that the reactor always flows full, and the residence time of any fluid block depends upon the velocity with which the fluid block behind it is moving.

On the assumption that the reactor is empty to begin with and the reactants are fed into the feed chamber with flow rates of F_{A0} and F_{B0} liter/min, and concentrations of C_{AI} and C_{BI} mole/liter, the actual concentration of component A in the first block of fluid entering the reactor will be $\frac{F_{A0}}{F_{A0}+F_{B0}} C_{AI}$ mole/liter, while the concentration of component B will be $\frac{F_{B0}}{F_{A0}+F_{B0}} C_{BI}$ mole/liter. This is due to the mixing and the subsequent dilution effect. The residence time of this fluid element in a reactor of volume V liter will be $\frac{V}{F_{A0}+F_{B0}}$ min.

As the first block progresses through the reactor, a second block follows and goes through the same process. Thus, one could look upon the fluid flowing in the reactor as a train of blocks moving through the reactor. Each block is autonomous as far as the reaction is concerned and does

not mix with the adjoining blocks. However, the speed with which a block moves will depend upon the speed with which the block behind is moving.

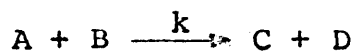
At time $t = 0$, the reactor start-up time, the measuring probe does not measure anything since no fluid element has reached point 9. Thus the concentration at the outlet of the reactor is going to remain at zero until the first fluid element reaches it, after passing through the reactor. This happens as soon as a time equivalent to the residence time lapses, and the concentration changes from 0 to C_{AS0} , where C_{AS0} is the concentration of component A in a batch reactor of volume V, at time t, with the following conditions.

$$t = T_0 = \frac{V}{F_{A0} + F_{B0}} \text{ min}$$

$$\text{Initial concentration of A} = C_{A0} = \frac{F_{A0}}{F_{A0} + F_{B0}} C_{AI}$$

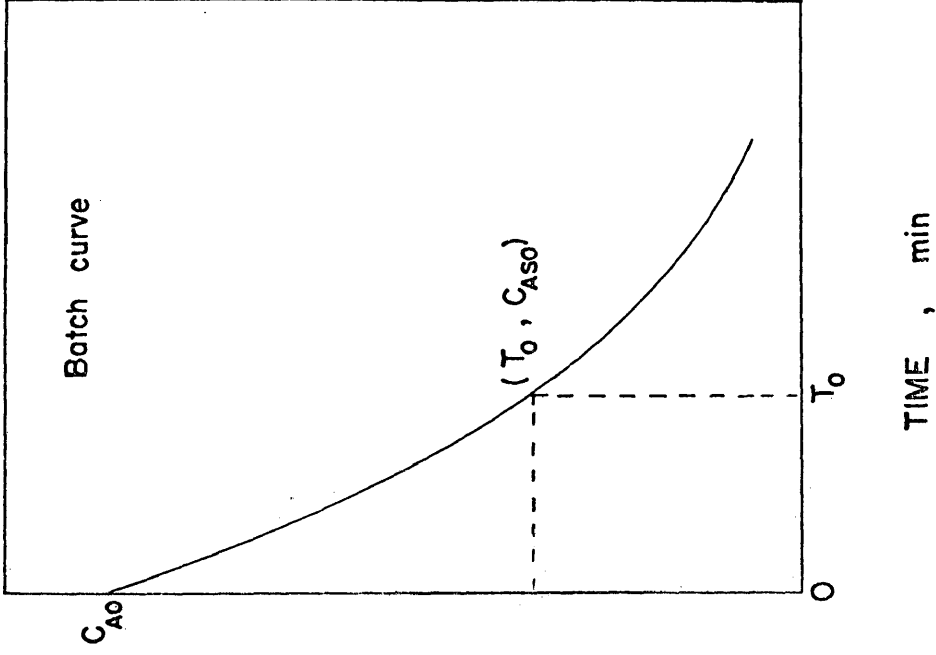
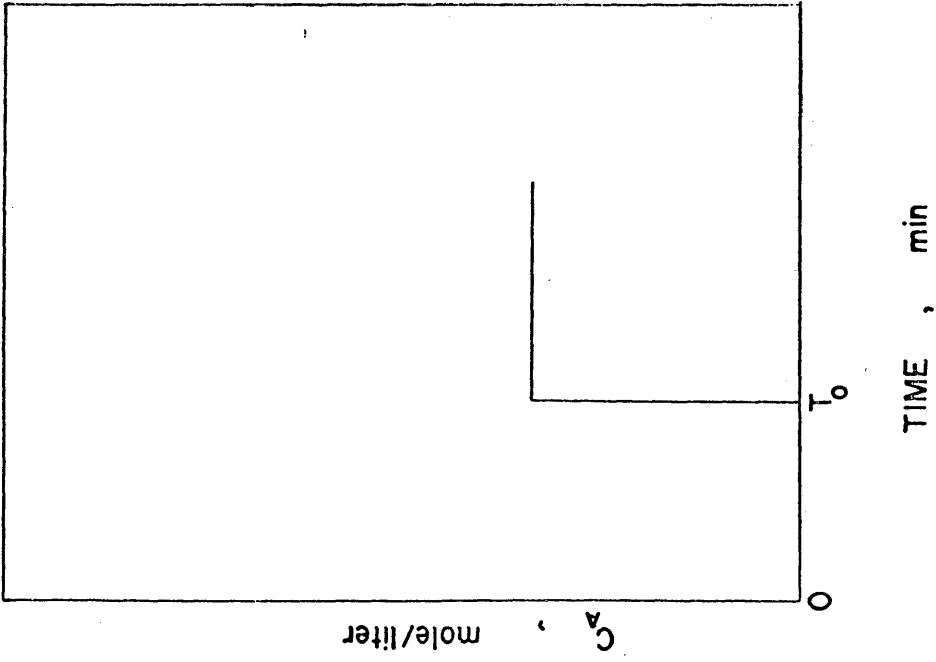
$$\text{Initial concentration of B} = C_{B0} = \frac{F_{B0}}{F_{A0} + F_{B0}} C_{BI}$$

The reaction taking place in the reactor is



Graphically this phenomenon of attaining steady state is shown in Figure 5. In the sections to follow specific cases will be discussed.

Figure 5. Approach to steady state.



Definitions

- C_{AI} : Concentration of sodium hydroxide entering reactor before upset, mole/liter (based on stream A)
 C_{BI} : Concentration of methyl acetate entering reactor before upset, mole/liter (based on stream B)
 F_{A0} : Flow rate of sodium hydroxide before upset, liter/min
 F_{B0} : Flow rate of methyl acetate before upset, liter/min
 T_0 : Residence time before upset, min
 C_{AF} : Concentration of sodium hydroxide entering reactor after upset, mole/liter (based on stream A)
 C_{BF} : Concentration of methyl acetate entering reactor after upset, mole/liter (based on stream B)
 F_{A1} : Flow rate of sodium hydroxide after upset, liter/min
 F_{B1} : Flow rate of methyl acetate after upset, liter/min
 T_1 : Residence time after upset, min
 C_{A0} : Actual concentration of sodium hydroxide at the inlet of the reactor before upset, mole/liter (based on mixed streams of A and B)
 C_{B0} : Actual concentration of methyl acetate at the inlet of the reactor, before upset, mole/liter (based on mixed streams of A and B)
 C_{A1} : Actual concentration of sodium hydroxide at the inlet of the reactor, after upset, mole/liter (based on mixed streams of A and B)
 C_{B1} : Actual concentration of methyl acetate at the inlet of the reactor, after upset, mole/liter (based on mixed streams of A and B)
 V : Volume of reactor, liter
 C_A : Concentration of sodium hydroxide at the outlet of the reactor, mole/liter
 C_{AS0} : Steady state concentration of sodium hydroxide at the outlet of the reactor before upset, mole/liter
 C_{AS1} : Steady state concentration of sodium hydroxide at the outlet of the reactor after upset, mole/liter

$$C_{A0} = \frac{F_{A0}}{F_{A0} + F_{B0}} C_{AI}$$

$$C_{B0} = \frac{F_{B0}}{F_{A0} + F_{B0}} C_{BI}$$

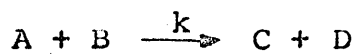
$$C_{A1} = \frac{F_{A1}}{F_{A1} + F_{B1}} C_{AF}$$

$$C_{B1} = \frac{F_{B1}}{F_{A1} + F_{B1}} C_{BF}$$

$$T_0 = \frac{V}{F_{A0} + F_{B0}}$$

$$T_1 = \frac{V}{F_{A1} + F_{B1}}$$

Reaction in reactor



If $C_{B0} = C_{A0}$,

$$C_{AS0} = \frac{1}{\frac{1}{C_{A0}} - kT_0}$$

If $C_{B0} \neq C_{A0}$,

$$C_{AS0} = \frac{M_0}{N_0 \exp(M_0 kT_0) - 1.0}$$

where $M_0 = C_{B0} - C_{A0}$

$$N_0 = \frac{C_{B0}}{C_{A0}}$$

If $C_{B1} = C_{A1}$

$$C_{AS1} = \frac{1}{\frac{1}{C_{A1}} - kT_1}$$

If $C_{B1} \neq C_{A1}$

$$C_{AS1} = \frac{M_1}{N_1 \exp(M_1 k T_1) - 1.0}$$

where $M_1 = C_{B1} - C_{A1}$

$$N_1 = \frac{C_{B1}}{C_{A1}}$$

It is assumed that an upset is made at $t = T_0$, which occurs when the initial steady state is attained. In the following discussion the time scale will be normalized, so that time will be zero at time of upset. The two time zones of interest are

- i) Response zone, $0 < t < T_1$
- ii) Final steady state zone, $t \geq T_1$

Single Concentration Upset

A single concentration upset in sodium hydroxide can be symbolically represented by the following equations:

$$\begin{aligned} C_{AI} &\neq C_{AF} \\ C_{BI} &= C_{BF} \\ F_{A0} &= F_{A1} \\ F_{B0} &= F_{B1} \end{aligned} \tag{4-13}$$

Referring back to the previous section on definitions and using equation 4-13, it is evident that

$$\begin{aligned} C_{B0} &= C_{B1} \\ C_{A0} &\neq C_{A1} \\ T_0 &= T_1 \end{aligned}$$

Since $T_0 = T_1$, all the fluid elements before and after upset are moving with the same velocity. Hence, the response curve should come in the form of a step given by the following equations:

$$\begin{aligned} \text{Zone i)} \quad 0 \leq t < T_1 \\ C_A = C_{AS0} \end{aligned}$$

$$\begin{aligned} \text{Zone ii)} \quad t \geq T_1 \\ C_A = C_{AS1} \end{aligned}$$

Single Flow Upset

Symbolically a single flow upset in sodium hydroxide can be given as,

$$C_{AI} = C_{AF}$$

$$C_{BI} = C_{BF}$$

$$F_{A0} \neq F_{A1}$$

$$F_{B0} = F_{B1}$$

Even though only one flow rate was changed, a close look at the actual concentrations and residence times, will show more than one change, viz.,

$$C_{A0} \neq C_{A1}$$

$$C_{B0} \neq C_{B1}$$

$$T_0 \neq T_1$$

This is, in effect, a triple upset as far as the reactor is concerned. Since the residence time before upset is not

the same as the residence time after upset, the fluid elements would have different velocity from one another and the response would not be in the form of a step.

The response in part can be obtained from the following equations:

$$t = 0 \quad , \quad C_A = C_{AS0}$$

$$t \geq T_1 \quad , \quad C_A = C_{AS1}$$

However, the region of interest is $0 < t < T_1$.

At time $t = 0$, the amount of time each fluid element in Figure 3 has spent inside the reactor can be given by the following equations:

$$\text{Block 2, } T = (1/7) T_0$$

$$\text{Block 3, } T = (2/7) T_0$$

$$\text{Block 4, } T = (3/7) T_0$$

$$\text{Block 5, } T = (4/7) T_0$$

$$\text{Block 6, } T = (5/7) T_0$$

$$\text{Block 7, } T = (6/7) T_0$$

where T = the amount of time spent in the reactor.

When the upset is made at $t = 0$, the effect due to the change is felt in three directions, viz., concentration changes in A and B at the inlet of the reactor and change in residence time. The effect due to change in residence time will be felt as soon as the upset is made. However, the effect due to the concentration change will not be

felt until a period of time equivalent to the new residence time (T_1) lapses.

Initially the change in residence time is felt. This effect is going to be felt merely as a change in the amount of time each fluid element spends inside the reactor. During this process the residence time gradually changes from T_0 to T_1 , and this change is accomplished in T_1 min.

This concept would become more clear if one took a closer look at a typical fluid element of Figure 3. Block 7 as seen before has spent $(6/7) T_0$ min inside the reactor at $t = 0$; and if no change in flow rate was made, this fluid element would have stayed in the reactor for T_0 min before hitting the measuring probe. But, since the flow rate has changed, the new residence time for this fluid element will be $(\frac{6}{7} T_0 + \frac{T_1}{7})$ min, and the concentration of this element as it leaves the reactor will be given by

$$C_A = \frac{M_0}{N_0 \exp \left\{ M_0 k \left(\frac{6T_0}{7} + \frac{T_1}{7} \right) \right\} - 1.0} \quad \text{if } C_{A0} \neq C_{B0}$$

or

$$C_A = \frac{1}{\frac{1}{C_{A0}} - k \left(\frac{6T_0}{7} + \frac{T_1}{7} \right)} \quad \text{if } C_{A0} = C_{B0}$$

This fluid element will be seen by the measuring probe at $t = T_1/7$. This argument can be extended to all the fluid elements. Hence, for the time zone $0 < t < T_1$ the concentration

of sodium hydroxide at the outlet of the reactor is given by equation 4-14.

$$t = \frac{n}{N} T_1$$

If $C_{A0} \neq C_{B0}$

$$C_A = \frac{M_0}{N_0 \exp \left\{ M_0 k \left(\frac{N-n}{N} T_0 + \frac{n}{N} T_1 \right) \right\} - 1}$$

(4-14)

If $C_{A0} = C_{B0}$

$$C_A = \frac{1}{\frac{1}{C_{A0}} - k \left(\frac{N-n}{N} T_0 + \frac{n}{N} T_1 \right)}$$

where N : Number of times reactor is divided (also can be looked upon as the number of points desired for the response curve)
 n : Block level, goes from 1 to N in increments of one

Thus, the overall response for a single flow upset can be given by equation 4-15.

$$t = 0 ; C_A = C_{AS0}$$

$$t \geq T_1 ; C_A = C_{AS1}$$

$$0 < t < T_1 ; C_A = \frac{M_0}{N_0 \exp \left\{ M_0 k \left(\frac{n-N}{N} T_0 + \frac{n}{N} T_1 \right) \right\} - 1}$$

if $C_{A0} \neq C_{B0}$

(4-15)

or

$$C_A = \frac{1}{\frac{1}{C_{A0}} - k \left(\frac{N-n}{N} T_0 + \frac{n}{N} T_1 \right)} \quad \text{if } C_{A0} = C_{B0}$$

Another way of viewing this would be to look at the corresponding batch curves. Figure 3 shows the batch concentration curves for the various conditions. Curve 1 in Figure 5 corresponds to C_{A0} , C_{B0} , and curve 2 corresponds to C_{A1} , C_{B1} . At the time of flow upset the concentration of sodium hydroxide being at C_{AS0} is represented by point A in Figure 3. When the upset is made, the flow rate is decreased. As a result the residence time is increased from T_0 to T_1 . Since the residence time is increased there is more time to react and the concentration decreases. The concentration follows the curve AB, and reaches B when $t = T_1$. But at $t = T_1$, the new concentration, viz., C_{A1} , C_{B1} , comes into play, and the concentration at the outlet of the reactor drops from B to C. Hence, the path followed by the response curve will be A - B - C. The amount of time taken by the response curve to move from A to B is T_1 min. The concentration, starting slowly, drops until $t = T_1$, but at $t = T_1$ the concentration plunges to a new value.

For a reverse upset, viz. flow increase, the path of the response curve would be C - D - A. In this case T_1 is smaller than T_0 , and C_{AS0} will be represented by point C while point A is C_{AS1} .

Simultaneous Upsets in Concentration

Once again in symbolic representation, simultaneous upsets in concentration can be represented as

$$C_{AI} \neq C_{AF}$$

$$C_{BI} \neq C_{BF}$$

$$F_{A0} = F_{A1}$$

$$F_{B0} = F_{B1}$$

Hence,

$$C_{A0} \neq C_{A1}$$

$$C_{B0} \neq C_{B1}$$

$$T_0 = T_1$$

Thus, simultaneous upsets in concentration change both of the incoming concentrations. However, since the residence time does not change, the response will be in the form of a step given by equation 4-16.

$$\begin{aligned} 0 < t < T_1 & \quad C_A = C_{AS0} \\ t \geq T_1 & \quad C_A = C_{AS1} \end{aligned} \tag{4-16}$$

Even though two concentrations were changed the effect was almost like the one obtained for a single concentration upset.

Simultaneous Flow Upset

In symbolic representation this upset would be

$$C_{AI} = C_{AF}$$

$$C_{BI} = C_{BF}$$

$$F_{A0} \neq F_{A1}$$

$$F_{B0} \neq F_{B1}$$

For this kind of upset two cases have to be considered.

Case I: In this case $(F_{A0}/F_{B0}) = (F_{A1}/F_{B1})$ and hence

$$C_{A0} = C_{A1}$$

$$C_{B0} = C_{B1}$$

$$T_0 \neq T_1$$

Thus, the only change in this kind of upset is in the residence time, and there is no change in concentrations at the reactor inlet. The response for this case would be given by

$$t = 0 \quad ; \quad C_A = C_{AS0}$$

$$t \geq T_1 \quad ; \quad C_A = C_{AS1}$$

$$0 < t < T_1 \quad ; \quad \text{If } C_{A0} = C_{B0}$$

$$C_A = \frac{1}{\frac{1}{C_{A0}} - k \left\{ \frac{N-n}{N} T_0 + \frac{n}{N} T_1 \right\}}$$

$$\text{If } C_{A0} \neq C_{B0}$$

$$C_A = \frac{M_0}{N_0 \exp \left\{ M_0 k \left(\frac{N-n}{N} T_0 + \frac{n}{N} T_1 \right) \right\} - 1.0}$$

The concentration slowly drops from C_{AS0} to C_{AS1} , and unlike the rapid change observed in the case of single flow upset before reaching the final steady state, no sudden change in concentration is seen at $t = T_1$ in this case.

Graphically, the response starts at A in Figure 3 and goes to B following the curve 1. For this case A corresponds to C_{AS0} and B corresponds to C_{AS1} .

Case II: In this case $\frac{F_{A0}}{F_{B0}} \neq \frac{F_{A1}}{F_{B1}}$

$$\begin{aligned} \therefore C_{A0} &\neq C_{A1} \\ C_{B0} &\neq C_{B1} \\ T_0 &\neq T_1 \end{aligned}$$

Because this is just like the case discussed for a single flow upset, it can be analyzed accordingly.

Combination Upsets

This constitutes a simultaneous upset in flow rate and concentration, and can be represented as

$$\begin{aligned} C_{AI} &\neq C_{AF} \\ C_{BI} &= C_{BF} \\ F_{A0} &= F_{B0} \\ F_{A1} &\neq F_{B1} \end{aligned}$$

Hence,

$$\begin{aligned} C_{A0} &\neq C_{A1} \\ C_{B0} &\neq C_{B1} \\ T_0 &\neq T_1 \end{aligned}$$

This kind of upset is once again like a single flow upset.

Summing up the discussion, one could say there are two cases which will describe all types of upsets in a

broad sense.

Case 1. This case occurs when the residence time before upset is equal to the residence time after upset. When $T_0 = T_1$ the response is given by

$$\begin{aligned} 0 < t < T_1 & \quad C_A = C_{AS0} \\ t \geq T_1 & \quad C_A = C_{AS1} \end{aligned}$$

Case 2. This case arises when the residence time before upset is not the same as the residence time after upset. When $T_0 \neq T_1$, the response is given by

$$\begin{aligned} t = 0 & \quad ; \quad C_A = C_{AS0} \\ t \geq T_1 & \quad ; \quad C_A = C_{AS1} \\ 0 < t < T_1 & \quad ; \quad \text{if } C_{A0} = C_{B0} \end{aligned}$$

$$C_A = \frac{1}{\frac{1}{C_{A0}} k \left(\frac{N-n}{N} T_0 + \frac{n}{N} T_1 \right)}$$

$$\text{if } C_{A0} \neq C_{B0}$$

$$C_A = \frac{M_0}{N_0 \exp\{M_0 k \left(\frac{N-n}{N} T_0 + \frac{n}{N} T_1 \right)\} - 1.0}$$

N : Number of points desired in response curve
 n : Positive integer, 1, 2, 3. ... N

RTD Model with Dispersion

Even though plug flow was assumed, dispersion was observed in certain cases. Dispersion was seen at low flow rates and whenever there was a sharp change in concentration inside the reactor. However, if the change in concentration

was gradual, no matter what the flow rate, the dispersion observed was negligible, e.g., response for simultaneous flow upset with $F_{A0}/F_{A1} = F_{B0}/F_{B1}$.

The dispersion observed was found to be a function of the flow rate of the reactants. Accordingly, the RTD model that includes dispersion is given by the following empirical equations:

$$t \leq 0.826 T_1, \quad C_A = \text{Same as calculated by RTD model without dispersion}$$

$$t = 0.826 T_1, \quad \text{dispersion effect starts}$$

$$t > 0.826 T_1$$

$$t = 0.826 T_1 + \Delta t$$

$$C_A = C_{A2} + (C_{A1} - C_{A2}) \left(1 - \exp\left(-\frac{\Delta t}{t_D}\right)\right)$$

where t_D = Time constant of dispersion
 $= 1.83 \exp(-17.78 (F_{A1} + F_{B1}))$

$$C_{A2} = \frac{1}{\frac{1}{C_{A0}} k(0.826 T_1)} \quad \text{if } C_{A0} = C_{B0}$$

$$C_{A2} = \frac{M_0}{N_0 \exp\{M_0 k(0.826 T_1)\} - 1.0} \quad \text{if } C_{A0} \neq C_{B0}$$

Δt : Time increment

Because this method is empirical, it has to be used with caution. This method accounts for dispersion as a function of flow rate alone and does not account independently for molecular diffusion. It seems to be necessary

to apply this dispersion model only when there is a sharp change in concentration inside the reactor. When there is no sudden change, the RTD model without dispersion predicts the data well.

RESULTS AND DISCUSSION

Table I lists the various runs made in the study and gives the experimental conditions. Figures 12 to 35 show the experimental data and the theoretical predictions. The RTD model was used exclusively for developing the theoretical curves as better fit was observed with this model.

Figure 6 shows the theoretical curve predicted by the lumped parameter model and the RTD model along with experimental data for run 3A. The RTD model without dispersion presents the exact solution for the PFTR. The lumped parameter model even with 8 axial divisions does not predict the response curve very well. The RTD model without dispersion also does not predict the data well; however, as can be seen in Figure 7, the RTD model with dispersion predicts the data very well. Another reason why the lumped parameter model was not used is that the amount of computer time needed to process a test was considerable.

Figures 8, 9 and 10 show typical response curves of the pH combination electrode used, for step changes in concentration, with a normalized concentration scale. The average time constant of the measurement lag was found to be 1.67 sec, which is very small compared with the reactor response time and the dispersion lag created mainly by back

mixing. Electrode response studies were conducted at different conditions to determine the effect of concentration and flow rate on measurement lag. In the concentration range studied, the time constant of the measurement lag is steady and does not depend upon the concentration or the flow rate. The maximum amount of deviation from the average value was 3.8 percent. One of the important factors which determines the lag of the electrode is the way it is prepared before measurement. It was found in the present study that pickling the electrode in strong alkaline solution overnight improved the response speed. The above-mentioned response data were obtained with the same pickling conditions used for obtaining transient response data in the tubular reactor. The pH combination electrode was highly efficient and the reproducibility was well within 3 percent.

Dispersion was observed in this study (Figures 12 to 35). According to Levenspiel (24), the non-ideality observed in reactors is due to three factors: intensity of fluid mixing, reaction rate, and reactor geometry. Since in the present study the reactor geometry and the reaction rate were fixed, the main factor which affects dispersion is the intensity of fluid mixing. Intensity of fluid mixing is directly related to the flow rate; thus dispersion should be related to the flow rate. This was witnessed in the present study. The non-ideality observed

in each run came out very close to first-order exponentials, and the time constants of these pseudo-first-order curves were an exponential function of flow rate as shown in Figure 11. Figure 11 is a semi-log plot of the time constant observed versus flow rate of the reactants. This is in keeping with findings of previous authors like Levenspiel (16), Danckwertz (15), and Wolf (23).

The time constant of the dispersion curves for the reactor system studied is given by

$$t_D = 1.83 \exp(-17.78F)$$

Where t_D : Time constant of the dispersion curve, min
 F : Total flow rate of the reactants, liter/min

It was observed that dispersion became prominent as the flow rate decreased. As can be seen from the experimental curves the effect of back mixing was more pronounced than forward mixing. This is due to the fact that there is a chemical reaction taking place in the reactor. The axial dispersion effect is made up of three things: molecular diffusion, bulk flow, and change in reaction rate due to concentration changes. In the case of forward mixing the bulk flow dominates and wipes out the general effect of the diffusion processes, whereas in the case of back mixing the bulk flow tends to increase the effects due to diffusion, since it is in the opposite direction.

Even though the measurement lag was considered to be negligible, the effect of measurement lag and molecular diffusion which can be seen at the break point of the response curves make the curves look like second-order curves. This accounts for the deviation of the data points at the break point of the response curves. Break point is defined as the point on the time scale when the effect of dispersion is seen. The break point is given by the following equation:

$$t = 0.826 T_1$$

where T_1 : Residence time after upset, min

The deviations observed between experimental and theoretical results were very small since the effect of back mixing due to flow overshadows the other effects.

A series of upsets was made in this study. Figures 12, 13, and 14 show concentration upsets in methyl acetate. As the concentration of methyl acetate is increased, the reaction rate increases and more sodium hydroxide is used; hence, the concentration of sodium hydroxide at the outlet of the reactor drops as can be seen from Figure 13. Figure 12 shows the reverse upset. As can be seen from Figures 12 and 13, the concentration remains at the old steady state value for a considerable length of time after the upset is made. This is due to the fact that the fluid elements with the older concentration history are still

in the reactor when the upset is made at the inlet and have to be displaced before the measuring element at the outlet sees the fluid elements with the new concentrations. The sodium hydroxide concentration was monitored at the outlet of the reactor by means of a pH meter, and the response curves shown in Figures 12, 13, and 14 are plots of sodium hydroxide concentration at the outlet of the reactor versus time. As these curves were plotted the abscissa was normalized by setting time equal to zero at the time of upset. Runs 10A, 10B, and 11A, 11B, presented in Figures 12, 13, and 14 were for single concentration upsets in methyl acetate. Runs 11A and 10B were identical concentration upsets. However, the throughput in run 10B was 48 cc/min and the throughput in run 11A was 104 cc/min. These runs were made at different throughputs to study the effect of throughput on concentration response. Though the residence time was changed from 2.29 min (run 10B) to 1.06 min (run 11A), the change in conversion was from 66 percent (run 10B) to 48 percent (run 11A). One of the reasons for this can be attributed to the non-linearity of the system which is caused by the second order chemical reaction. As can be seen from Figures 12, 13, and 14, the RTD model with dispersion fits the data very well.

Runs 15A, 15B, and 12A, 12B, were performed to study the response when the concentration of the incoming sodium

hydroxide stream was changed. The response obtained for these runs is shown in Figures 15, 16, and 17.

Response to simultaneous concentration upsets are shown in Figures 18, 19, and 20. For simultaneous upsets the response curves obtained are almost like the the ones obtained for single concentration upsets. This is so because in effect there is just a concentration change in the inlet stream and since the flow rates have not changed, there is no change in the residence time.

The transportation lags for all runs were small compared with the overall response and have been accounted for in the presentation of all experimental results. The transportation lag of each of the feed lines was equal. Also, for the case of simultaneous concentration upsets, tests were made at different flow rates, and the theory predicts the response well as is evident from Figures 18, 19, 20, and 21.

One of the most interesting response curves observed was for single-flow upsets. When a flow upset is made, there is more than one inlet condition change. First, there is a residence time change, and second there is a concentration change. Therefore, a single flow upset actually gives simultaneous upsets in inlet concentration and residence time. This yields the interesting response curves observed in Figures 7, 22, 23, 24, and 25 for single

flow upsets in both methyl acetate and sodium hydroxide.

Figure 7 shows the response curve obtained for run 3A. In run 3A the flow rate of sodium hydroxide was decreased. As soon as the flow rate was decreased, the residence time of the fluid elements in the reactor increased. Accordingly, the reaction time increased and the sodium hydroxide concentration at the outlet of the reactor started dropping slowly. This was followed by a noticeably sharp change in concentration. This is one of the reasons why the conventional methods like lumped parameter models do not predict the concentration response well. The actual solution must come out in two time zones (where $t < \text{residence time}$ and $t > \text{residence time}$) and the boundary conditions are different in each time zone.

Figure 22 shows the response for an increase in the flow rate of sodium hydroxide. When sodium hydroxide flow is increased, the overall residence time decreases, and the concentration of the sodium hydroxide at the inlet of the reactor increases ($C_{A1} > C_{A0}$). Both these effects increase the effluent concentration of sodium hydroxide, as can be seen in Figure 22. The fit between data and theory is very good. As was mentioned before, the deviation observed is due to molecular diffusion and measurement lag.

Runs 1A, 1B, and 4A, 4B presented in Figures 23 and 24 were single-flow upsets in methyl acetate. As the methyl

acetate flow is decreased, the overall residence time is increased and the concentration of methyl acetate at the inlet of the reactor is decreased ($C_{B1} < C_{B0}$). Since the overall residence time is increased, there is more time for reaction; hence, more sodium hydroxide is used, and the concentration of sodium hydroxide at the outlet of the reactor starts dropping, as can be seen in Figures 23 and 24. But as soon as a time equivalent to the new residence time lapses, the concentration effect comes into play and the sodium hydroxide concentration increases. The response curve takes a reverse direction when methyl acetate flow is increased, as can be seen in Figures 24 and 25. The tests were conducted at different flow rates; it was found that for even small changes in flow rate the response followed the pattern described above.

Another interesting response was observed in runs 2A and 2B, presented in Figures 26 and 27. In runs 2A and 2B, the flow rates of both sodium hydroxide and methyl acetate were changed to the same extent ($F_{A1}/F_{A0} = F_{B1}/F_{B0}$). In run 2A the flow rates were increased from 52 cc/min to 79 cc/min for both of the reactants. Hence, the residence time was decreased from 1.05 min to 0.7 min, but since the flow rates were changed to the same extent, the concentrations at the inlet of the reactor did not change. So, the only effect seen was due just to a reduction in residence

time. As the residence time is reduced, there is less time for reacting and the amount of sodium hydroxide used up is less. So the concentration of sodium hydroxide at the outlet of the reactor started increasing as soon as the upset was made and after a time equivalent to the new residence time leveled off at the new steady state. The effect of dispersion was negligible in this case, as expected since there is no sharp change in concentration in the reactor at any time or position. Excellent agreement was observed between the data and the RTD model without dispersion, as can be seen from Figures 26 and 27.

Simultaneous upsets in concentration and flow rate were also made. In the case of simultaneous upsets, the response, as before, comes out in two time zones. When a flow rate and concentration were changed, the net result on the system was a residence time change and change in concentrations of the reactants at the inlet of the reactor. The effect due to residence time change is felt as soon as the upset is made. If the residence time decreases after upset, the amount of time available for reaction is reduced, and the concentration of sodium hydroxide at the outlet of the reactor starts increasing. If the residence time increases the reverse will happen. This effect is felt until a time period equivalent to the residence time lapses after upset. At this point, the

effect due to the concentration change is seen. The direction which the response curve follows at this point depends entirely upon the net change in concentration of the reactants at the inlet of the reactor, at the time of the upset. Theoretically, the effect due to concentration change is felt when time equals the new residence time. In practice, this effect is seen sooner due to dispersion.

In run 5A, presented in Figure 28, the sodium hydroxide concentration was decreased and the flow rate of methyl acetate was also decreased. Since the flow rate was decreased, the residence time was increased. In this case, the residence time was increased from 0.81 to 1.11 min. This increase of residence time increased the amount of time available for reaction and the concentration of sodium hydroxide at the outlet of the reactor decreased, as can be seen in Figure 28. A decrease of sodium hydroxide concentration in the incoming stream has a negative effect on the sodium hydroxide concentration at the inlet of the reactor; however, decreasing the flow rate of methyl acetate has a positive effect. Thus, these two effects oppose each other and the shape of the response curve will depend upon the net result of these two effects. A similar argument can also be extended for the concentration of methyl acetate at the inlet of the reactor. In this particular case, the effect due to sodium hydroxide concentration decrease was greater

than the effect due to methyl acetate flow rate decrease and the concentration of sodium hydroxide at the inlet of the reactor was reduced from 0.1235 to 0.0835 mole/liter. Hence, the concentration of sodium hydroxide at the outlet kept dropping until it reached the final steady state, as shown in Figure 28. In run 5B the upset described above was made in the reverse direction and the response is shown in Figure 29. In runs 5A and 5B, the effects of the upsets on the inlet concentrations of sodium hydroxide and methyl acetate were opposing one another.

In run 6A, shown in Figure 30, the concentration of the incoming methyl acetate was increased, and the flow rate of the incoming sodium hydroxide was decreased. Since the overall residence time was increased, the concentration of sodium hydroxide at the outlet of the reactor started decreasing as soon as the upset was made. An increase in the incoming concentration of methyl acetate in the feed stream increases the concentration of methyl acetate at the inlet of the reactor, and a decrease in the incoming sodium hydroxide flow rate also increases the methyl acetate concentration at the inlet of the reactor. In this case, both the effects are complementing each other and the net result is seen as a big drop in the concentration of sodium hydroxide at the outlet of the reactor, as shown in Figure 30. As is evident from Figure 30, the total outlet

concentration change due to inlet concentration change is much larger than the effect due to the change in residence time. In run 6B, the upset was made in the reverse direction, and the response is shown in Figure 31. It is clear from the above discussion that the shape and magnitude of the response curves depend upon a wide variety of system parameters and boundary conditions.

In run 9B, shown in Figure 32, the incoming methyl acetate concentration was decreased, and the methyl acetate flow was also decreased. The overall residence time was increased, so the sodium hydroxide concentration at the outlet of the reactor started decreasing. In this case, the effects due to change in flow rate and concentration complement one another and the net result is an increase in the concentration of sodium hydroxide at the inlet of the reactor. Hence, the response curve first drops due to the increased residence time and then increases due to the sodium hydroxide concentration increase, as shown in Figure 32. In run 9A, the methyl acetate concentration and flow rate were increased; the response is shown in Figure 33.

Runs 8A and 8B were also simultaneous upsets. These runs were very similar to runs 9A and 9B; in these runs both the concentration and flow rate of sodium hydroxide were changed. The response of runs 8A and 8B are recorded

in Figures 34 and 35.

As mentioned before, there are many factors which affect reactor outlet concentration response. But the important factors that determined the shape of the response curves were the change in residence time and the changes in concentration of the reactants at the inlet of the reactor at the time of upset.

Table 1
Experimental Inlet Reactor Operating Conditions

Run	CAI	C _{BI}	F _{AO}	F _{BO}	C _{AF}	C _{BF}	F _{AI}	F _{BI}	Figure no.
<u>Single Flow Upset (methyl acetate)</u>									
1 A	0.2486	0.2221	0.052	0.079	0.2486	0.2221	0.052	0.052	23
1 B	0.2486	0.2221	0.052	0.052	0.2486	0.2221	0.052	0.079	25
<u>Simultaneous Flow Upset</u>									
2 A	0.1235	0.1216	0.052	0.052	0.1235	0.1216	0.079	0.079	26
2 B	0.1235	0.1216	0.079	0.079	0.1235	0.1216	0.052	0.052	27
<u>Single Flow Upset (sodium hydroxide)</u>									
3 A	0.2486	0.2221	0.079	0.031	0.2486	0.2221	0.016	0.031	7
3 B	0.2486	0.2221	0.016	0.031	0.2486	0.2221	0.079	0.031	22
<u>Single Flow Upset (methyl acetate)</u>									
4 A	0.2486	0.1216	0.031	0.016	0.2486	0.1216	0.031	0.052	24
4 B	0.2486	0.1216	0.031	0.052	0.2486	0.1216	0.031	0.016	24
<u>Simultaneous Upset (sodium hydroxide concentration & methyl acetate flow)</u>									
5 A	0.2470	0.2275	0.068	0.068	0.1215	0.2275	0.068	0.031	28
5 B	0.1215	0.2275	0.068	0.031	0.2470	0.2275	0.068	0.068	29

Table 1 (continued)

Run	C _{AI}	C _{BI}	F _{A0}	F _{B0}	C _{AF}	C _{BF}	F _{A1}	F _{B1}	Figure no.
<u>Simultaneous Upset (sodium hydroxide flow & methyl acetate concentration)</u>									
6 A	0.1215	0.1187	0.068	0.068	0.1215	0.2275	0.031	0.068	30
6 B	0.1215	0.2275	0.031	0.068	0.1215	0.1187	0.068	0.068	31
<u>Simultaneous Concentration Upset</u>									
7 A	0.1258	0.1216	0.079	0.079	0.2486	0.2221	0.079	0.079	21
7 B	0.2486	0.2221	0.079	0.079	0.1258	0.1216	0.079	0.079	21
<u>Simultaneous Upset (sodium hydroxide concentration & flow)</u>									
8 A	0.2470	0.2275	0.068	0.068	0.1215	0.2275	0.031	0.068	35
8 B	0.1215	0.2275	0.031	0.068	0.2470	0.2275	0.068	0.068	34
<u>Simultaneous Upset (methyl acetate concentration & flow)</u>									
9 A	0.2486	0.1216	0.052	0.052	0.2486	0.2221	0.052	0.079	33
9 B	0.2486	0.2221	0.052	0.079	0.2486	0.1216	0.052	0.052	32
<u>Single Concentration Upset (methyl acetate)</u>									
10 A	0.2486	0.2390	0.024	0.024	0.2486	0.1216	0.024	0.024	12
10 B	0.2486	0.1216	0.024	0.024	0.2486	0.2390	0.024	0.024	13

Table 1 (continued)

Run	C _{AI}	C _{BI}	F _{A0}	F _{B0}	C _{AF}	C _{BF}	F _{AI}	F _{BI}	Figure no.
<u>Single Concentration Upset (methyl acetate)</u>									
11 A	0.2486	0.2390	0.052	0.052	0.2486	0.1216	0.052	0.052	14
11 B	0.2486	0.1216	0.052	0.052	0.2486	0.2390	0.052	0.052	14
<u>Single Concentration Upset (sodium hydroxide)</u>									
12 A	0.1235	0.1216	0.052	0.052	0.2460	0.1216	0.052	0.052	15
12 B	0.2460	0.1216	0.052	0.052	0.1235	0.1216	0.052	0.052	15
<u>Simultaneous Concentration Upset</u>									
13 A	0.2486	0.1216	0.031	0.031	0.1258	0.2390	0.031	0.031	18
13 B	0.1258	0.2390	0.031	0.031	0.2486	0.1216	0.031	0.031	19
<u>Simultaneous Concentration Upset</u>									
14 A	0.1258	0.1216	0.044	0.044	0.2486	0.2390	0.044	0.044	20
14 B	0.2486	0.2390	0.044	0.044	0.1258	0.1216	0.044	0.044	20
<u>Single Concentration Upset (sodium hydroxide)</u>									
15 A	0.0235	0.1216	0.024	0.024	0.2460	0.1216	0.024	0.024	16
15 B	0.2460	0.1216	0.024	0.024	0.1235	0.1216	0.024	0.024	17

Figure 6. Transient response of outlet sodium hydroxide concentration to single flow upset (decrease) in sodium hydroxide (Run 3A)

Comparison between lumped parameter model and RTD model.

X Lumped parameter model (N = 8)

. Lumped parameter model (N = 4)

— RTD model without dispersion

■ Experimental data

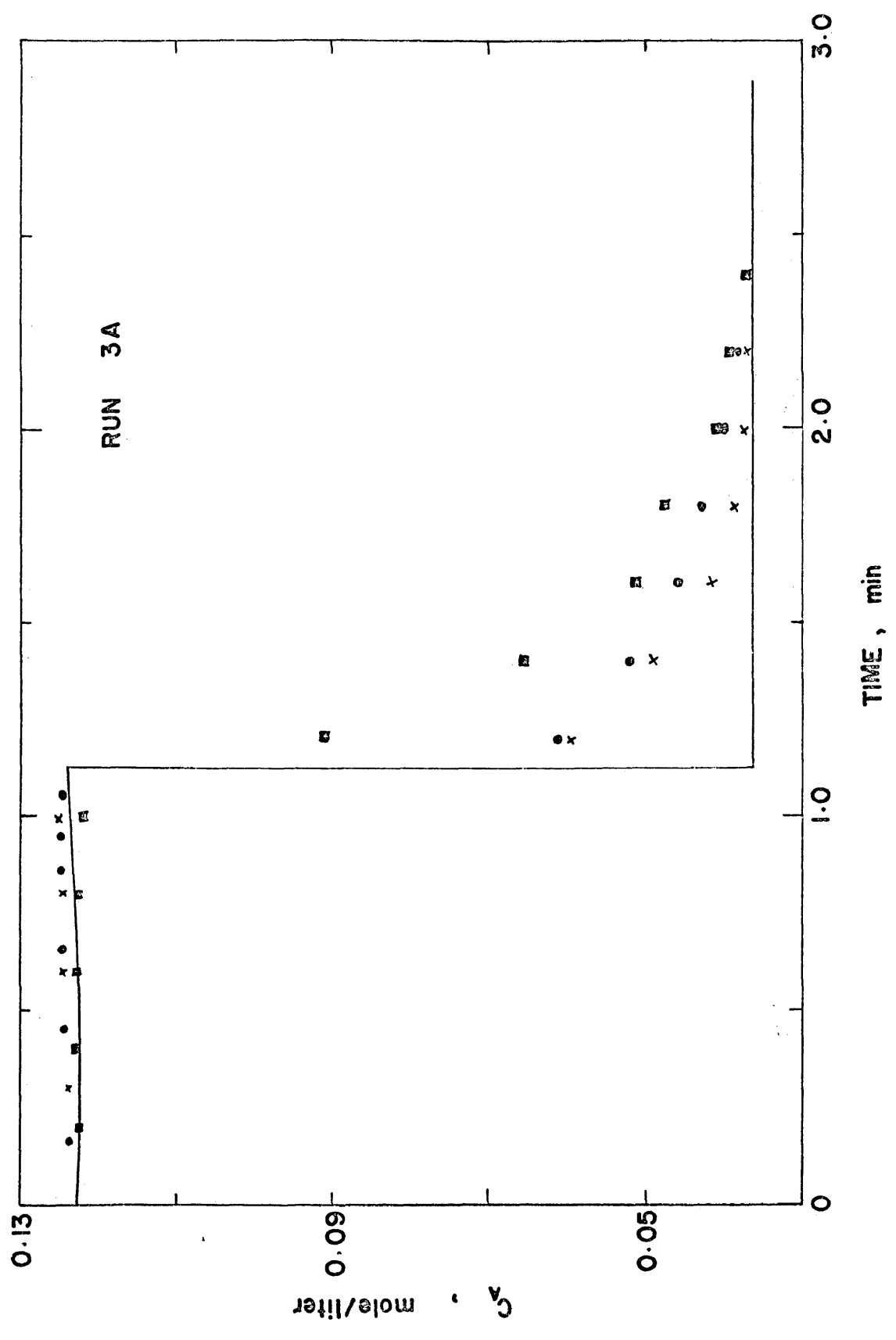
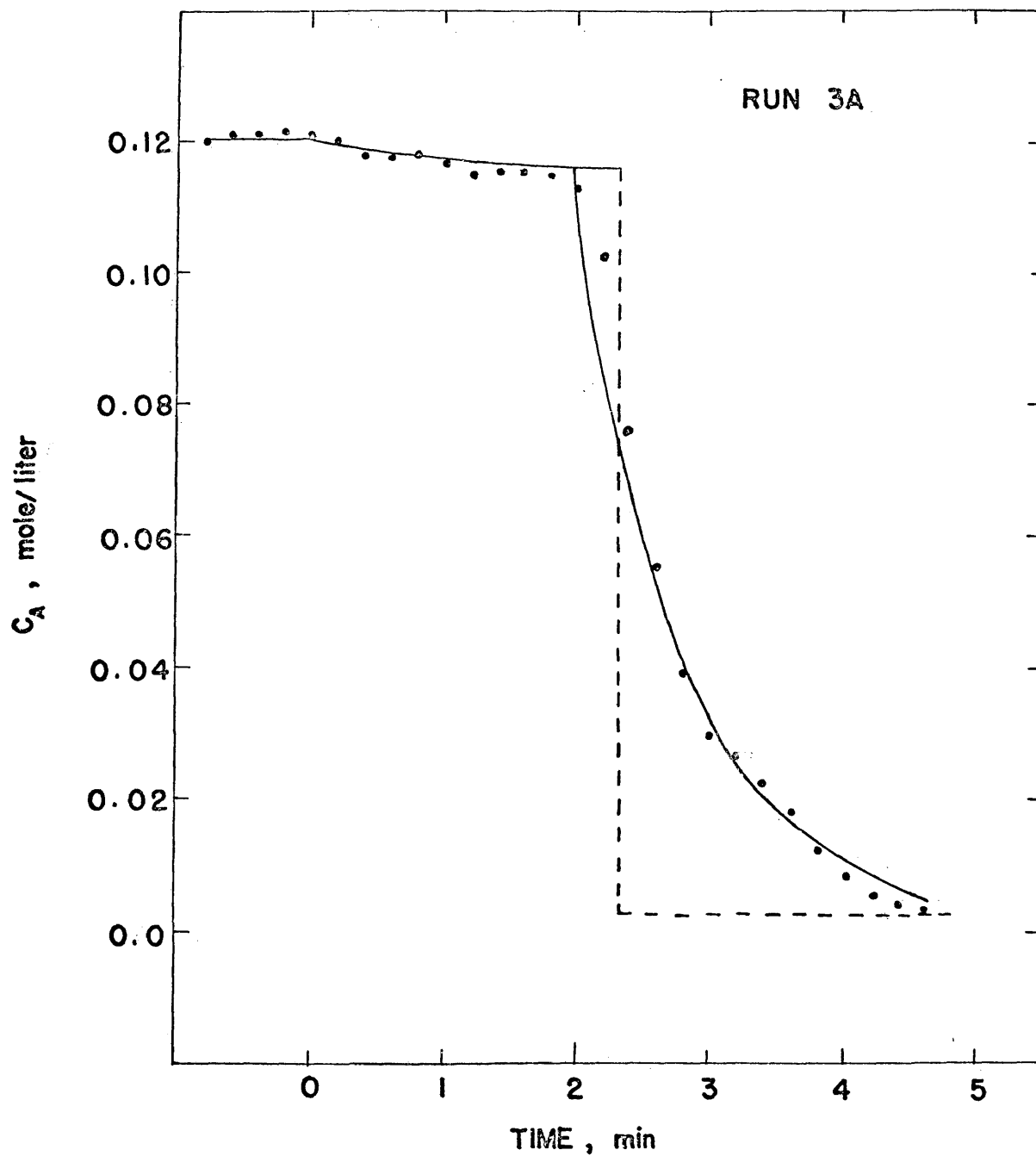


Figure 7. Transient response of outlet sodium hydroxide concentration to single flow upset (decrease) in sodium hydroxide (Run 3A).

- RTD model without dispersion
- _____ RTD model with dispersion
- . Experimental data

See Table 1 for operating conditions



- RTD model without dispersion
- RTD model with dispersion
- Experimental data

Figure 8. Response of pH combination electrode
(Run RES-1).

Time constant = 1.65 sec

Concentration changed from 0.032 to 0.125 mole/liter

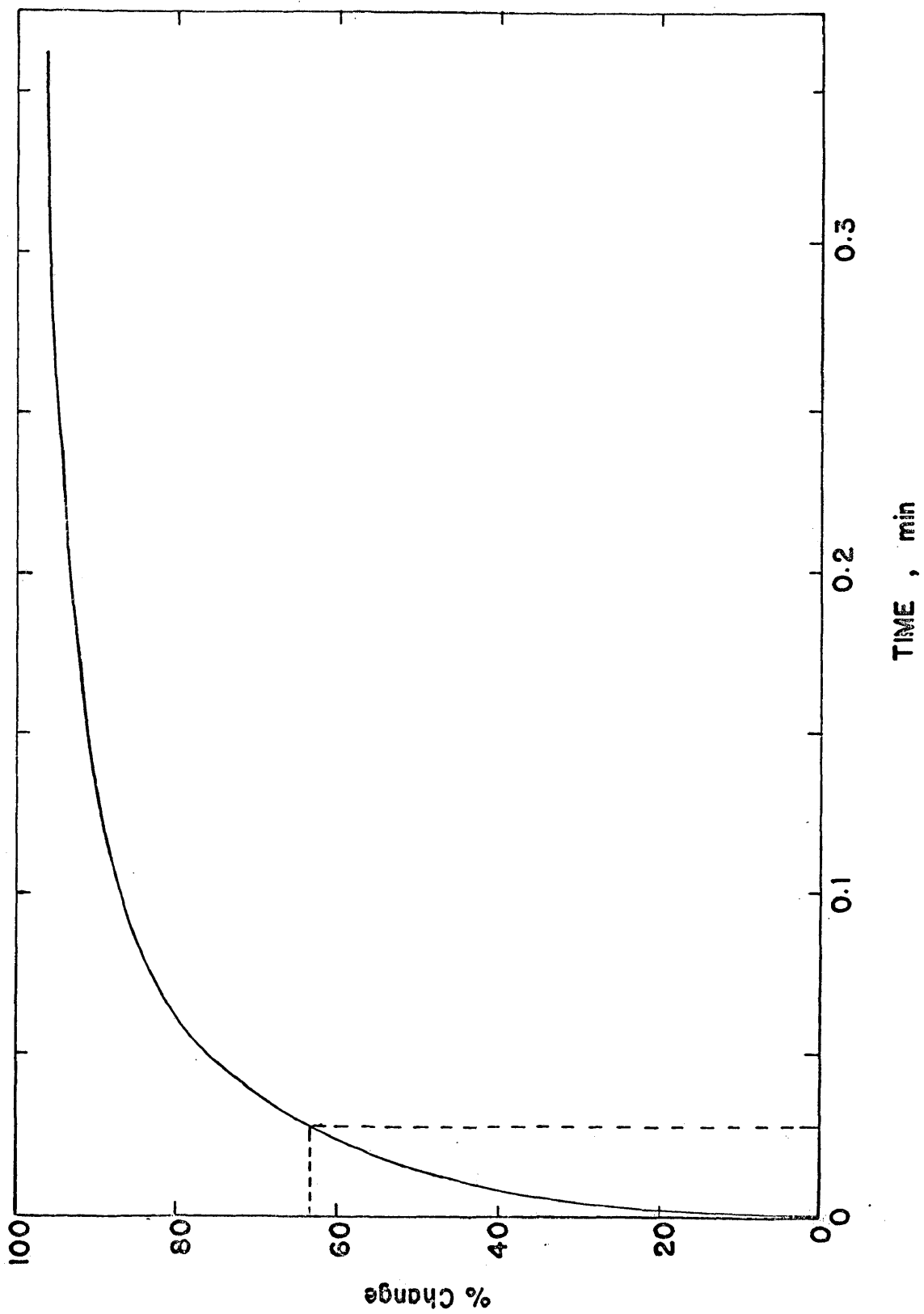


Figure 9. Response of pH combination electrode
(Run RES-2)

Time constant = 1.72 sec

Concentration changed from 0.065 to 0.25 mole/liter

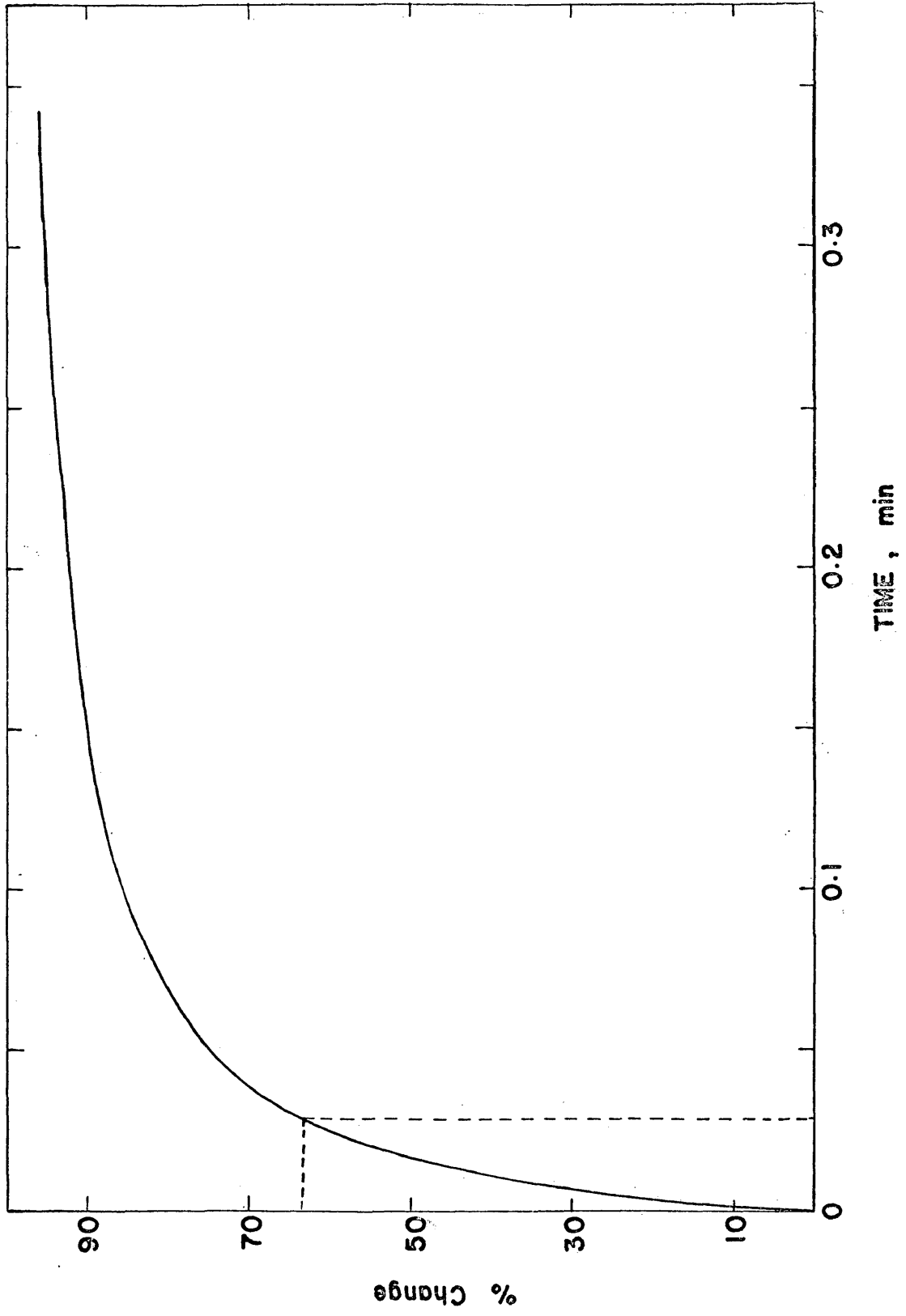


Figure 10. Response of pH combination electrode
(Run RES-3)

Time constant = 1.65 sec

Concentration changed from 0.25 to 0.065 mole/liter

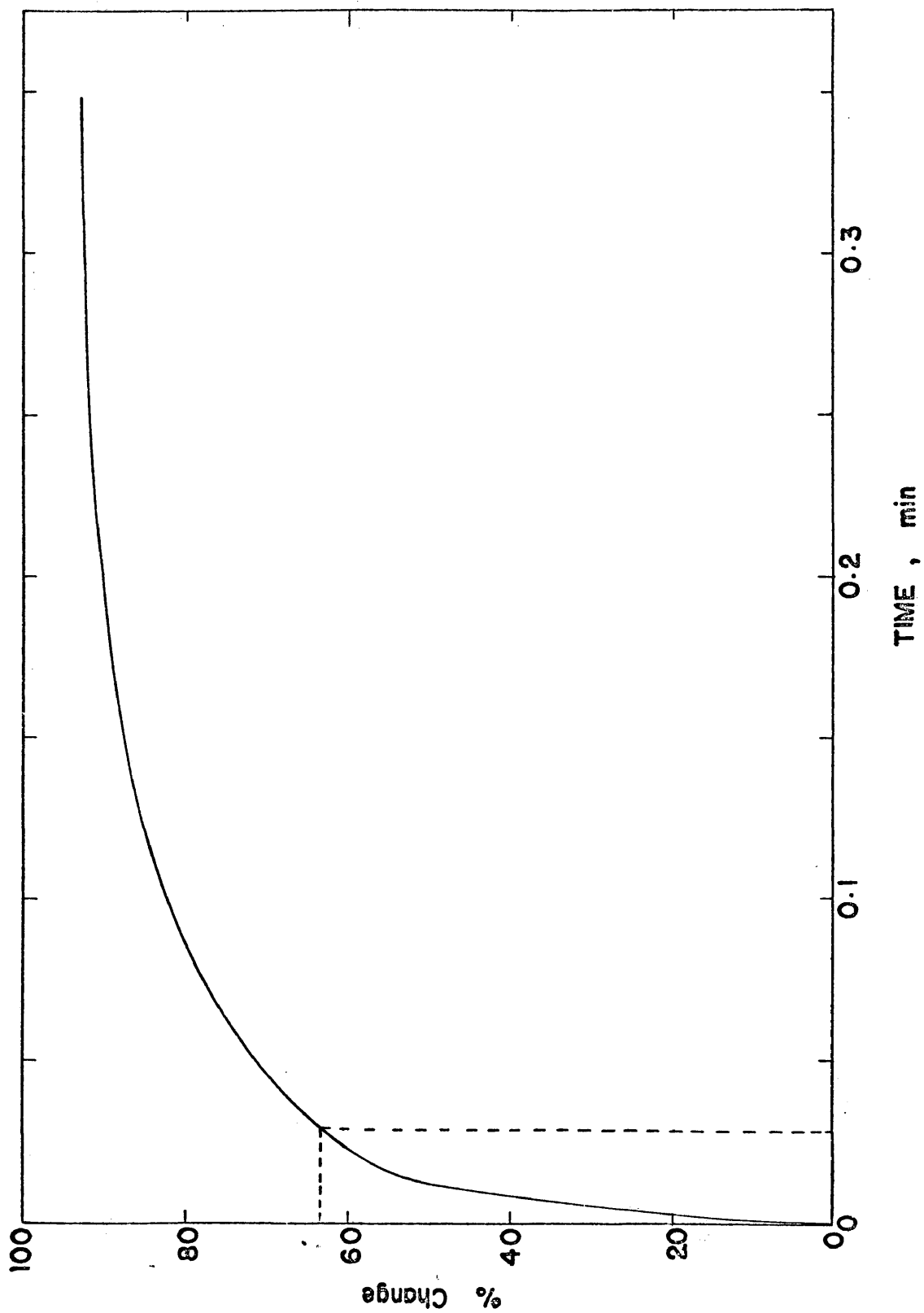


Figure 11. Effect of flow rate on dispersion

t_D = Time constant of dispersion curves, min
(as obtained from the different runs)

$$= 1.83 \exp (-17.78 F)$$

F = Flow rate, liter/min

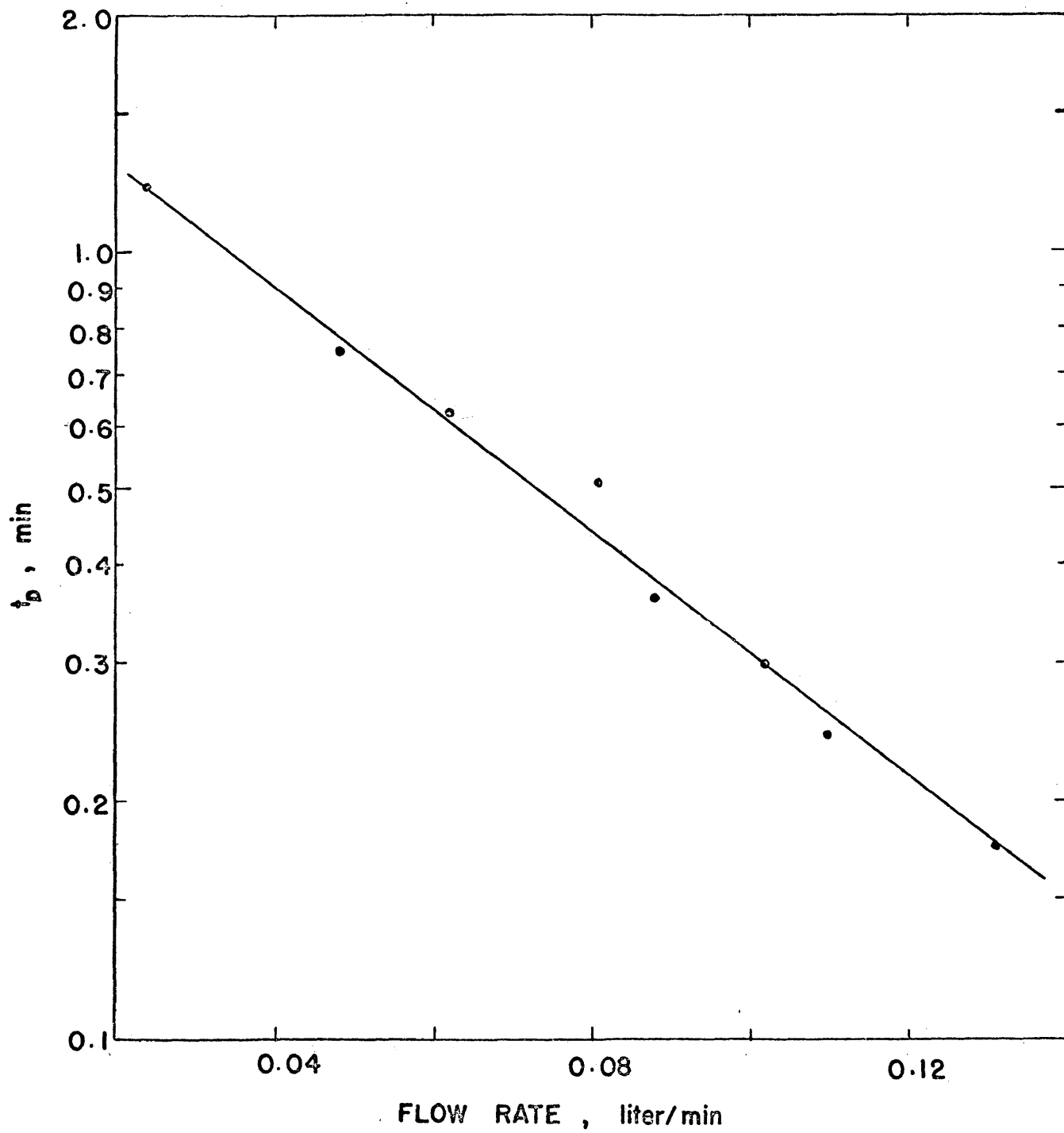


Figure 12. Transient response of outlet sodium hydroxide concentration to single concentration upset (decrease) in methyl acetate (Run 10A)

---- RTD model without dispersion
_____ RTD model with dispersion
• Experimental data

See Table 1 for operating conditions

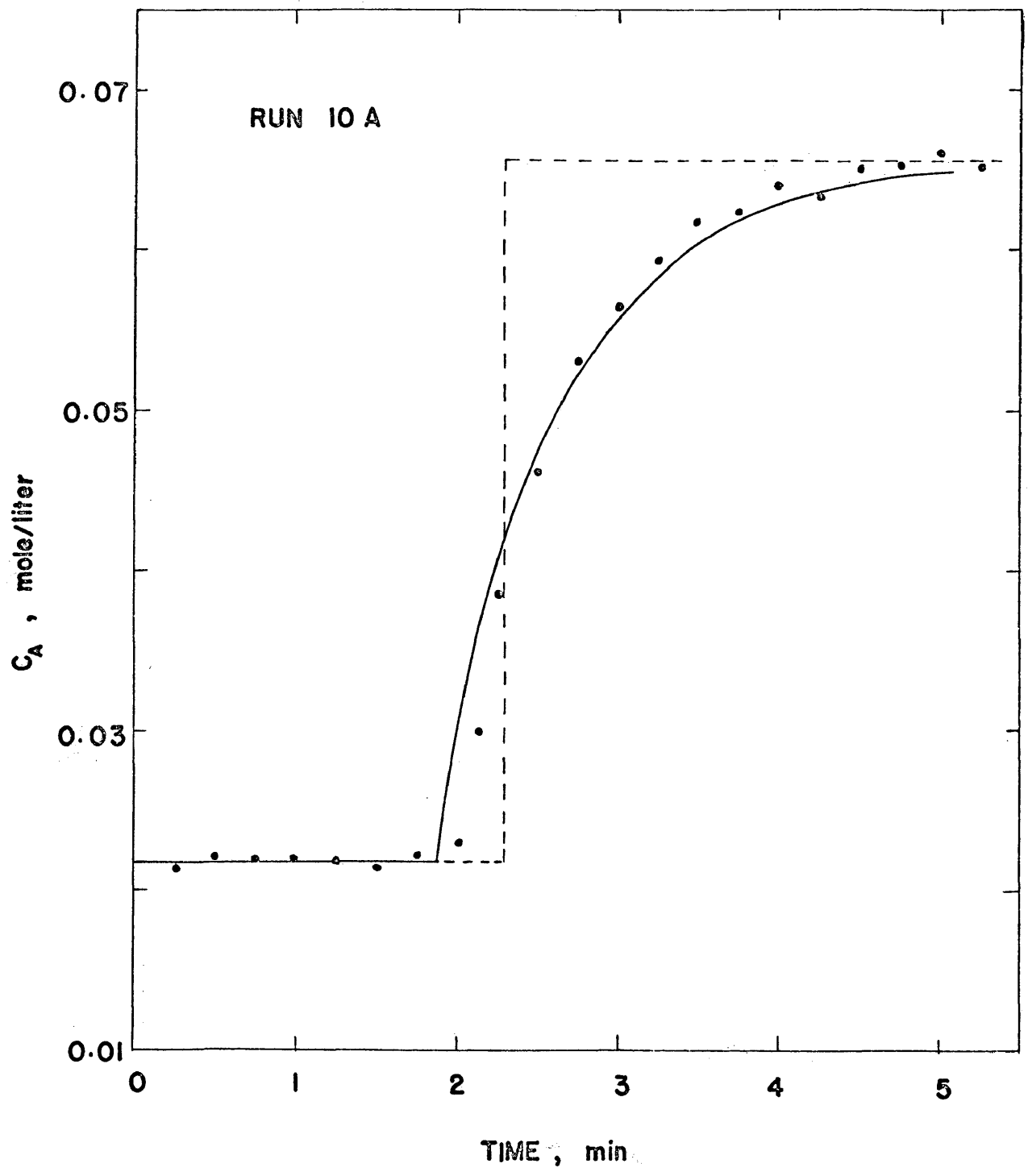


Figure 13. Transient response of outlet sodium hydroxide concentration to single concentration upset (increase) in methyl acetate (Run 10B)

----- RTD model without dispersion

_____ RTD model with dispersion

. Experimental data

See Table 1 for operating conditions

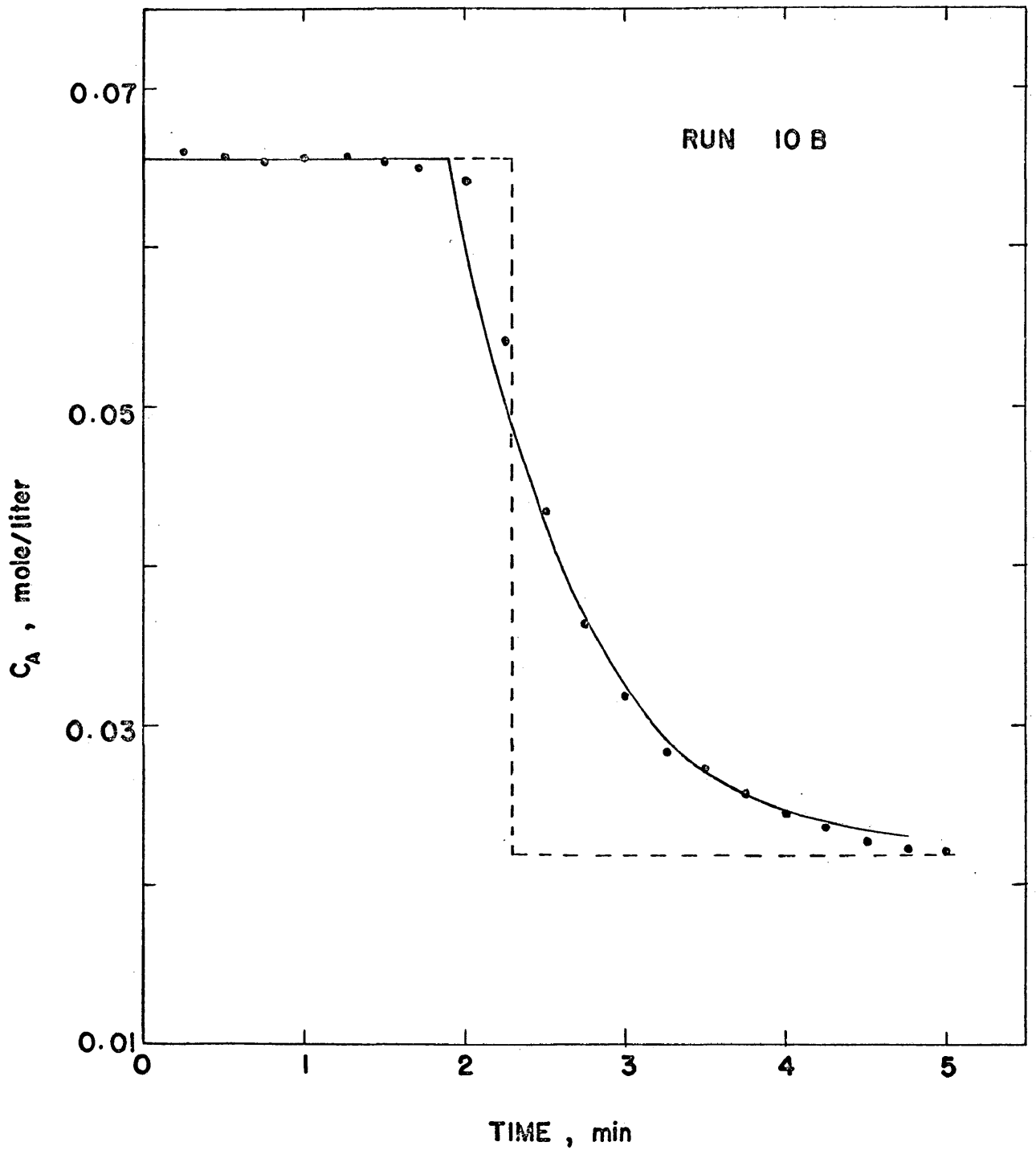


Figure 14. Transient response of outlet sodium hydroxide concentration to single concentration upset in methyl acetate (Runs 11A and 11B)

- RTD model without dispersion
- _____ RTD model with dispersion
- . Experimental data

See Table 1 for operating conditions

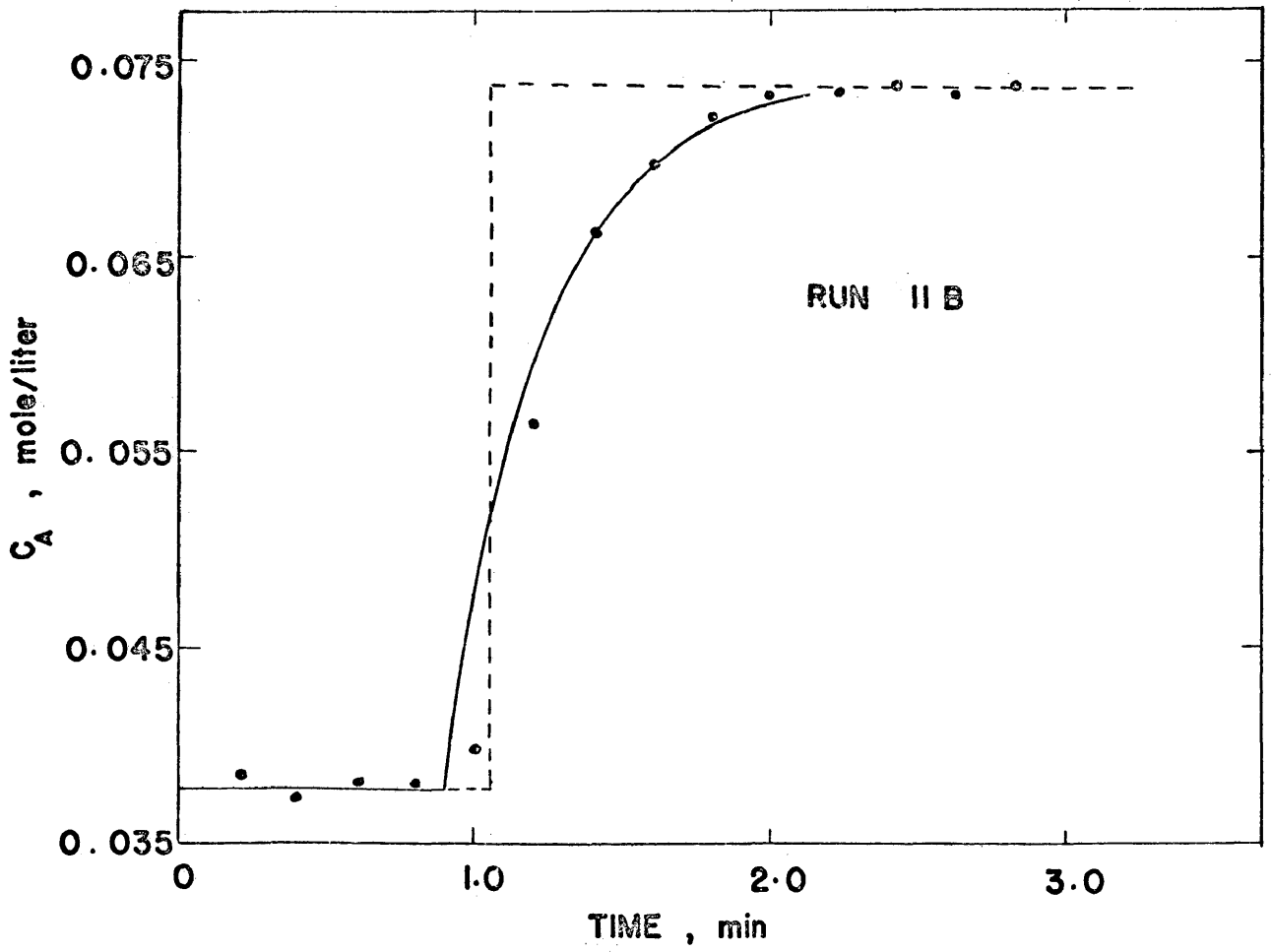
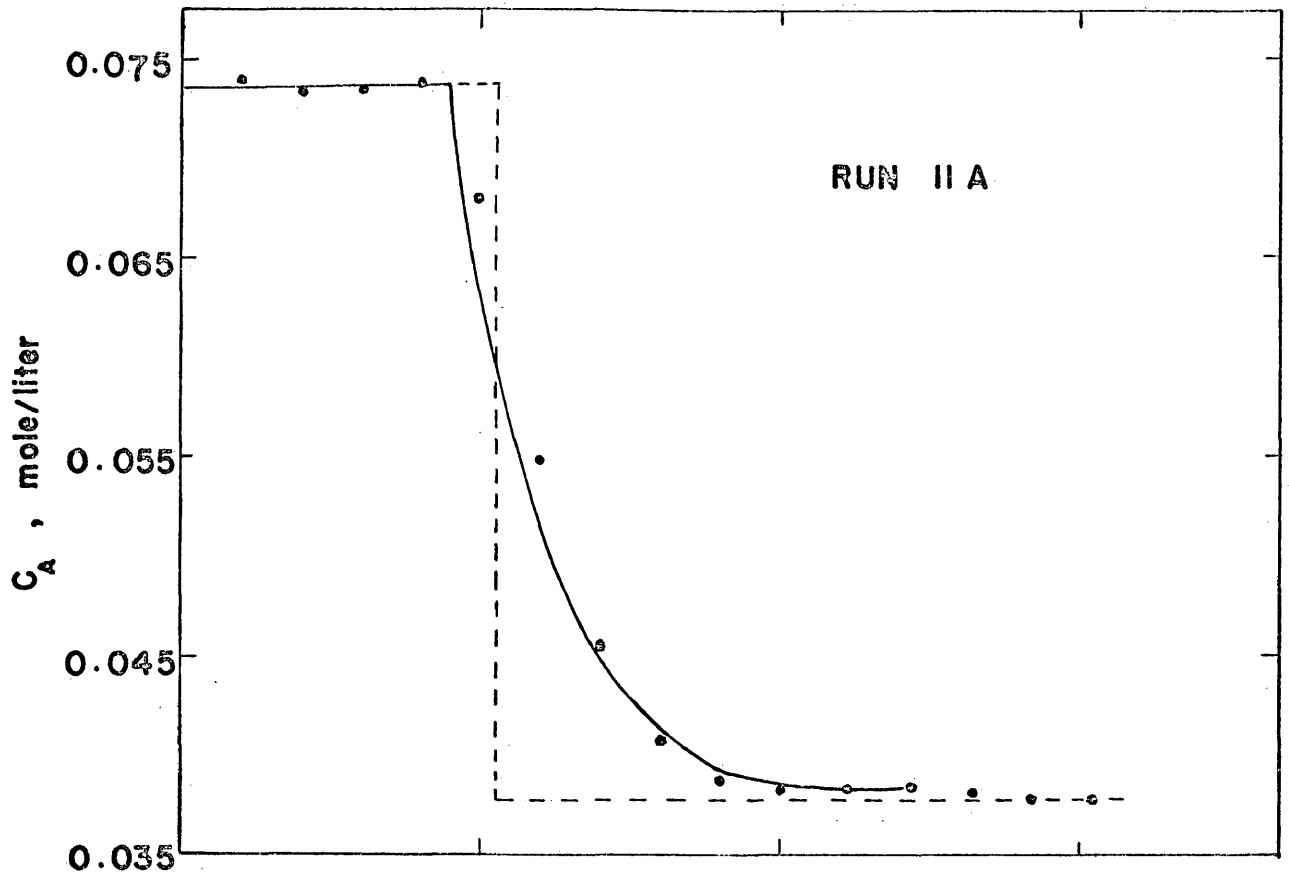


Figure 15. Transient response of outlet sodium hydroxide concentration to single concentration upset in sodium hydroxide (Runs 12A and 12B)

- RTD model without dispersion
- _____ RTD model with dispersion
- . Experimental data

See Table 1 for operating conditions

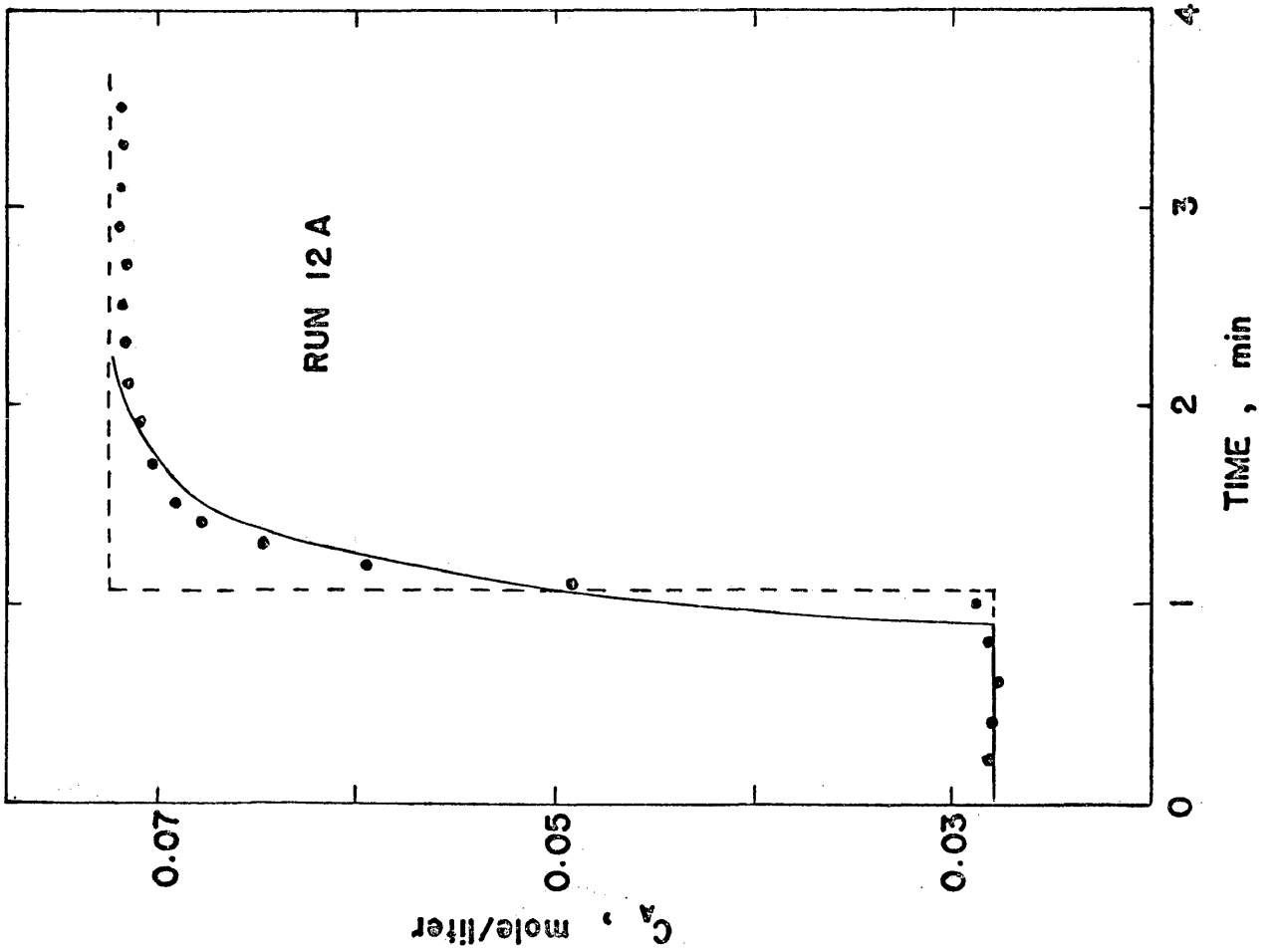
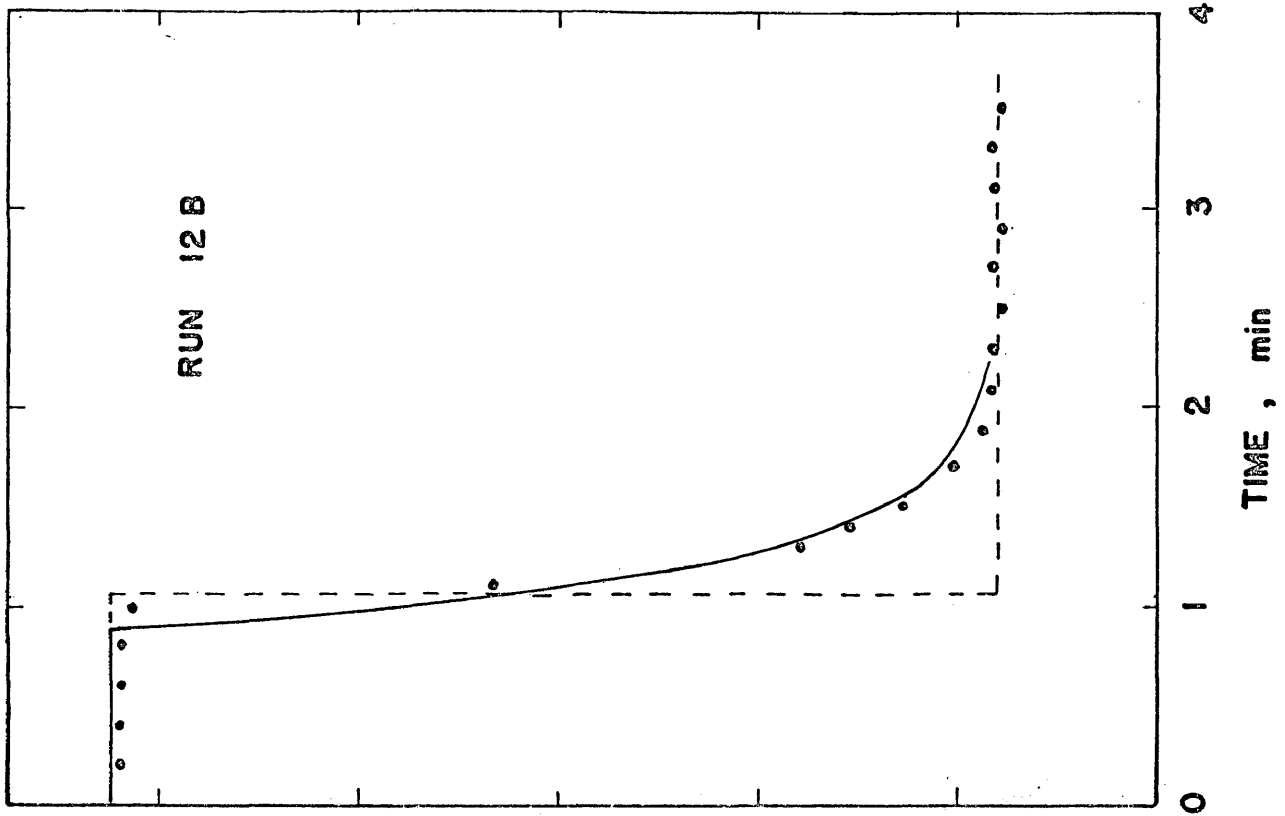


Figure 16. Transient response of outlet sodium hydroxide concentration to single concentration upset (increase) in sodium hydroxide (Run 15A)

- RTD model without dispersion
- RTD model with dispersion
- . Experimental data

See Table 1 for operating conditions

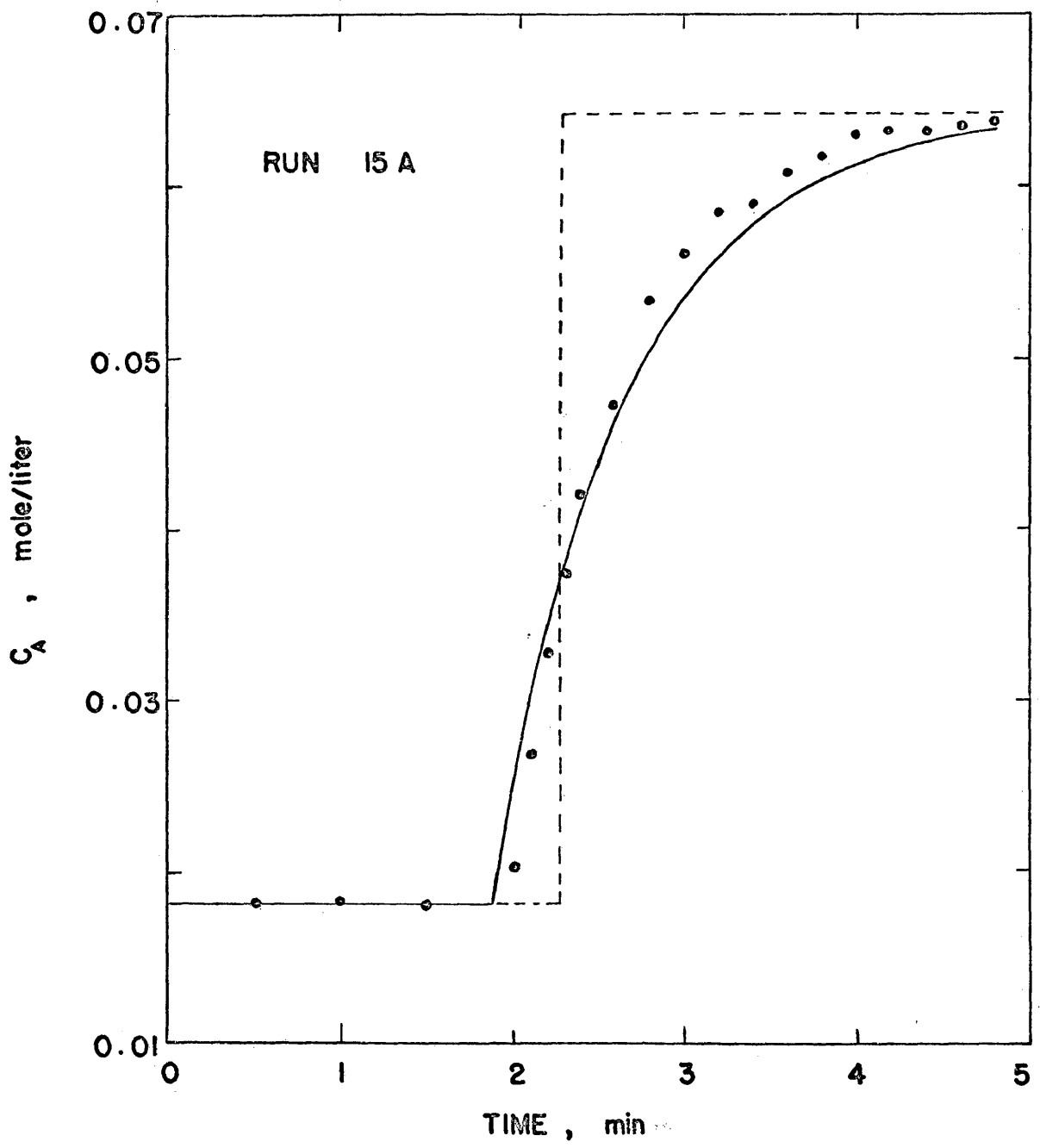


Figure 17. Transient response of outlet sodium hydroxide concentration to single concentration upset (decrease) in sodium hydroxide (Run 15B)

- RTD model without dispersion
- RTD model with dispersion
- Experimental data

See Table 1 for operating conditions

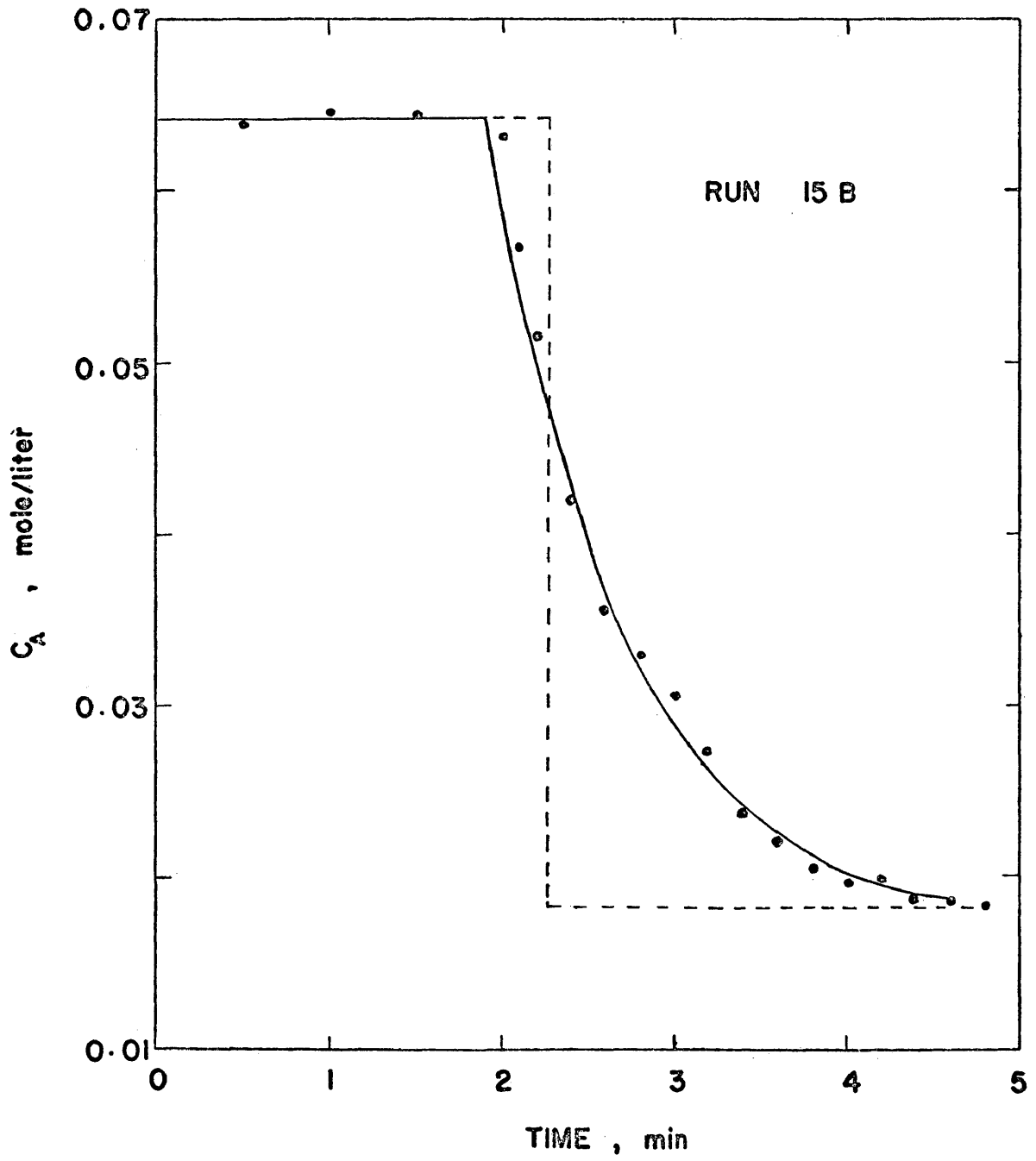


Figure 18. Transient response of outlet sodium hydroxide concentration to simultaneous concentration upset (Run 13A)

- RTD model without dispersion
- RTD model with dispersion
- . Experimental data

See Table 1 for operating conditions

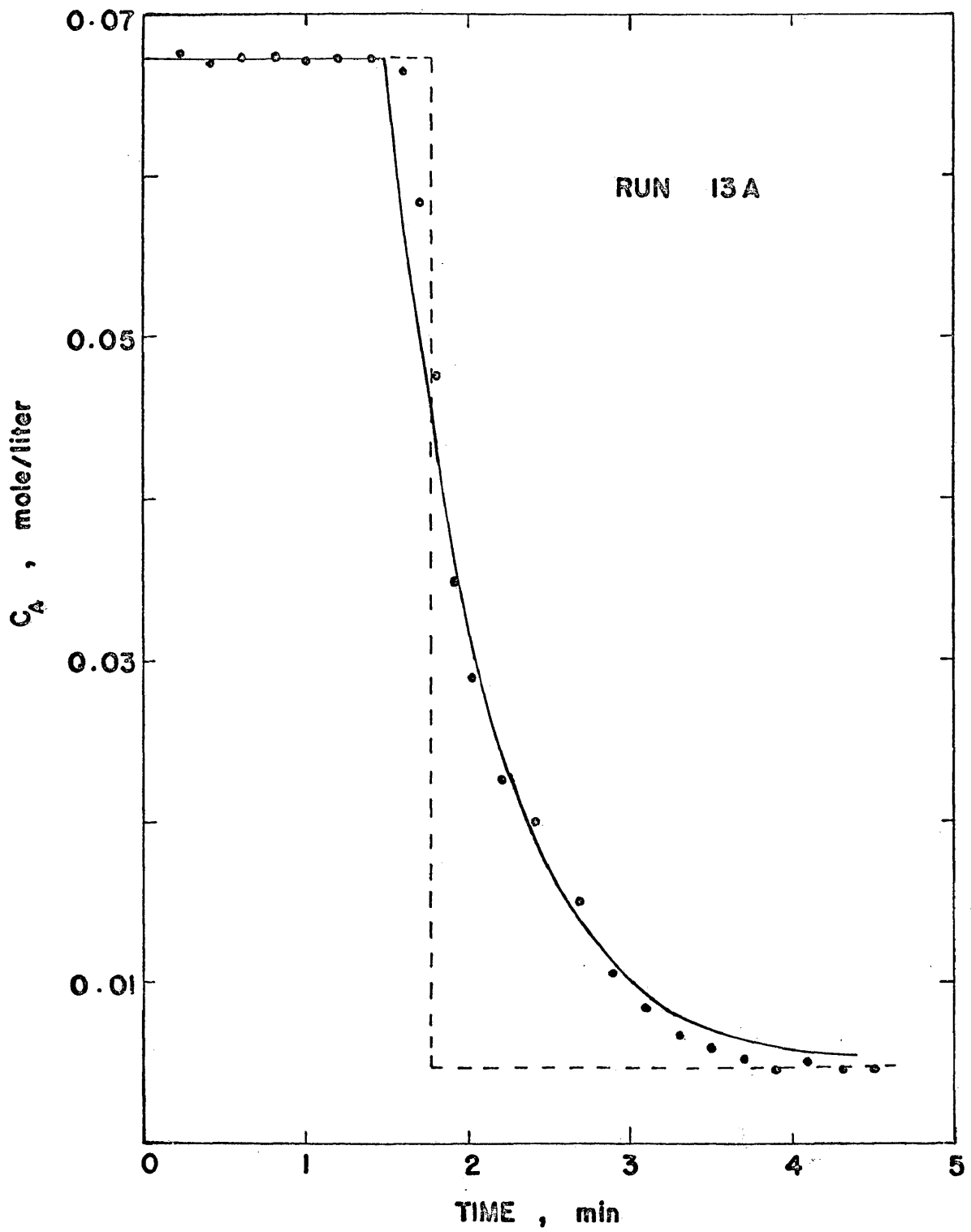


Figure 19. Transient response of outlet sodium hydroxide concentration to simultaneous concentration upset (Run 13B)

- RTD model without dispersion
- RTD model with dispersion
- . Experimental data

See Table 1 for operating conditions

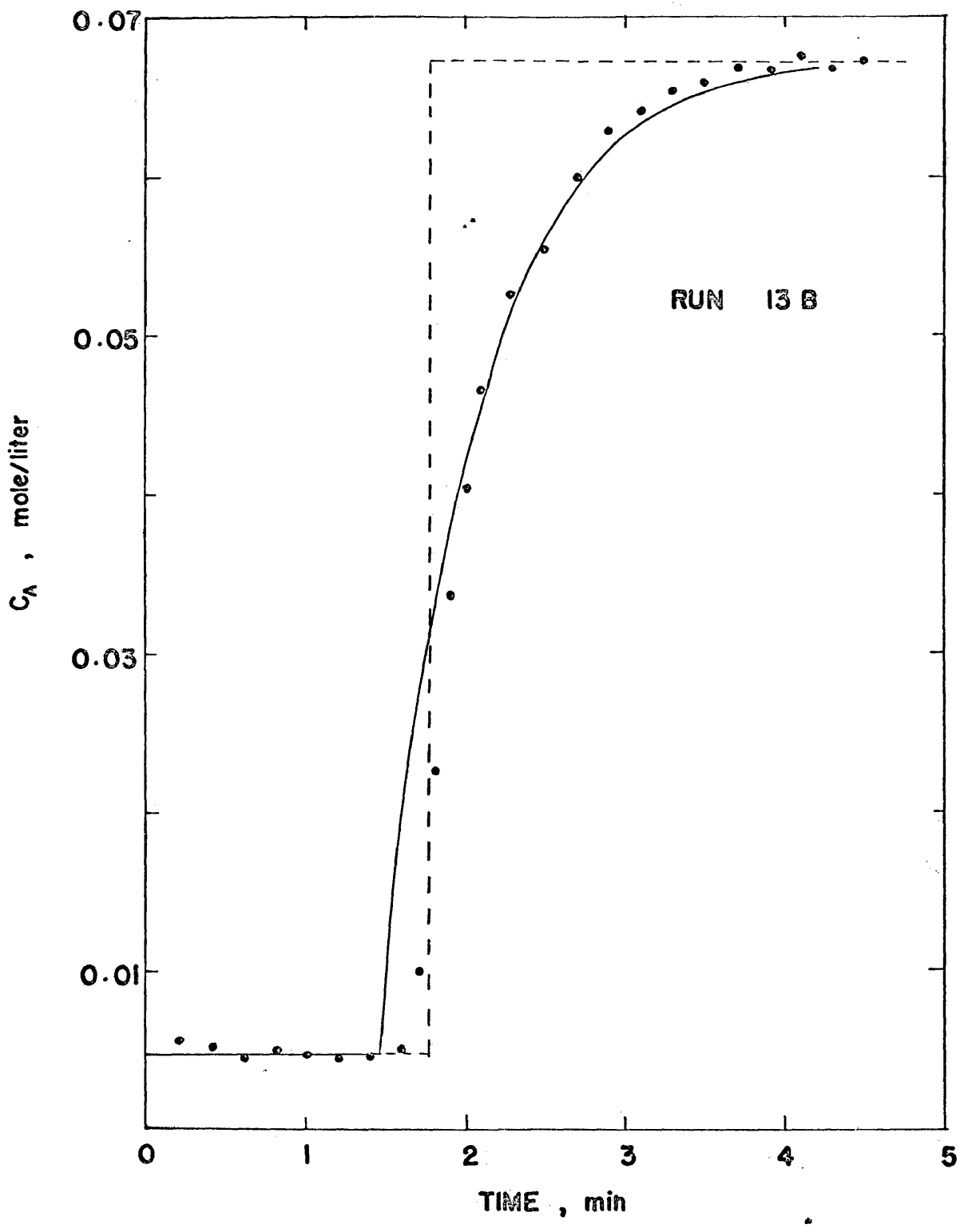


Figure 20. Transient response of outlet sodium hydroxide concentration to simultaneous concentration upset (Runs 14 A and 14 B)

- RTD model without dispersion
- RTD model with dispersion
- . Experimental data

See Table 1 for operating conditions

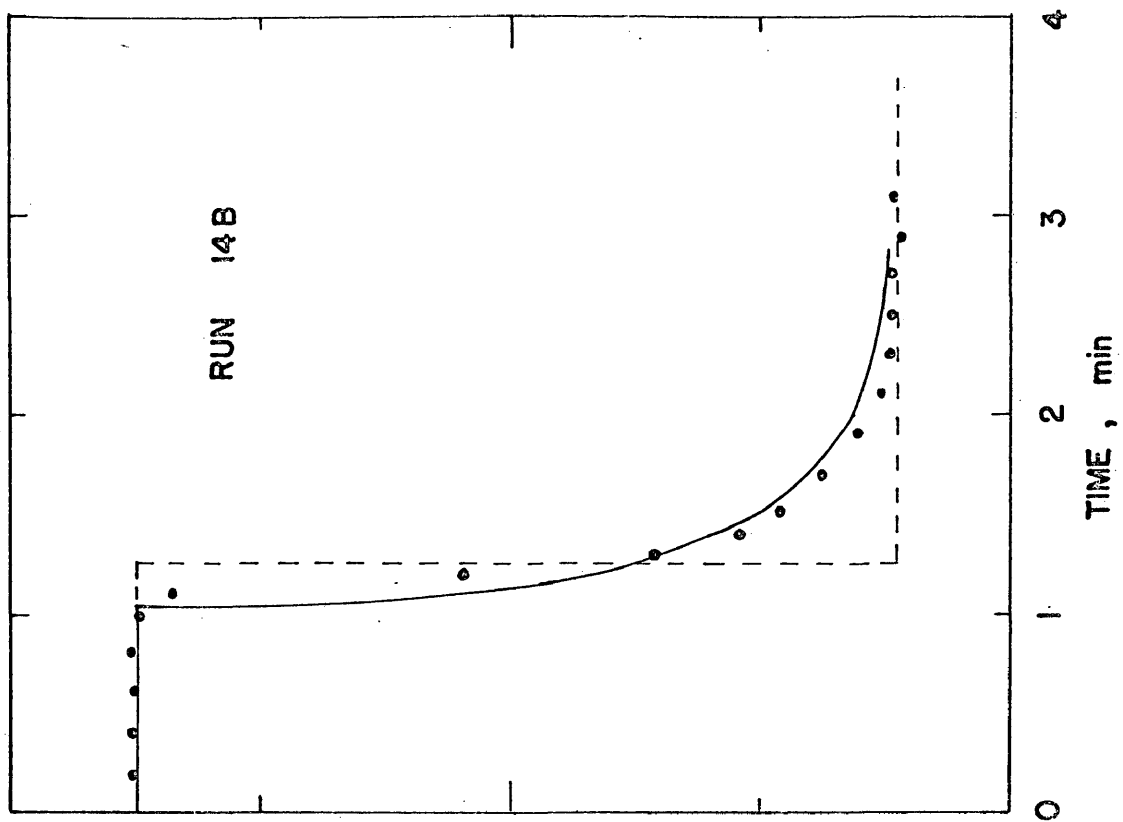
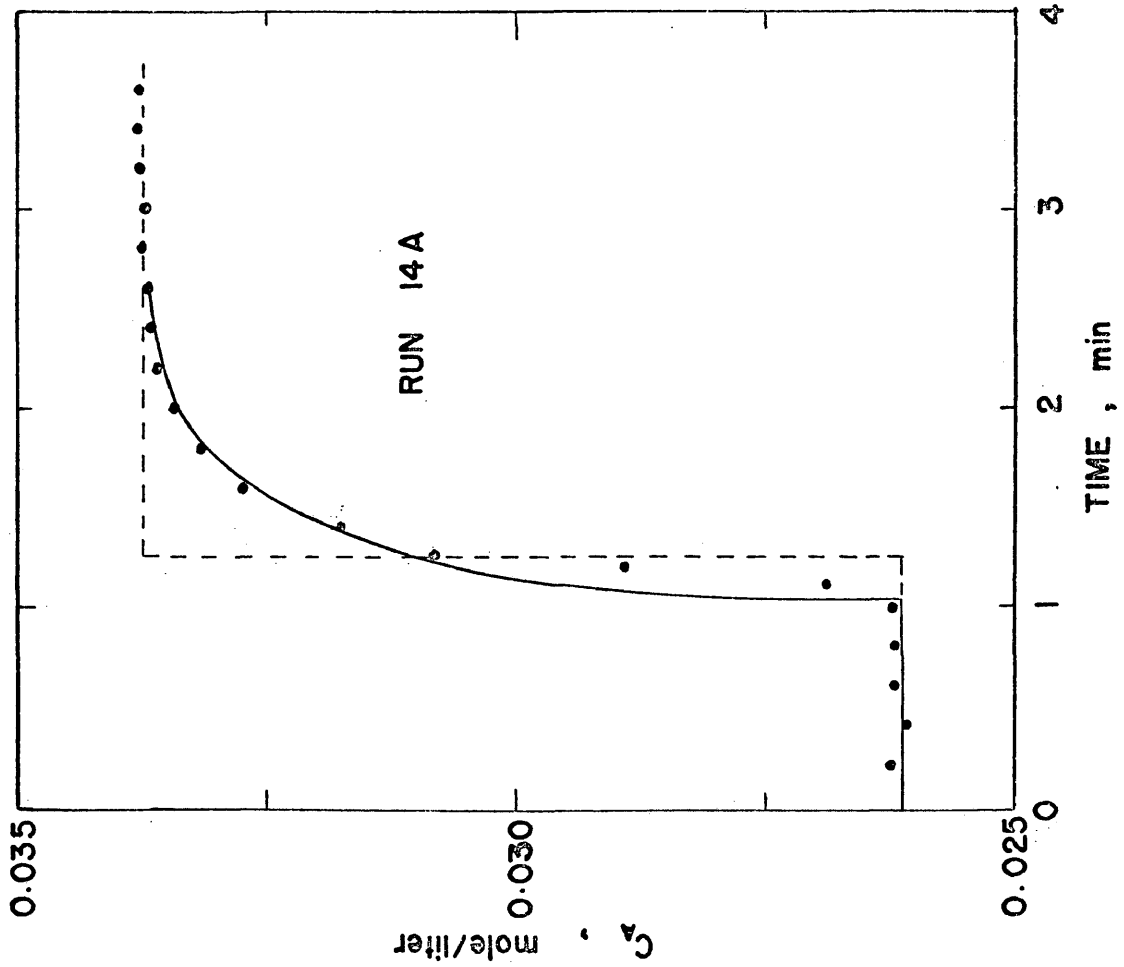


Figure 21. Transient response of outlet sodium hydroxide concentration to simultaneous concentration upset (Runs 7A and 7B)

- RTD model without dispersion
- _____ RTD model with dispersion
- . Experimental data

See Table 1 for operating conditions

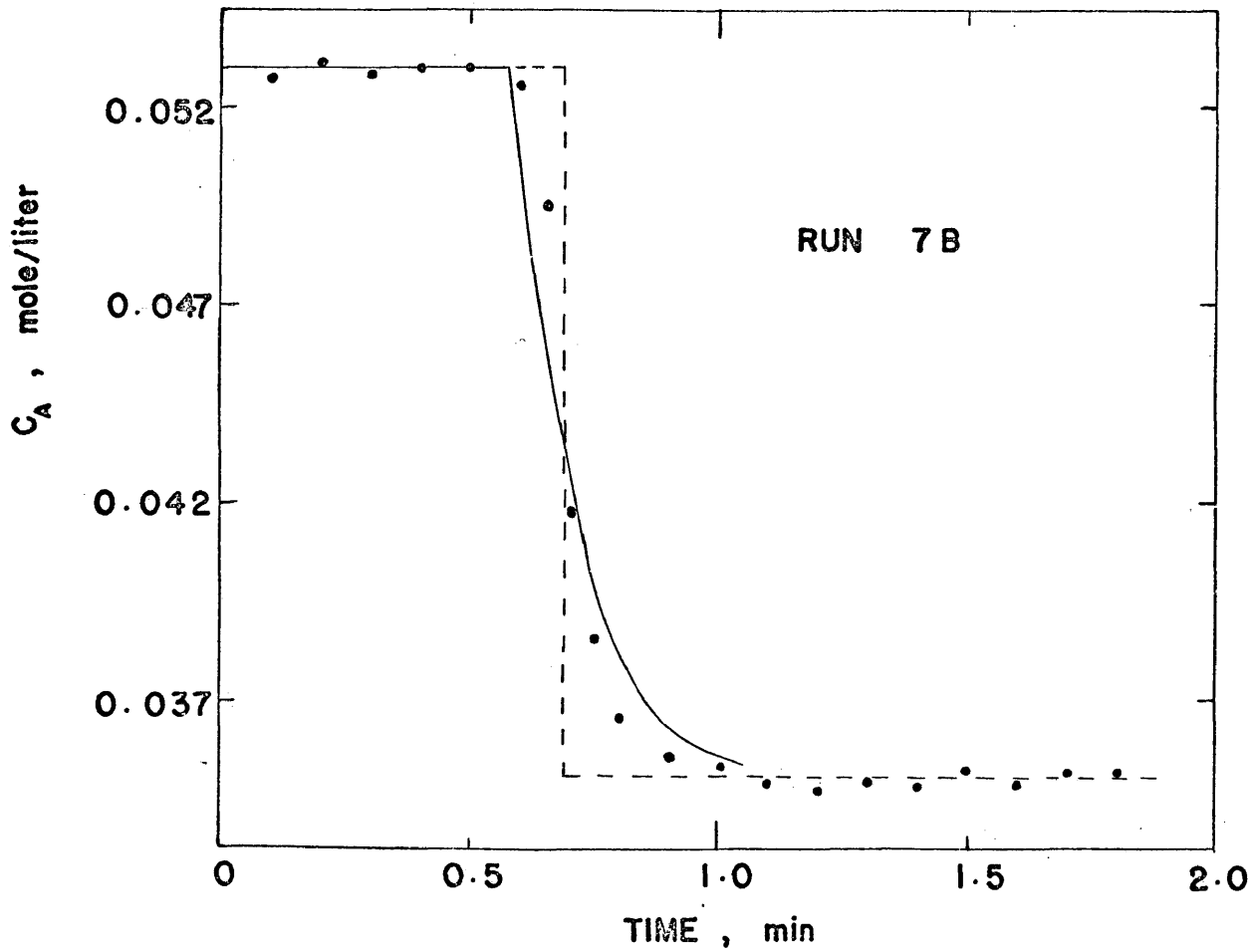
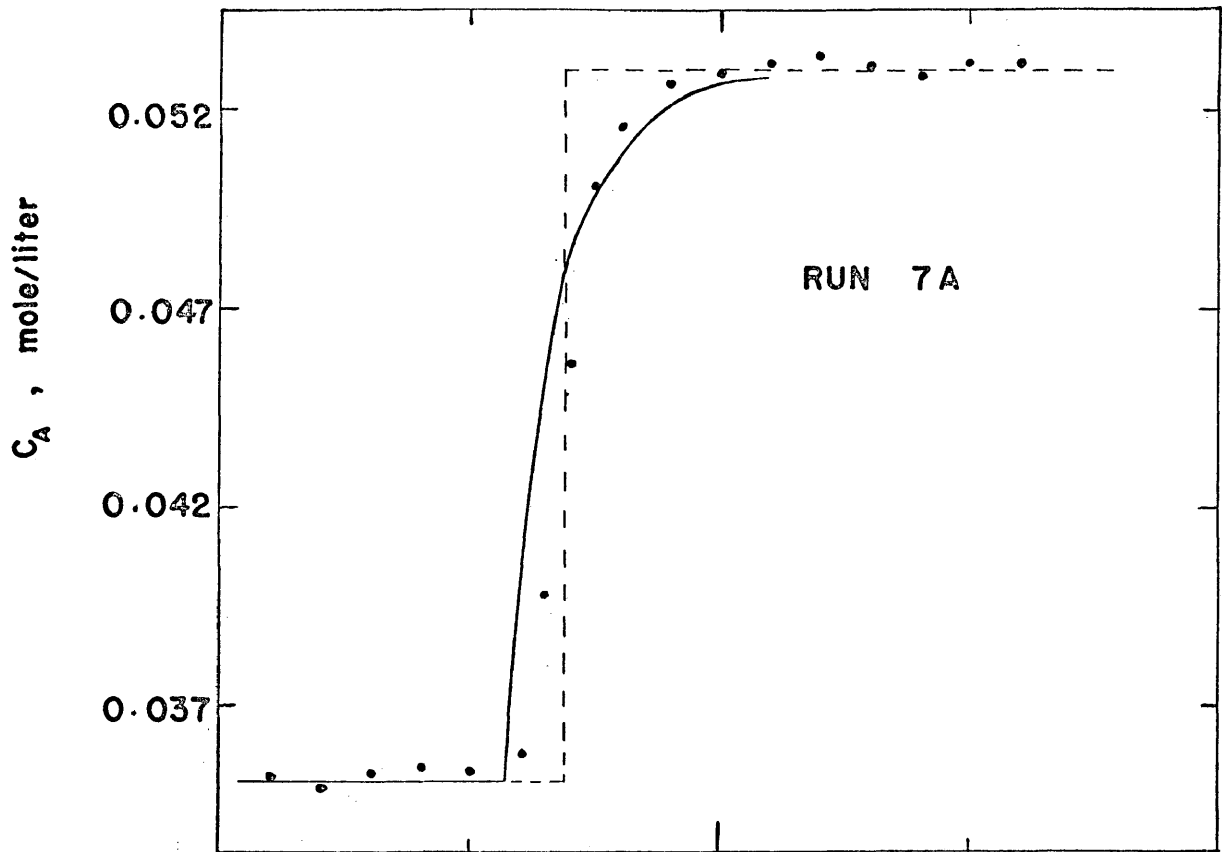
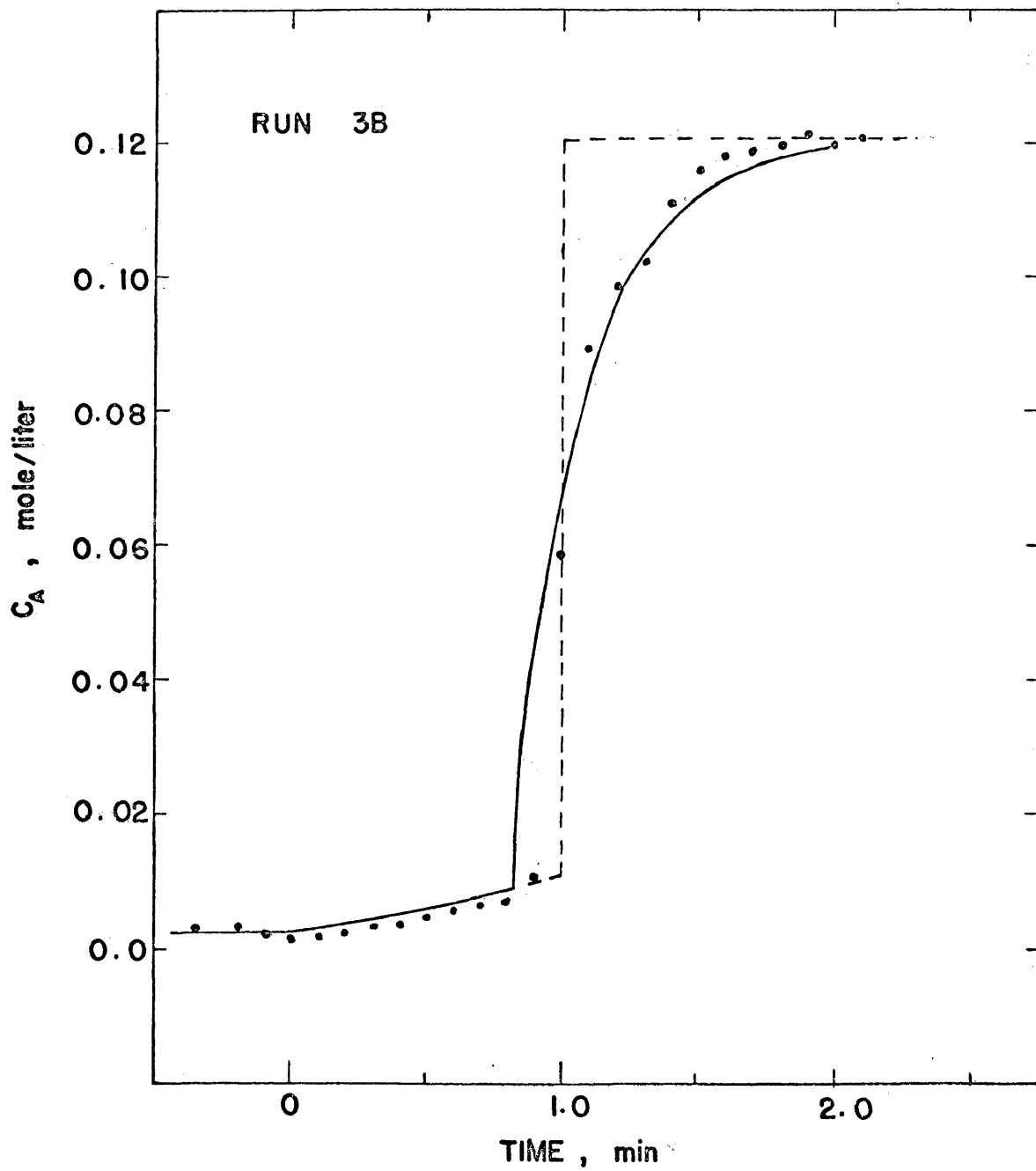


Figure 22. Transient response of outlet sodium hydroxide concentration to single flow upset (increase) in sodium hydroxide (Run 3B)

- RTD model without dispersion
- RTD model with dispersion
- . Experimental data

See Table 1 for operating conditions



- RTD model without dispersion
- RTD model with dispersion
- Experimental data

Figure 23. Transient response of outlet sodium hydroxide concentration to single flow upset (decrease) in methyl acetate (Run 1A)

- RTD model without dispersion
- RTD model with dispersion
- Experimental data

See Table 1 for operating conditions

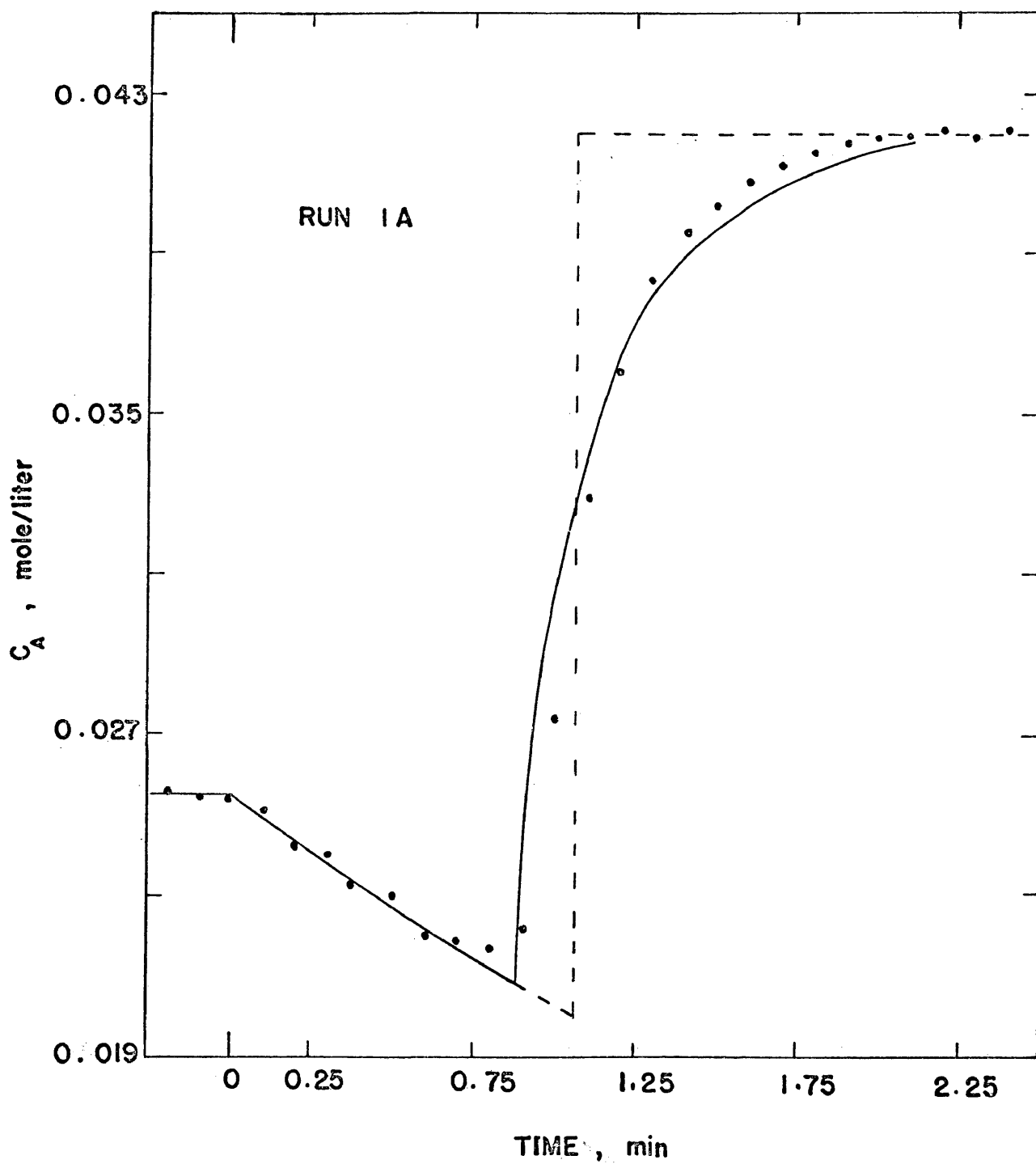


Figure 24. Transient response of outlet sodium hydroxide concentration to single flow upset in sodium hydroxide (Runs 4A and 4B)

- RTD model without dispersion
- _____ RTD model with dispersion
- . Experimental data

See Table 1 for operating conditions

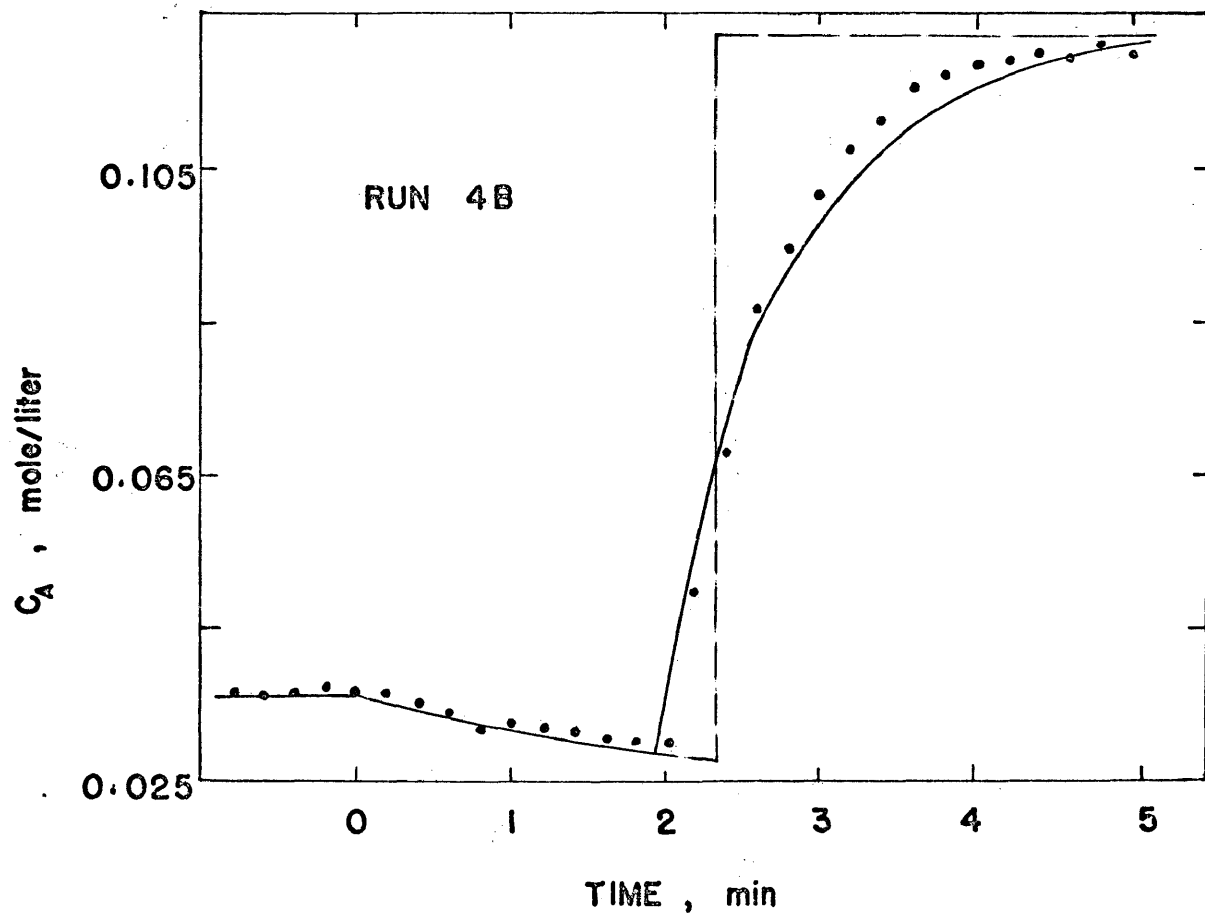
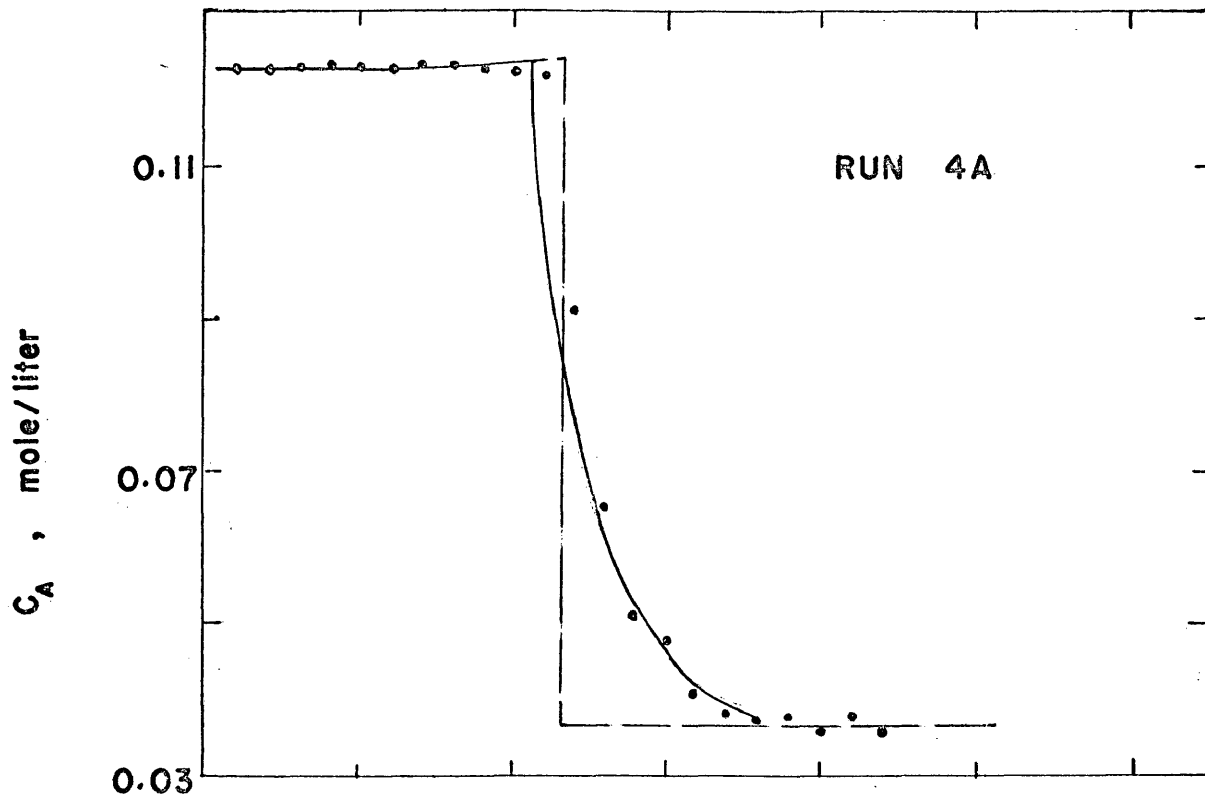


Figure 25. Transient response of outlet sodium hydroxide concentration to single flow upset (increase) in methyl acetate (Run 1B)

- RTD model without dispersion
- RTD model with dispersion
- . Experimental data

See Table 1 for operating conditions

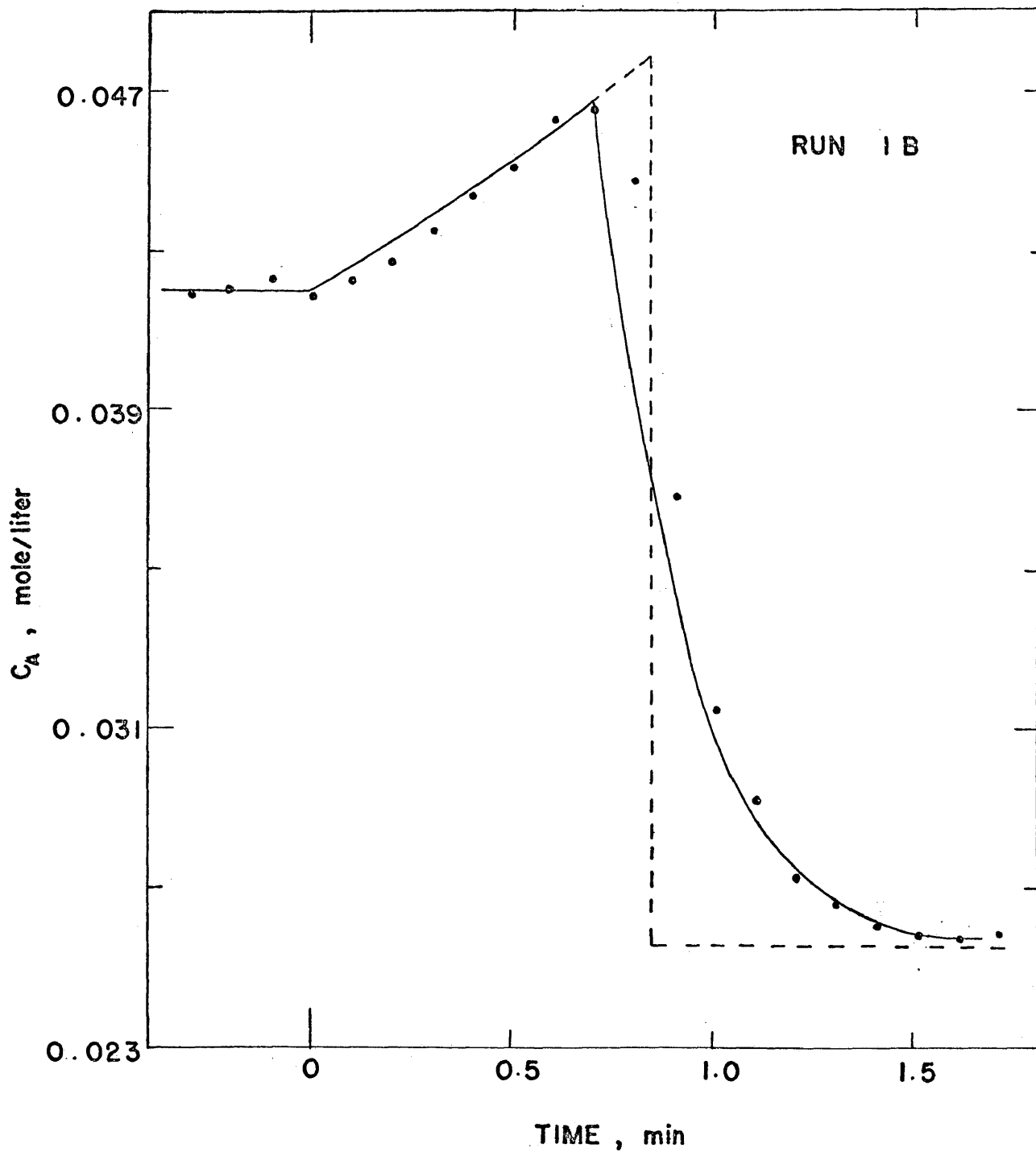


Figure 26. Transient response of outlet sodium hydroxide concentration to simultaneous flow upset (increase) (Run 2B)

See Table 1 for operating conditions

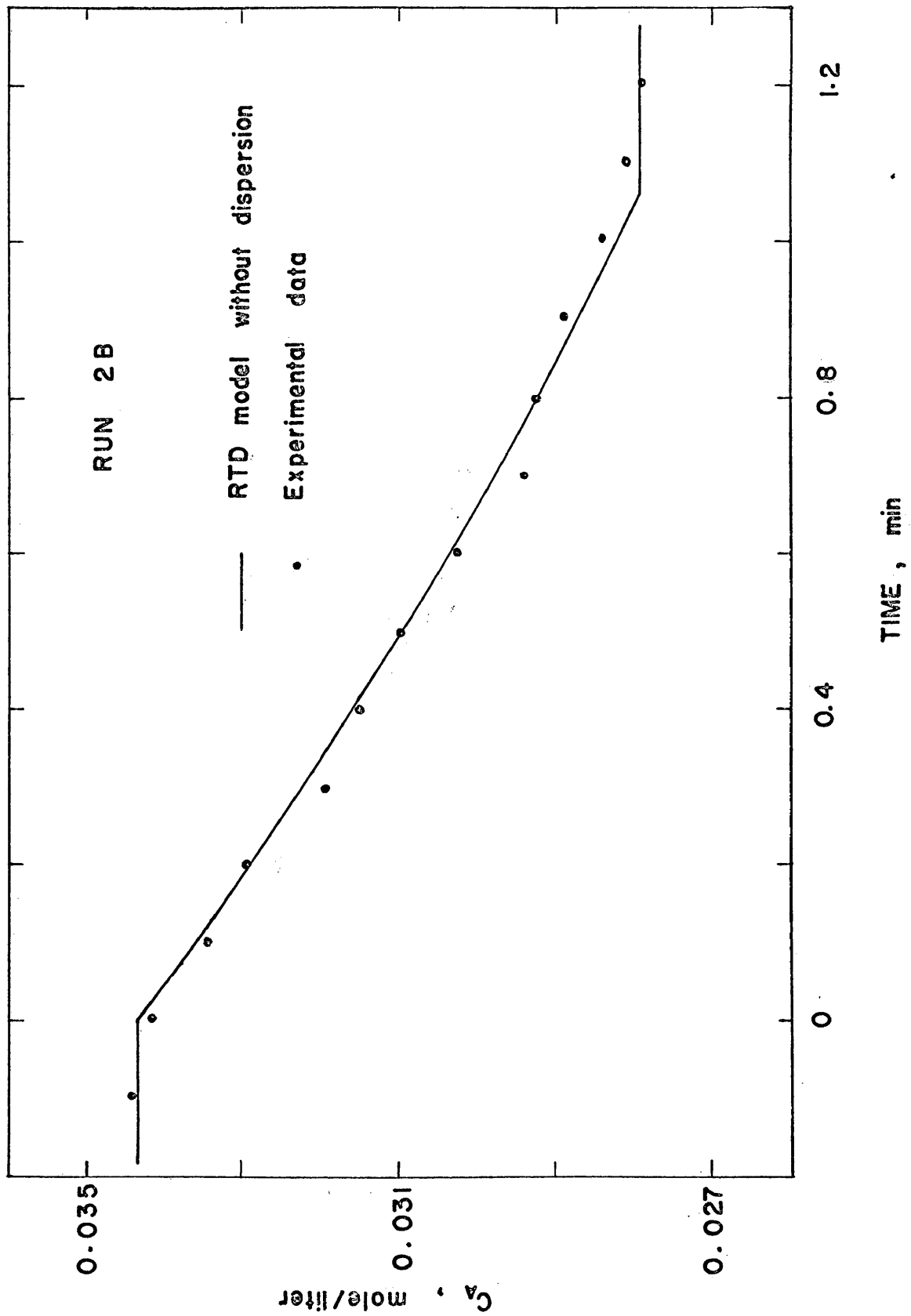


Figure 27. Transient response of outlet sodium hydroxide concentration to simultaneous flow upset (decrease) (Run 2A)

See Table 1 for operating conditions

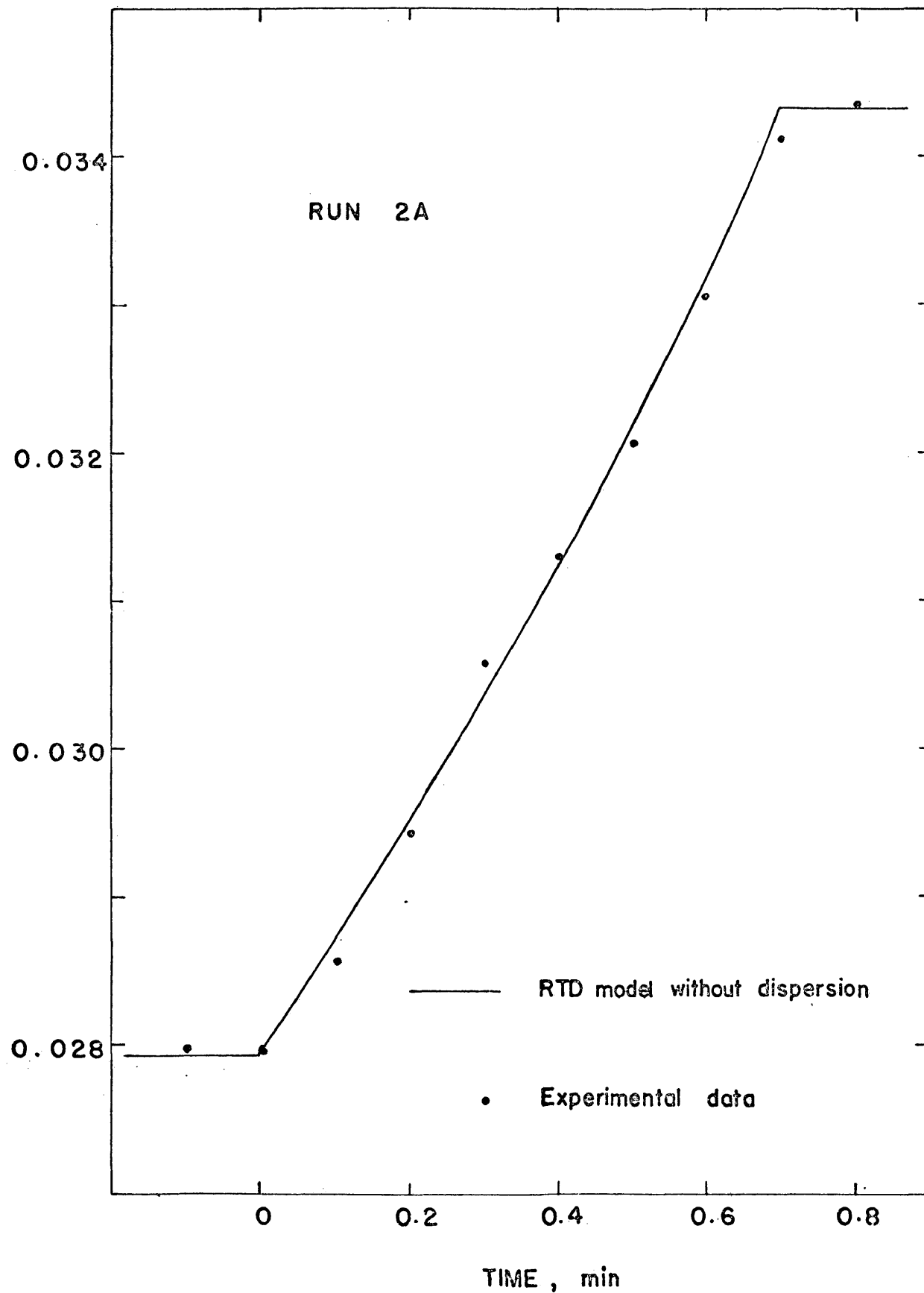


Figure 28. Transient response of outlet sodium hydroxide concentration to sodium hydroxide concentration decrease and methyl acetate flow decrease (Run 5A)

- RTD model without dispersion
- RTD model with dispersion
- Experimental data

See Table 1 for operating conditions

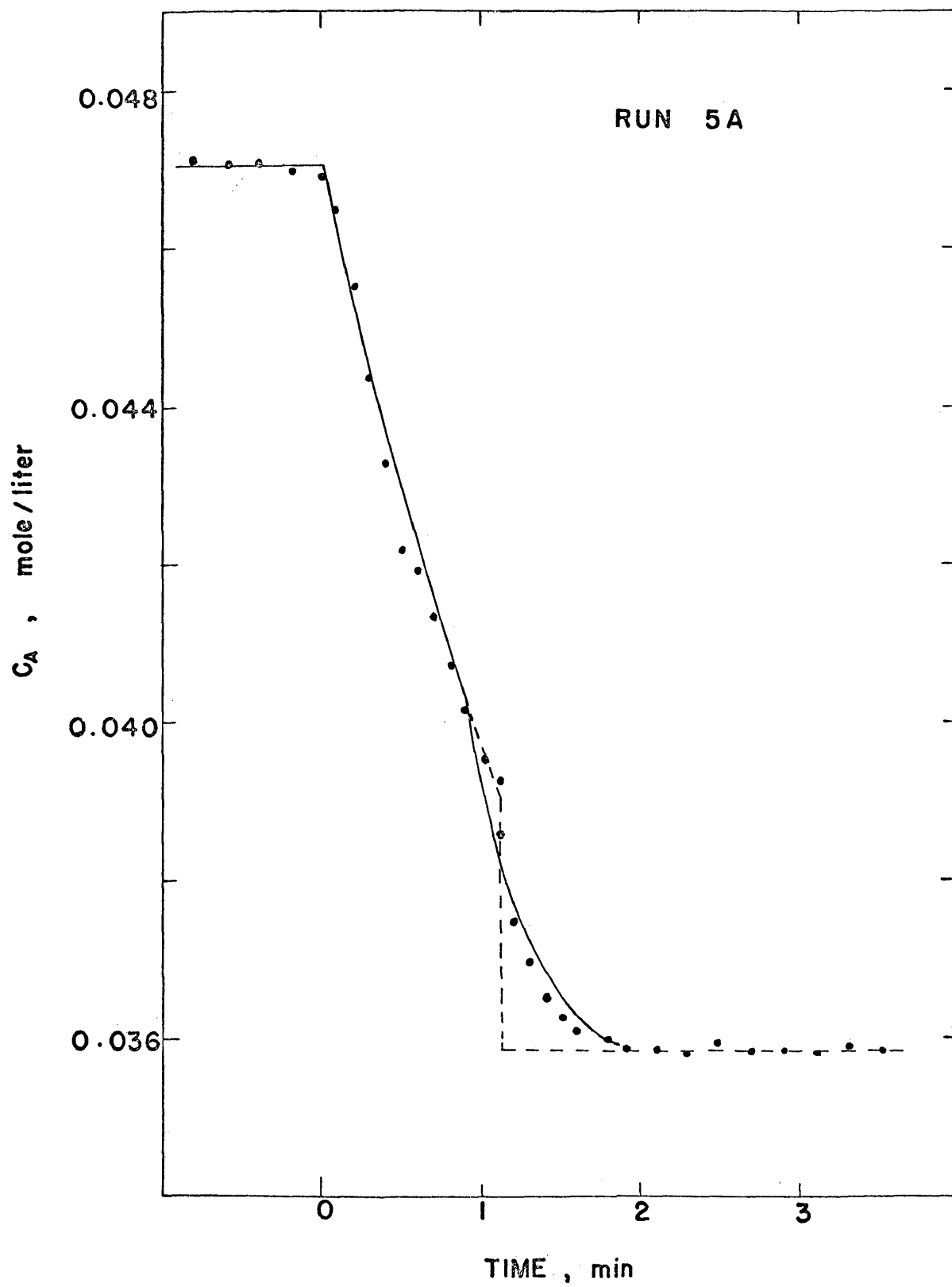


Figure 29. Transient response of outlet sodium hydroxide concentration to sodium hydroxide concentration increase and methyl acetate flow increase (Run 5B)

- RTD model without dispersion
- RTD model with dispersion
- . Experimental data

See Table 1 for operating conditions

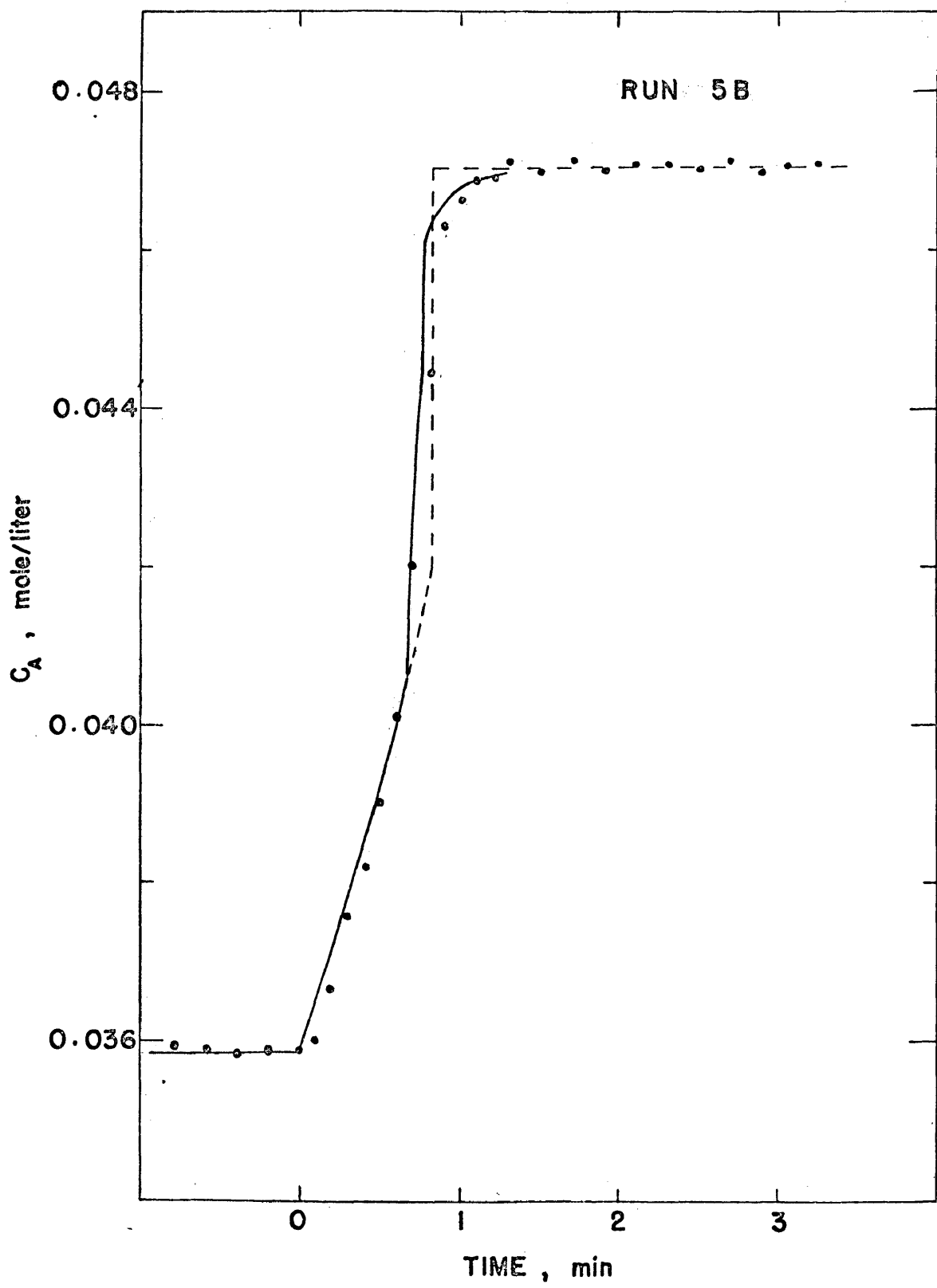


Figure 30. Transient response of outlet sodium hydroxide concentration to methyl acetate concentration increase and sodium hydroxide flow decrease (Run 6A)

----- RTD model without dispersion
——— RTD model with dispersion
. Experimental data

See Table 1 for operating conditions

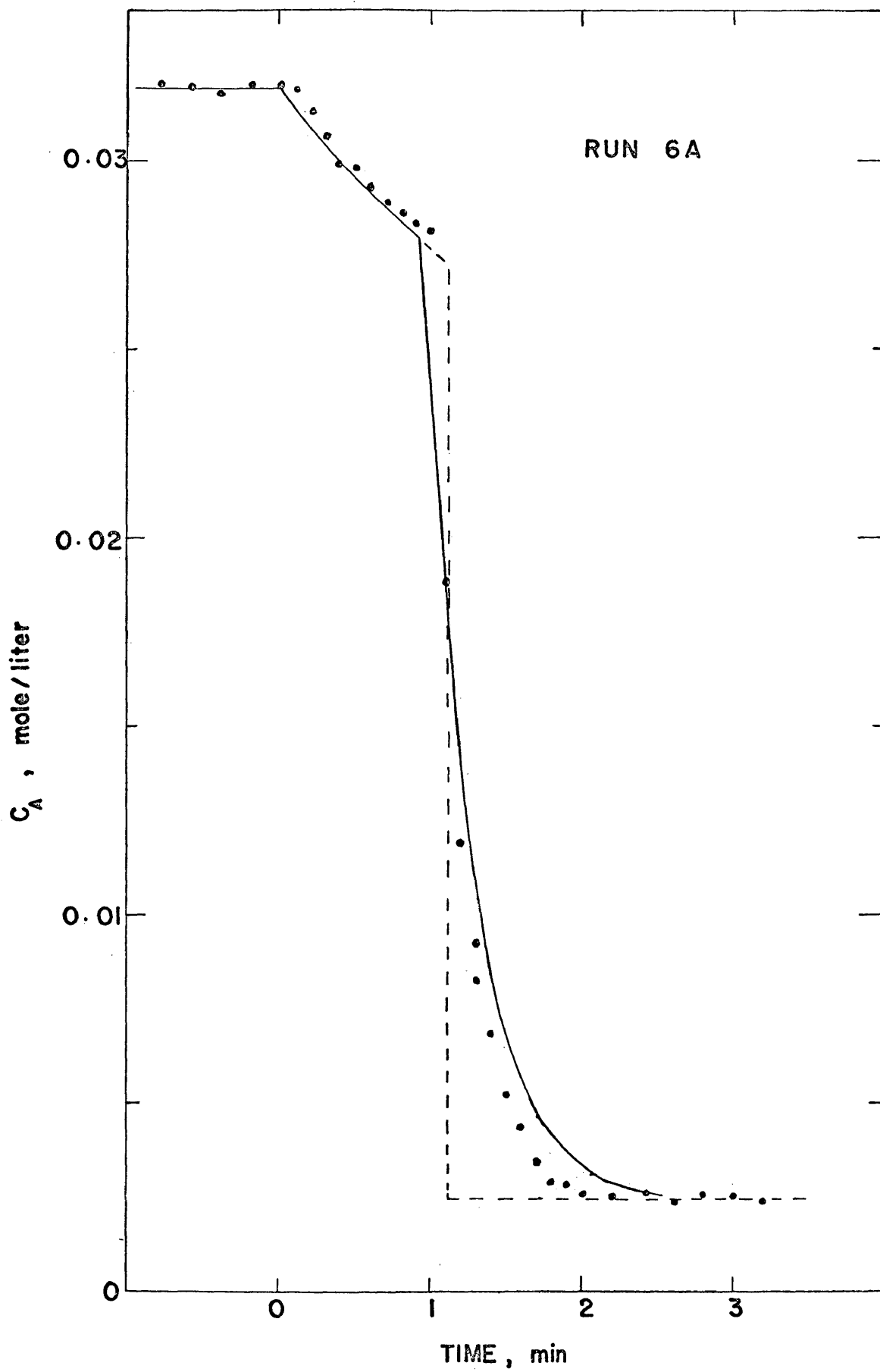


Figure 31. Transient response of outlet sodium hydroxide concentration to methyl acetate concentration decrease and sodium hydroxide flow increase (Run 6B)

----- RTD model without dispersion
——— RTD model with dispersion
. Experimental data

See Table 1 for operating conditions

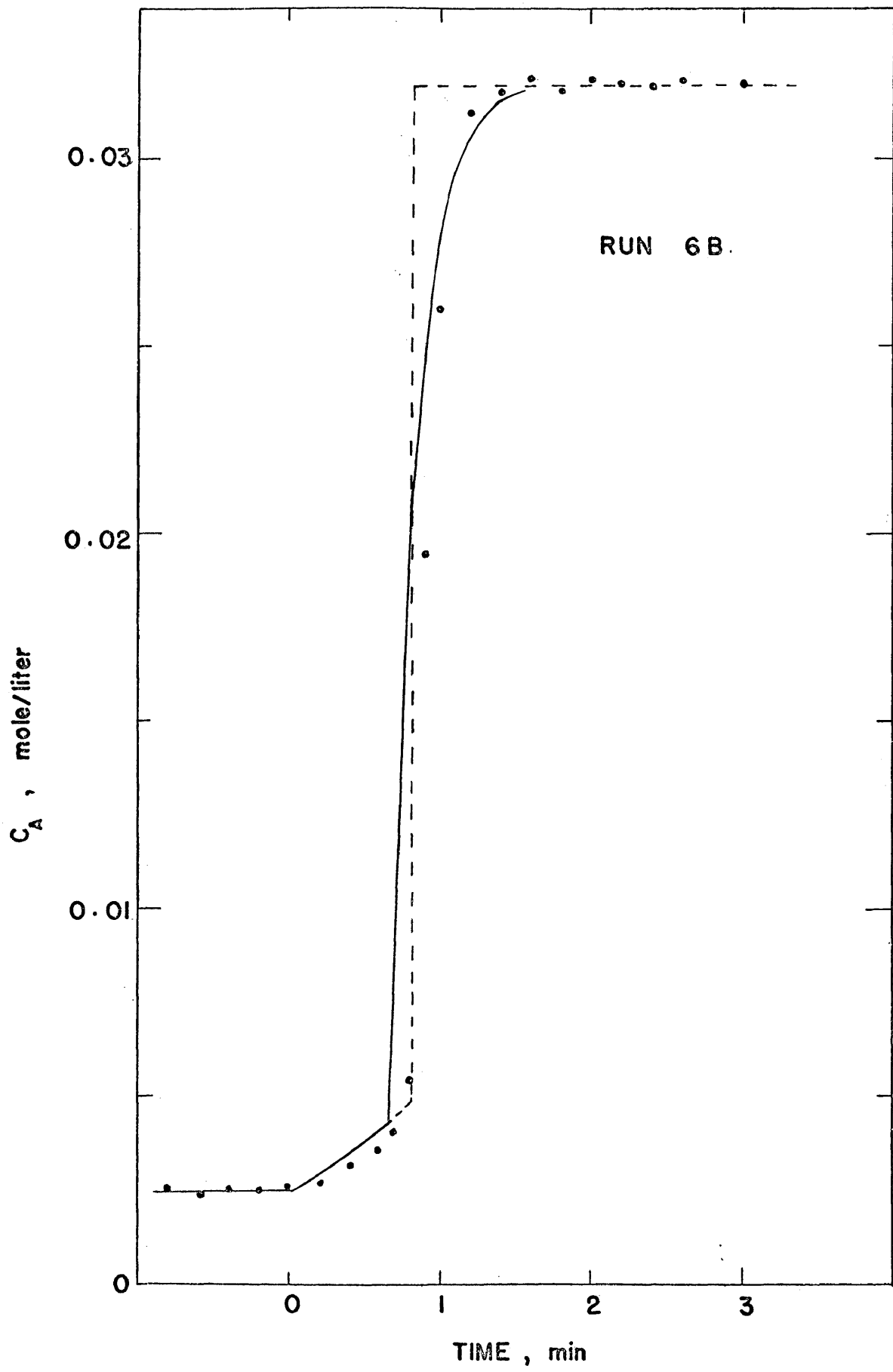


Figure 32. Transient response of outlet sodium hydroxide concentration to simultaneous decrease in methyl acetate concentration and flow (Run 9B)

- RTD model without dispersion
- RTD model with dispersion
- . Experimental data

See Table 1 for operating conditions

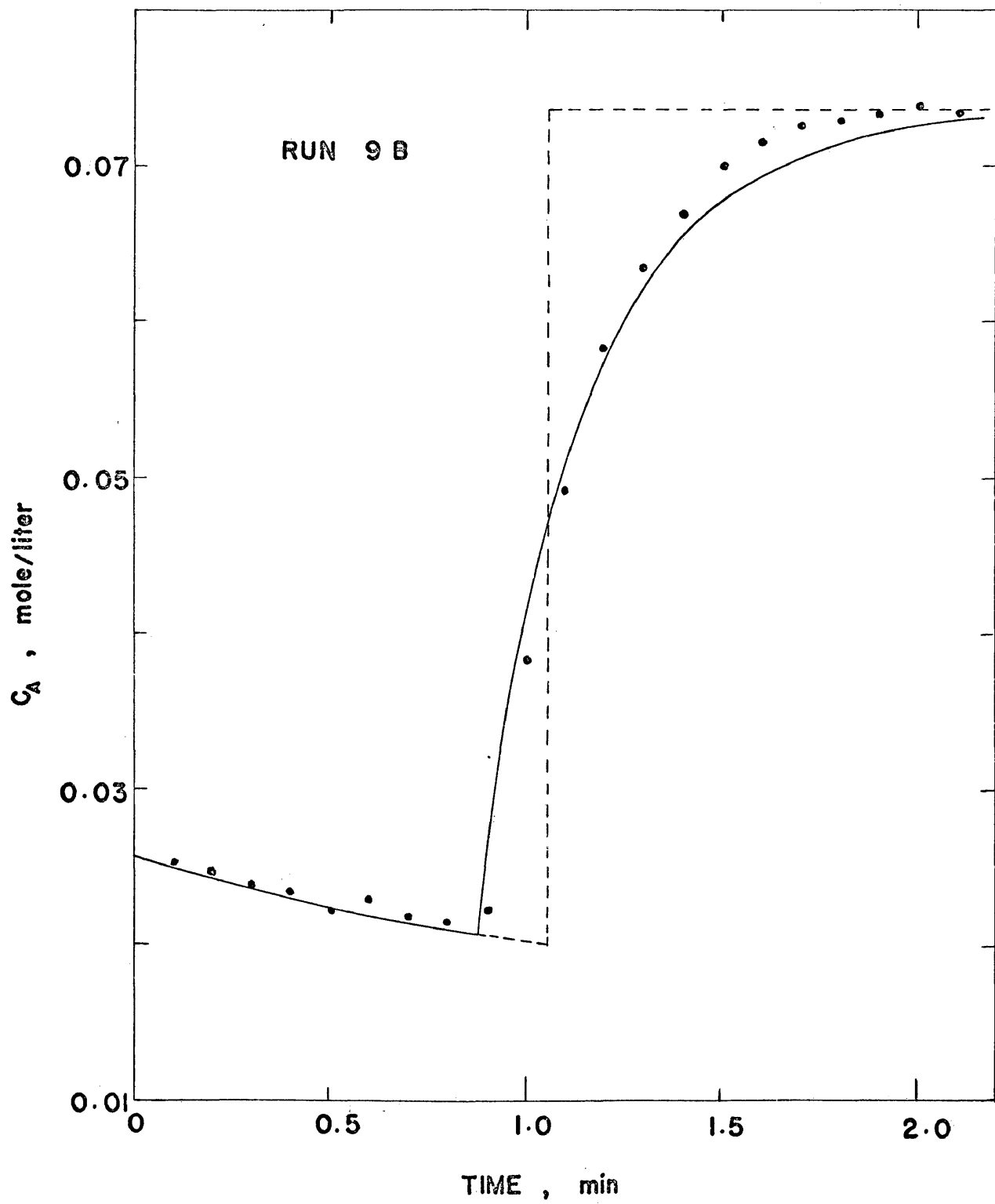


Figure 33. Transient response of outlet sodium hydroxide concentration to simultaneous increase in methyl acetate concentration and flow (Run 9A)

- RTD model without dispersion
- _____ RTD model with dispersion
- Experimental data

See Table 1 for operating conditions.

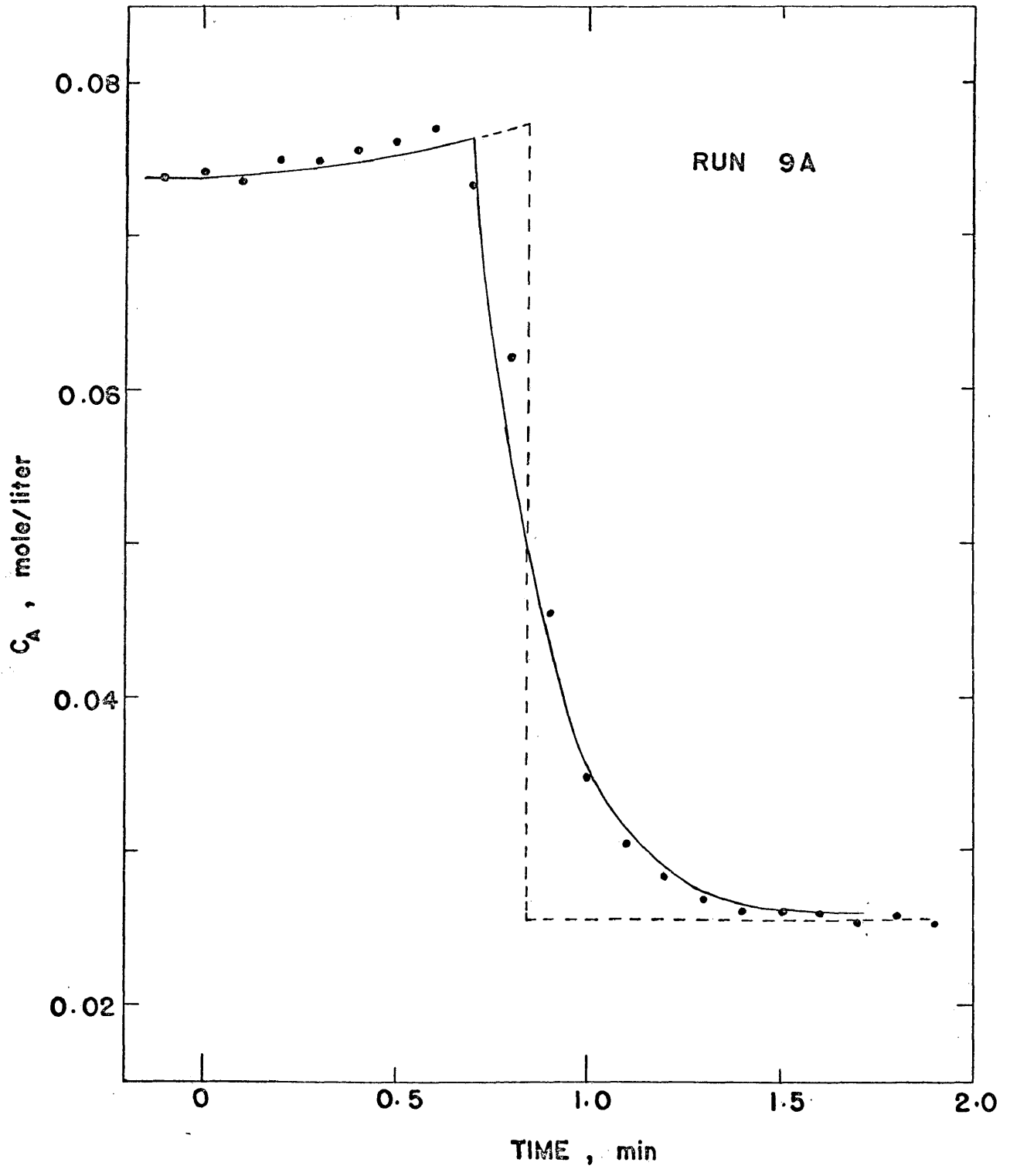


Figure 34. Transient response of outlet sodium hydroxide concentration to sodium hydroxide concentration increase and sodium hydroxide flow decrease (Run 8B)

- RTD model without dispersion
- RTD model with dispersion
- . Experimental data

See Table 1 for operating conditions

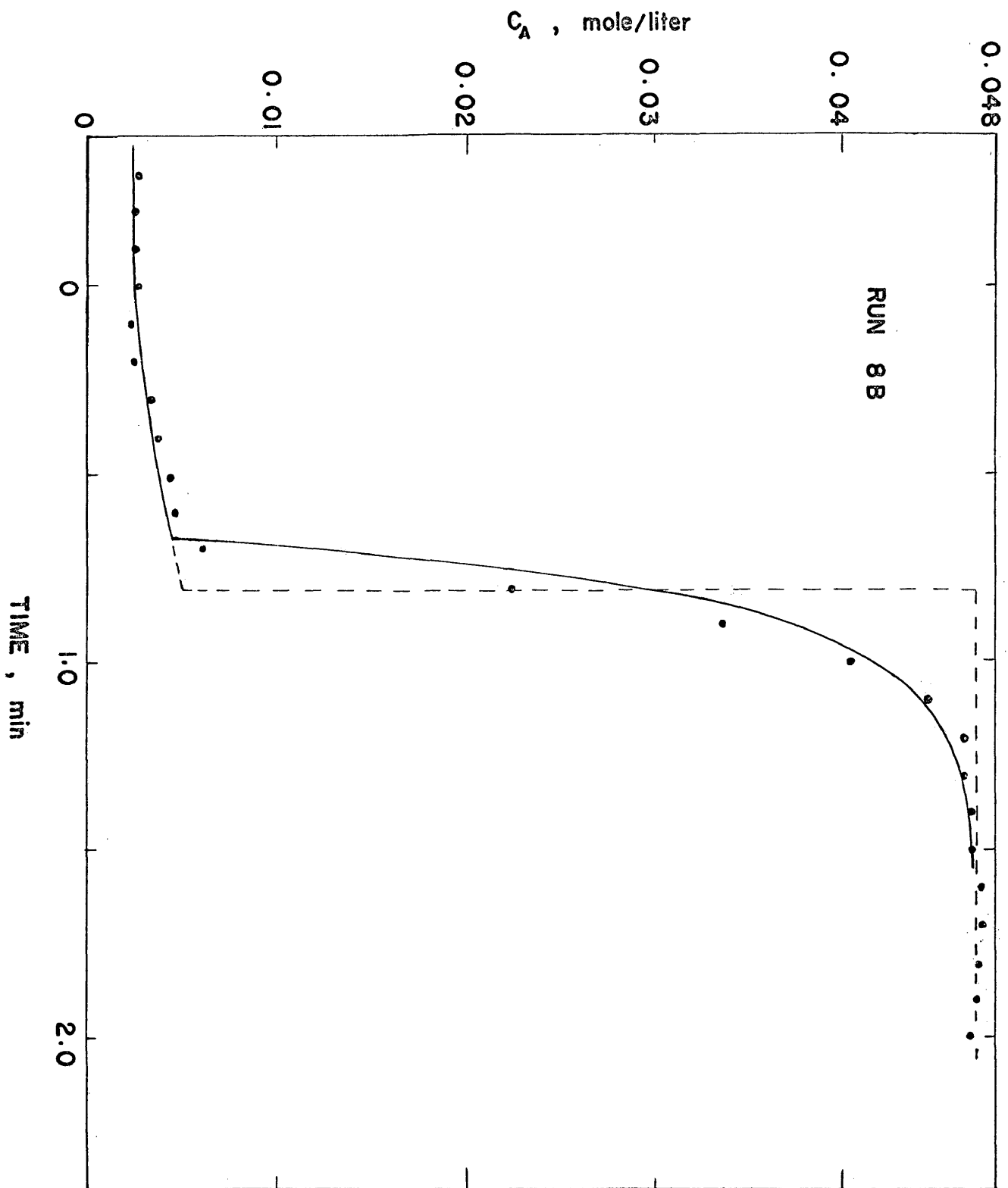
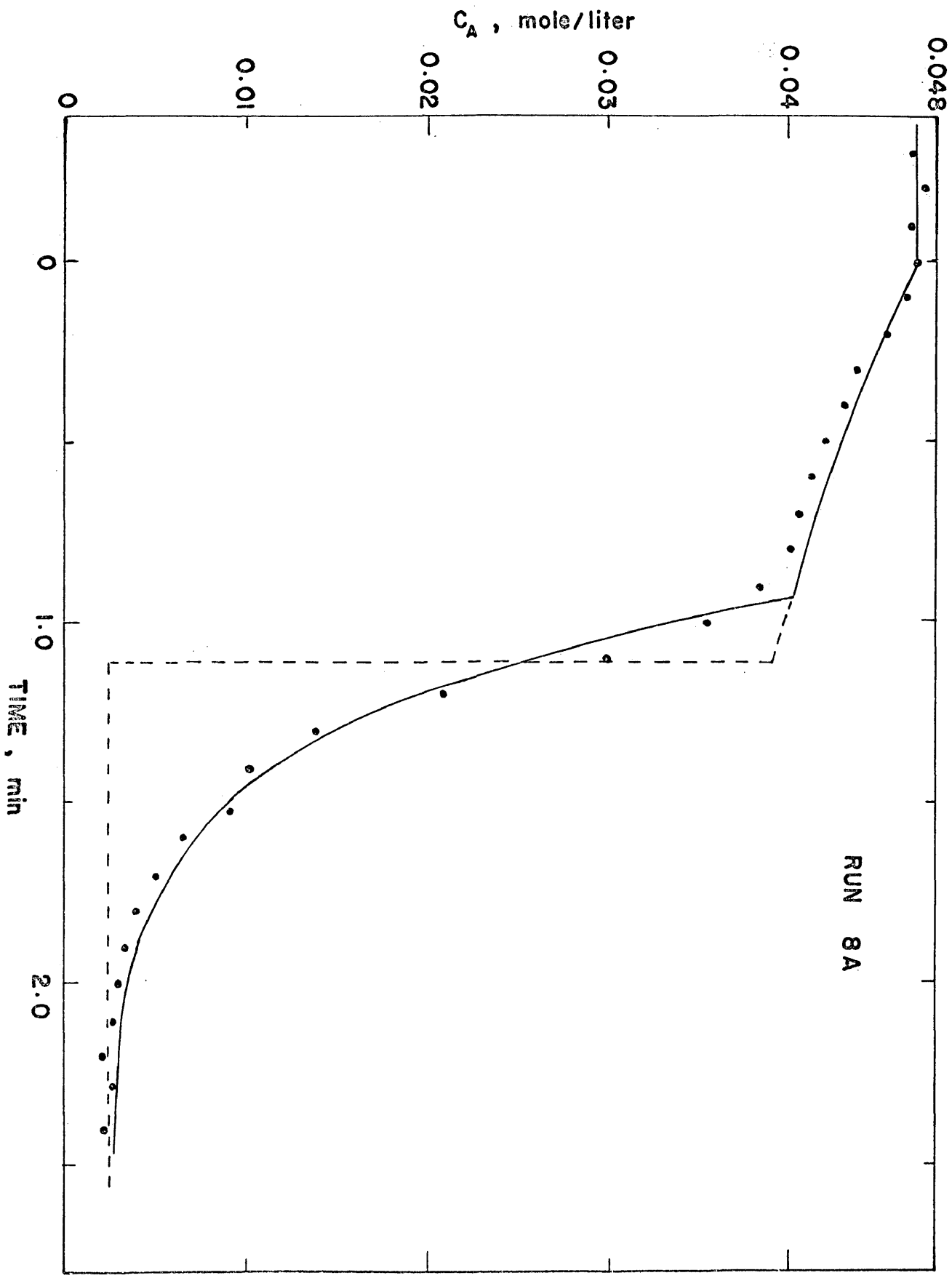


Figure 35. Transient response of outlet sodium hydroxide concentration to sodium hydroxide concentration increase and sodium hydroxide flow decrease (run 8A)

- RTD model without dispersion
- RTD model with dispersion
- . Experimental data

See Table 1 for operating conditions



RUN 8A

NON-ISOTHERMAL SYSTEMS

The RTD model developed in this dissertation can also be used for studying non-isothermal distributed parameter systems. The equations describing the concentration and temperature in an adiabatic tubular reactor with a non-isothermal second-order reaction are highly non-linear because of the reaction term. The describing equations are:

$$\frac{\partial C_a}{\partial t} + v \frac{\partial C_a}{\partial x} = k_0 e^{-\frac{\Delta E}{R_1 T}} C_a C_b$$

$$\frac{\partial C_b}{\partial t} + v \frac{\partial C_b}{\partial x} = k_0 e^{-\frac{\Delta E}{R_1 T}} C_a C_b \quad (6-1)$$

$$\frac{\partial T}{\partial t} + v \frac{\partial T}{\partial x} = \frac{k_0}{\rho C_p} e^{-\frac{\Delta E}{R_1 T}} C_a C_b (-\Delta H)$$

- where C_a : Concentration of component A (function of x and t)
 C_b : Concentration of component B (function of x and t)
 T : Temperature
 k_0 : Frequency factor
 ΔE : Activation energy
 R_1 : Universal gas constant
 ρ : Density of the reactants
 C_p : Heat capacity of the reactants
 $-\Delta H$: Heat of reaction
 v : Velocity of reactants in reactor

x : Length variable

t : Time variable

It is exceptionally difficult to obtain an analytical solution to the above set of equations. Even obtaining a numerical solution would be complicated. Hence, it would be very difficult to obtain response information from the above set of equations. In cases like this the RTD model is most useful; in the following sections a few cases will be discussed.

First Order Reaction

For the use of the RTD model, it is essential to have knowledge of the batch reactor theory. The basic equations that give concentration and temperature as a function of time for an adiabatic batch reactor with a first order reaction $A \xrightarrow{k} B$ are:

$$\frac{dC_A}{dt} = k_0 e^{-\frac{\Delta E}{R_1 T}} C_A \quad (6-2)$$

$$\frac{dT}{dt} = \left(\frac{dC_A}{dt}\right) \frac{-\Delta H}{V\rho C_p}$$

The definition of terms is the same as for equation (6-1).

An analytical solution can be obtained for the above equations by simplifying the exponential term using Taylor series expansion giving the following general form of solution for the above equations:

$$\frac{C_A}{C_{A0}} = \frac{C}{(DC_{A0} + C) \exp(Ct)} - DC_{A0} \quad (6-3)$$

where $D = k_0 B' A_1$

$$C = k_0 (A' - B' A_1 C_{A0} + B' T_1)$$

k_0 = Frequency factor

$$A_1 = (-\Delta H) / v \rho C_p$$

V = Volume of the reactor

$$A' = \exp(-\Delta E / RT_i) \left(1 + \frac{T_i R_1}{\Delta E \ln T_i} \right)$$

$$B' = -\exp(-\Delta E / RT_i) \left(\frac{R_1}{\Delta E \ln T_i} \right)$$

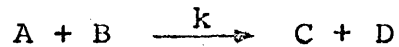
C_{A0} = Initial concentration of component A

T_i = Initial temperature of reactive mixture

Using equation 6-3 the batch data can be generated. Figure 36 is a schematic diagram for typical non-isothermal concentration curves plotted as a function of time in an adiabatic non-isothermal batch reactor. To define one curve, it is necessary to know the initial concentration of the reactant and also the initial temperature of the reactant. In Figure 36, curve 1 corresponds to the conditions before an upset and curve 2 corresponds to conditions after upset. The response curve can be either graphically obtained or analytically derived by using the method developed in the theoretical section. In Figure 36 the path followed for a concentration upset will be A-B, and for flow upset the path would be A-C-D.

Second Order Reaction

In the case of a second-order system with the reaction



the batch equations are:

$$-\frac{dC_B}{dt} = -\frac{dC_A}{dt} = k_0 (A'+B'T) C_A C_B$$

* (6-4)

$$\frac{dT}{dt} = \left(\frac{dC_A}{dt}\right) \frac{-\Delta H}{V\rho C_p}$$

Though the analytical solution for the above equations is difficult, the solution can be easily obtained by programming these equations on a digital computer or an analog computer. An unscaled analog program for equations 6-4 is shown in Figure 37.

The scaling of these equations should be done very carefully since there is a successive multiplication. Through this analog circuit a series of batch curves can be generated for various conditions, and from these curves the response data can easily be derived.

*The definition of the terms in equation (6-4) is the same as in equation (6-3).

Figure 36. Batch curves for predicting response.

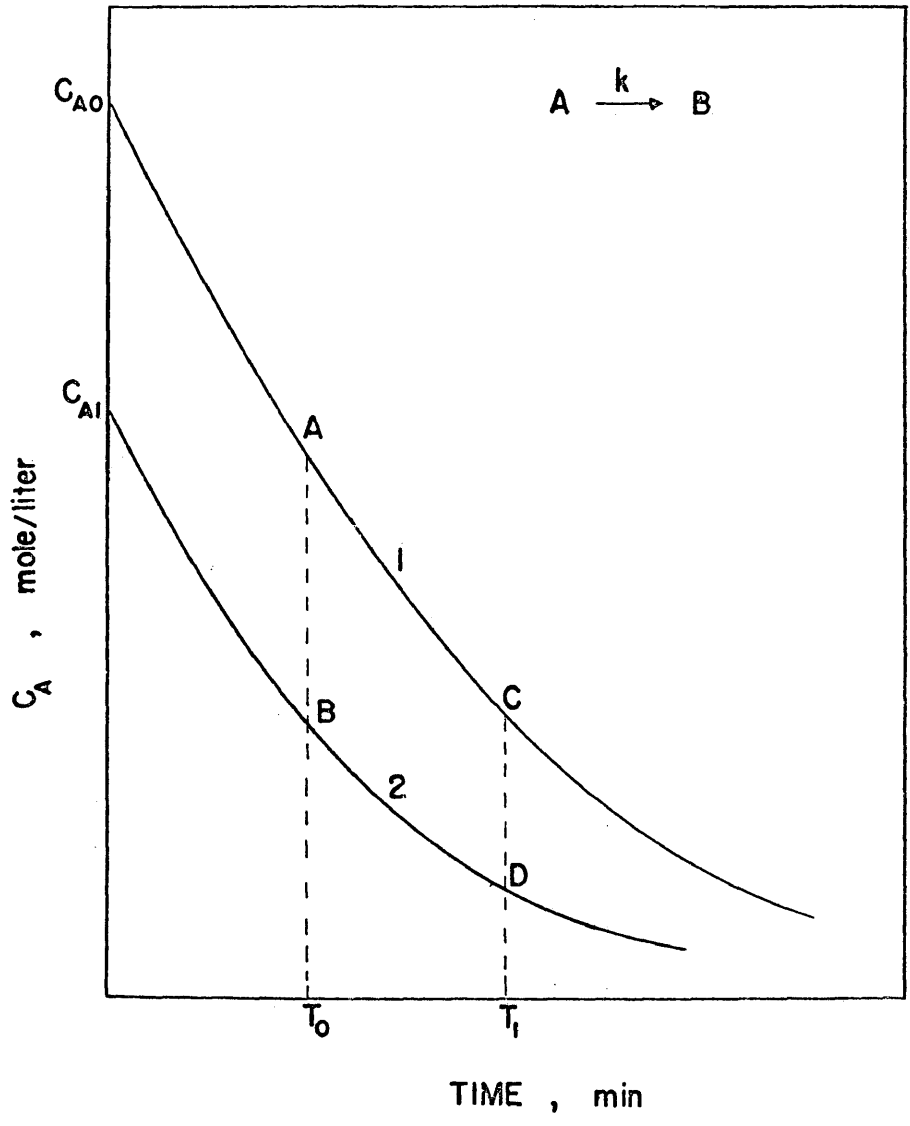
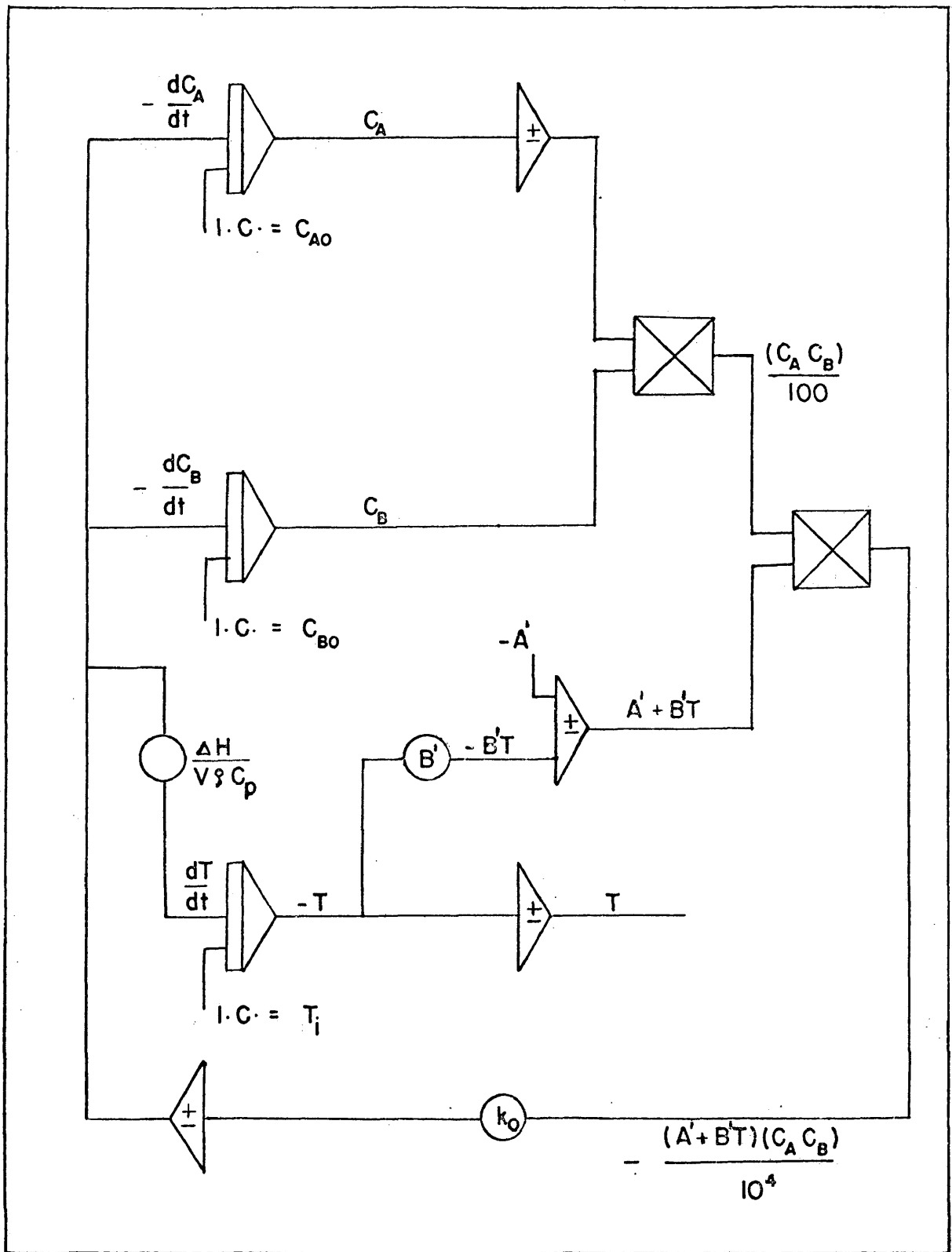


Figure 37. Analog circuit for solving equations 6-4.



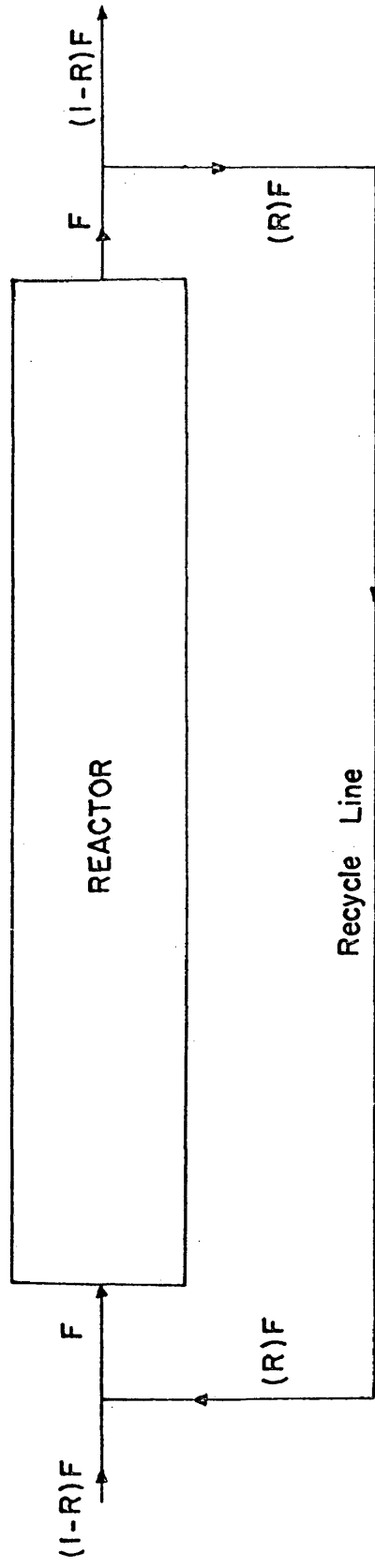
RECYCLE REACTOR

The recycle reactor has drawn a lot of attention recently, and has been used widely in industry. This type of reactor is very useful in case of reactions, where the reaction rate constant is small. The basic advantage in recycling is derived through greater conversion of raw material. This is obtained by giving fluid elements more residence time in the reactor. However, recycling does not give any significant advantage if the reaction rate constant was large. In the sections to follow, it will be shown how the RTD model can be used to predict the response for concentration upsets in a reactor with recycle. Figure 38 schematically shows a tubular reactor with recycle, and the recycle ratio is R .

Assumptions

1. The reaction taking place in the reactor is a second-order isothermal irreversible reaction.
2. Initially the reactor is at a given steady state.
3. Plug flow conditions exist in the reactor.
4. The reactants and products are incompressible.
5. There is no reaction in the recycle line. This is valid for very short recycle lines with negligible transportation lags.

Figure 38. Schematic diagram of a tubular reactor with recycle.



R Recycle Ratio
 F Total Throughput

Definitions

C_{AI}	Concentration of A entering reactor (based on stream A) before upset, mole/liter
C_{BI}	Concentration of B entering reactor (based on stream B) before upset, mole/liter
F_{A0}	Flow rate of A before upset, liter/min
F_{B0}	Flow rate of B before upset, liter/min
C_{AF}	Concentration of A entering reactor (based on stream A) after upset, mole/liter
C_{BF}	Concentration of B entering reactor (based on stream B) after upset, mole/liter
F_{A1}	Flow rate of A after upset, liter/min
F_{B1}	Flow rate of B after upset, liter/min
V	Volume of reactor, liter
T_1	Residence time after upset, min
C_{Ain}	Concentration of A at the inlet of recycle reactor @ $(n-1)T_1 \leq t < n T_1$, mole/liter
C_{Aon}	Concentration of A at the outlet of recycle reactor @ $(n-1)T_1 \leq t < n T_1$, mole/liter
C_{Bin}	Concentration of B at the inlet of recycle reactor @ $(n-1)T_1 \leq t < n T_1$, mole/liter
C_{Bon}	Concentration of B at the outlet of recycle reactor @ $(n-1)T_1 \leq t < n T_1$, mole/liter
	$t = 0$, at time of upset
R	Recycle ratio = Recycle flow/Reactor throughput
n	Positive integer, 0, 1, 2, 3, ... ∞

Concentration Upsets

Initially the reactor is at a given steady state before a concentration upset is made at $t = 0$.

For $t < 0$, the outlet steady state concentration values are C_{Ao1} and C_{Bo1} . The corresponding inlet conditions are

$$C_{Ai0} = (1-R) \frac{F_{A0}}{F_{A0} + F_{B0}} C_{AI} + R C_{Ao1}$$

$$C_{Bi0} = (1-R) \frac{F_{B0}}{F_{A0} + F_{B0}} C_{BI} + R C_{Bo1}$$

At time $t = 0$, a concentration upset is made in either C_{AI} or C_{BI} , or both. The new inlet concentrations to the reactor based upon total throughput for the time zone $0 \leq t < T_1$ are

$$C_{Ai1} = (1-R) \frac{F_{A1}}{F_{A1} + F_{B1}} C_{AF} + R C_{Ao1}$$

$$C_{Bi1} = (1-R) \frac{F_{B1}}{F_{A1} + F_{B1}} C_{BF} + R C_{Bo1}$$

where $R = \text{Recycle ratio}$
 $\quad = \text{Recycle flow/Reactor throughput}$

Since the residence time does not change when a concentration upset is made, the concentrations at the outlet of the reactor remain at the old steady state values until one residence-time lapses.

Thus, at $t = T_1$, there will be a concentration change at the outlet of the reactor. Since it is assumed in this

case that there is no transportation lag in the recycle line, a concentration change will be felt at the same time at the inlet of the reactor due to change in recycle concentration.

Accordingly, the inlet and outlet concentrations for the time zone

$$T_1 \leq t < 2 T_1$$

will be given by the following equations:

Case 1: $\underline{C_{Ai_1} \neq C_{Bi_1}}$

$$C_{Ao_2} = \frac{M_1}{N_1 \exp(M_1 k T_1) - 1.0}$$

where $M_1 = C_{Bi_1} - C_{Ai_1}$

$$N_1 = \frac{C_{Bi_1}}{C_{Ai_1}}$$

$$C_{Bo_2} = M_1 + C_{Ao_2}$$

Case 2: $\underline{C_{Ai_1} = C_{Bi_1}}$

$$C_{Ao_2} = \frac{1}{\frac{1}{C_{Ai_1}} - k T_1}$$

$$C_{Bo_2} = C_{Ao_2}$$

$$C_{Ai_2} = (1-R) \frac{F_{A1}}{F_{A1} + F_{B1}} C_{AF} + R C_{Ao_2}$$

$$C_{Bi_2} = (1-R) \frac{F_{B1}}{F_{A1} + F_{B1}} C_{BF} + R C_{Bo_2}$$

Similarly for the time zone

$$2T_1 \leq t < 3T_1$$

the concentration will be given by

Case 1: $\underline{C_{Ai_2} \neq C_{Bi_2}}$

$$C_{Ao_3} = \frac{M_2}{N_2 \exp(M_2 kT_1) - 1.0}$$

where $M_2 = C_{Bi_2} - C_{Ai_2}$

$$N_2 = \frac{C_{Bi_2}}{C_{Ai_2}}$$

$$C_{Bo_3} = M_2 + C_{Ao_3}$$

Case 2: $\underline{C_{Ai_2} = C_{Bi_2}}$

$$C_{Ao_3} = \frac{1}{\frac{1}{C_{Ai_2}} - kT_1}$$

$$C_{Bo_3} = C_{Ao_3}$$

$$C_{Ai_3} = (1-R) \frac{F_{A1}}{F_{A1} + F_{B1}} C_{AF} + R C_{Ao_3}$$

$$C_{Bi_3} = (1-R) \frac{F_{B1}}{F_{A1} + F_{B1}} C_{BF} + R C_{Bo_3}$$

This calculation can be extended to any length of time. In a more general form, one could write the following equations.

$$(n-1) T_1 \leq t < nT_1$$

Case 1: $\underline{C_{Ai(n-1)} \neq C_{Bi(n-1)}}$

$$C_{Ao_n} = \frac{M_{(n-1)}}{N_{(n-1)} \exp\{M_{(n-1)} kT_1\} - 1.0}$$

where $M_{(n-1)} = C_{Bi(n-1)} - C_{Ai(n-1)}$

$$N_{(n-1)} = \frac{C_{Bi(n-1)}}{C_{Ai(n-1)}}$$

Case 2: $\underline{C_{Ai(n-1)} = C_{Bi(n-1)}}$

$$C_{Ao_n} = \frac{1}{\frac{1}{C_{Ai(n-1)}} - kT_1}$$

$$C_{Bo_n} = C_{Ao_n}$$

$$C_{Ai_n} = (1-R) \frac{F_{A1}}{F_{A1} + F_{B1}} C_{AF} + R C_{Ao_n}$$

$$C_{Bi_n} = (1-R) \frac{F_{B1}}{F_{A1} + F_{B1}} C_{BF} + R C_{Bo_n}$$

Thus, for both single and multiple concentration upsets the response of a tubular reactor with recycle will come out in the form of steps. This is due to the residence time effect coupled with the effect caused by recycle.

Some typical responses of outlet sodium hydroxide concentration to concentration upsets are shown in Figures 39, 40, and 41. The reaction used for these case studies was the saponification of methyl acetate. It is evident from Figures 39, 40, and 41 that as the recycle rate is increased, the concentration of sodium hydroxide at the outlet decreases. Also, the system reaches a defined steady state much faster for a smaller recycle ratio than a higher recycle ratio. As the recycle ratio is increased, the defined steady state decreases; and in the limiting case when the recycle ratio becomes one, the steady state goes to zero. When the recycle ratio is one the residence time of all the fluid elements becomes infinity. The effect of reaction rate can also be seen in the figures. Increasing the reaction rate decreases the value of the two steady state reached. Figures 39, 40, and 41 also show approach to the initial steady state, starting with an empty reactor. The calculations for approach to initial steady state can be made in the same fashion as the one used for obtaining the response.

The RTD model can also be extended to single flow upsets and multiple upsets. In these cases, the response

curve will not come out in steps as in the case of the concentration upset. Instead, the response curve obtained will be a smooth continuous curve. This occurs because the effluent concentration from the reactor keeps continuously changing in value due to the residence time effect; thus, the dilution effect at the inlet of the reactor does not remain the same for any length of time.

Figure 39. Transient response of outlet sodium hydroxide concentration to simultaneous concentration upset in a tubular reactor with recycle ratio of 0.3 ($k = 10$)

$$C_{AI} = 0.25 \text{ mole/liter}$$

$$C_{AF} = 0.50 \text{ mole/liter}$$

$$C_{BI} = 0.25 \text{ mole/liter}$$

$$C_{BF} = 0.50 \text{ mole/liter}$$

$$F_{A0} = 0.05 \text{ liter/min}$$

$$F_{A1} = 0.05 \text{ liter/min}$$

$$F_{B0} = 0.05 \text{ liter/min}$$

$$F_{B1} = 0.05 \text{ liter/min}$$

Note: Upset made at $t = 0$ min

The discontinuous line shows the response curve when there is no recycle.

———— RTD model without dispersion.

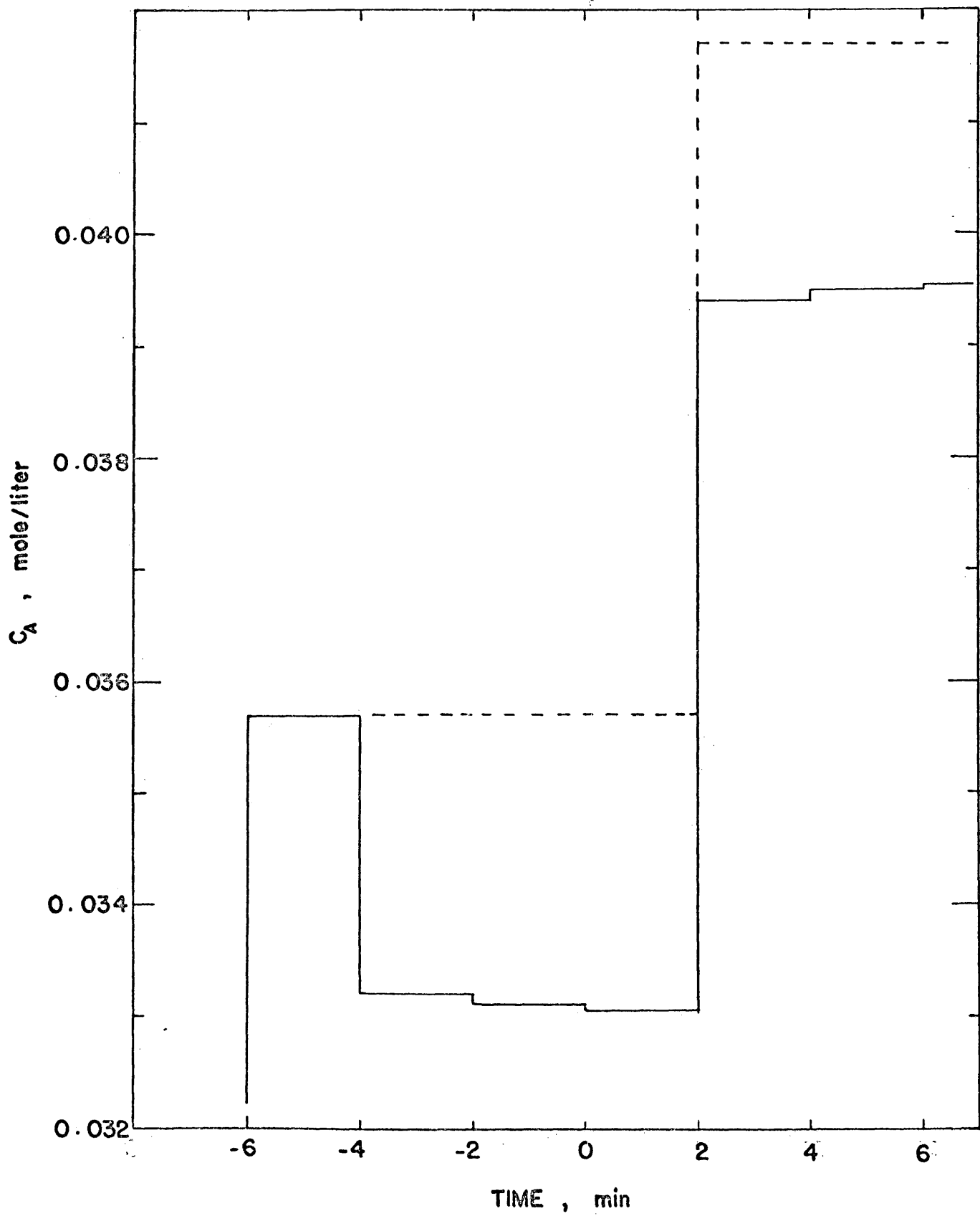


Figure 40. Transient response of outlet sodium hydroxide concentration to simultaneous concentration upset in a tubular reactor with recycle ratio of 0.7 ($k = 2$)

$$C_{AI} = 0.25 \text{ mole/liter}$$

$$C_{AF} = 0.50 \text{ mole/liter}$$

$$C_{BI} = 0.25 \text{ mole/liter}$$

$$C_{BF} = 0.50 \text{ mole/liter}$$

$$F_{A0} = 0.05 \text{ liter/min}$$

$$F_{A1} = 0.05 \text{ liter/min}$$

$$F_{B0} = 0.05 \text{ liter/min}$$

$$F_{B1} = 0.05 \text{ liter/min}$$

Note: Upset made at $t = 0$ min

———— RTD model without dispersion

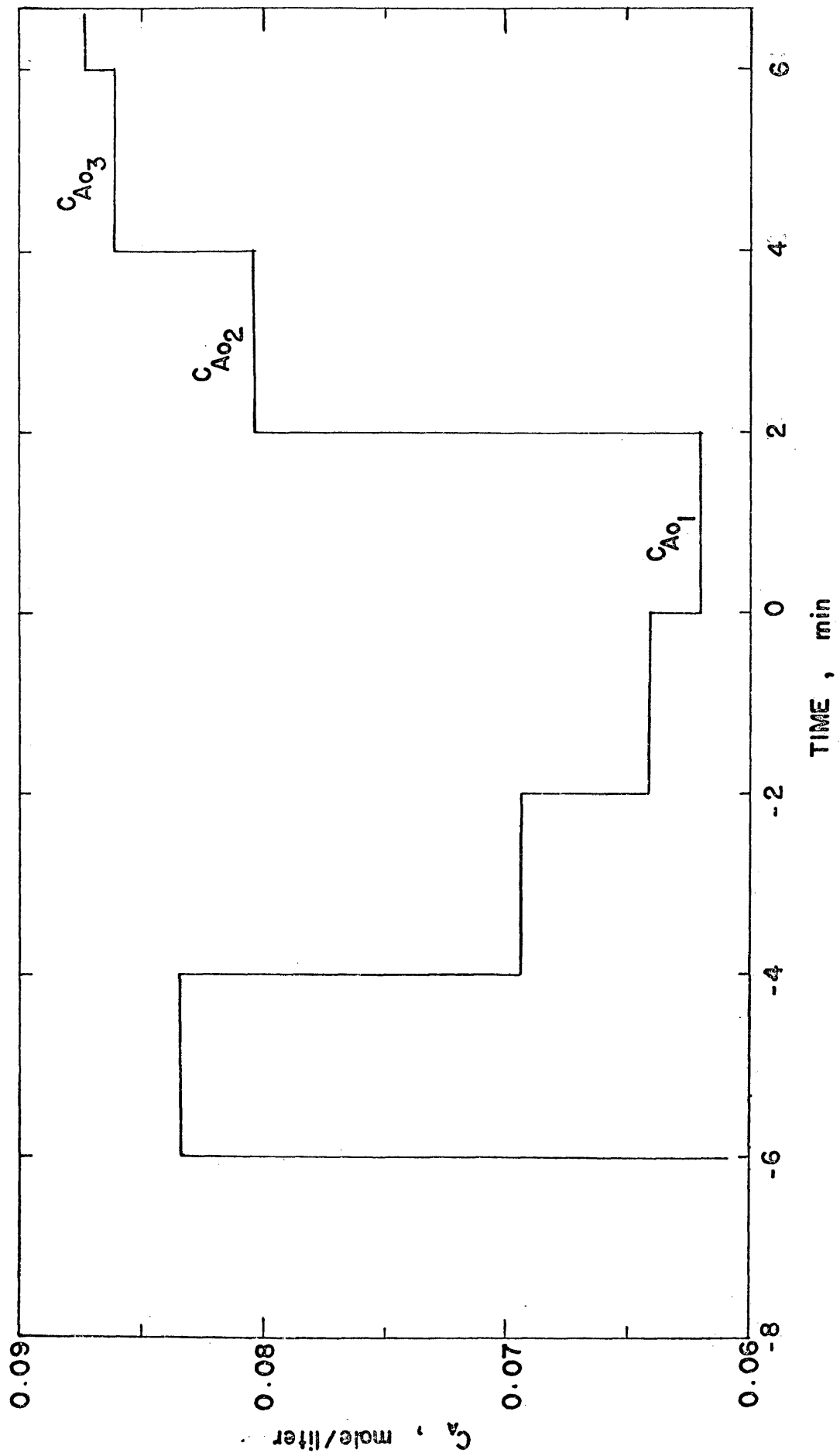


Figure 41. Transient response of outlet sodium hydroxide concentration to simultaneous concentration upset in a tubular reactor with recycle ratio of 0.3 ($k = 2$)

$$C_{AI} = 0.25 \text{ mole/liter}$$

$$C_{AF} = 0.50 \text{ mole/liter}$$

$$C_{BI} = 0.25 \text{ mole/liter}$$

$$C_{BF} = 0.50 \text{ mole/liter}$$

$$F_{A0} = 0.05 \text{ liter/min}$$

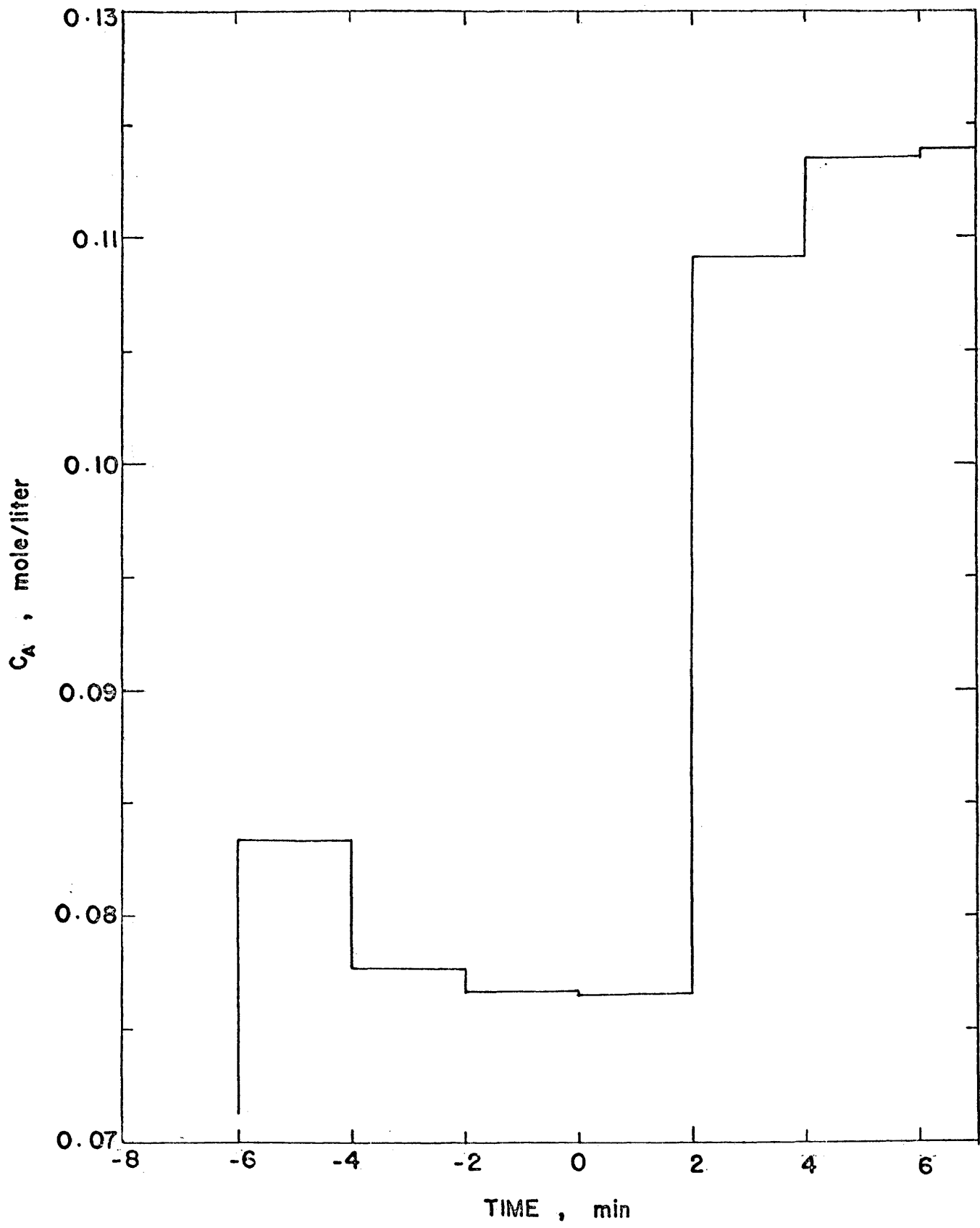
$$F_{A1} = 0.05 \text{ liter/min}$$

$$F_{B0} = 0.05 \text{ liter/min}$$

$$F_{B1} = 0.05 \text{ liter/min}$$

Note: Upset made at $t = 0$ min

———— RTD model without dispersion



CONCLUSIONS AND RECOMMENDATIONS

The RTD model is most effective in predicting the response of distributed parameter reactor system. For the second-order isothermal system studied the data were predicted very well. However, deviations were observed at certain portions of the response curve, especially when large changes in concentrations took place in the system. This was due to dispersion. In this study it was observed that because dispersion was mainly dependent upon flow rate, a correlation was possible. Although molecular diffusion contributes toward non-ideality, in this system the effect due to molecular diffusion seem to be of little consequence. The overall dispersion observed was shown to be first order and behaved just like a first-order mixing lag. This behavior is in keeping with observations made by some of the previous workers who have investigated non-ideality in flow systems (15, 23). In future studies it would be interesting to investigate the effect of reaction rate and reaction geometry on dispersion.

In this study a wide variety of upsets was made and the responses obtained for the different cases were varied and interesting. The important factors that decided the shape of the response curve were the concentrations of the reactants at the inlet of the reactor and the residence

time. The concentrations of the reactants at the inlet of the reactor depend upon the flow rates of the feed streams and their respective concentrations.

When the flow rate of one of the inlet streams is changed, the concentrations of the reactants at the inlet of the reactor change and the residence time also changes. Hence, when one flow rate changes the reactor essentially sees a triple upset. (The triple upset is a change in the residence time and changes in the concentrations of both the reactants at the inlet of the reactor.) The response curve obtained for a single flow upset comes out in two stages. When the flow upset is made, the residence-time effect is felt first followed by the effect due to concentration change. The first stage starts as soon as the upset is made and ends after a time equivalent to the new residence time. The second stage takes over at this point.

For example, if the methyl acetate flow was increased, the net result would be an increase of methyl acetate concentration and decrease of sodium hydroxide concentration at the inlet of the reactor. The residence time after upset would be smaller than the residence time before upset. Since the residence time has decreased, there is less time for reaction; so less sodium hydroxide is used by the reaction, and the concentration of sodium hydroxide at the outlet starts increasing. It keeps increasing

until time becomes equal to the new residence time, but at this point the fluid elements with the new concentrations hit the measuring probe and the concentration of sodium hydroxide at the outlet starts dropping. For a reverse upset, unlike the concentration upsets, the response obtained is not a mirror image. This is due to the residence time effect.

Another interesting response curve was observed for simultaneous flow upset. The upset was made in such a way that both the flow rates were changed at the same time and to the same extent. For a change made in this fashion, the only change seen by the system is a residence time change, and there is no change in concentrations at the inlet of the reactor. Hence, the response observed was a smooth curve. When the residence time increased, the concentration at the outlet of the reactor decreased, and vice versa. For a simultaneous flow upset where the flow rates were not changed to the same extent, the response curve observed would be very similar to the one observed for a single flow upset.

Simultaneous upsets in flow and concentration have the same effect on the system as a single-flow upset. But, some interesting observations can be made about these kinds of upsets. In the case of a single-flow upset, it is possible to predict qualitatively, without making any

calculations, the shape of the curve. It is also possible to predict whether or not the response curve is going to have a maximum or minimum. A similar prediction cannot be made for a simultaneous upset in flow and concentration without making calculations. For example, in the case where the sodium hydroxide concentration was increased and the flow rate of methyl acetate was increased, there were two effects opposing each other. Increasing the sodium hydroxide concentration has a positive effect on the concentration of sodium hydroxide at the inlet of the reactor, but increasing the flow rate of methyl acetate has a negative effect on the concentration of sodium hydroxide at the inlet of the reactor. Since these two effects oppose each other, it is very difficult to draw any meaningful conclusions without making calculations. However, if the two effects were complementing each other, qualitative predictions could be made as before. The deciding factors which control the nature of the response curve are the final inlet concentrations and the difference between the initial and final residence times.

In the case of concentration upsets, since there is no change in the residence time, the ideal response should be in the form of a step. However, due to dispersion, the response curves came out in the form of an exponential curve.

It was observed that plug-flow conditions could be obtained with Reynolds Numbers of 250 or greater for the reactor used in this study. The reactor, in the form of a spiral, had a length-to-diameter ratio of 820. It would be of interest to obtain quantitative information about the relationship between the different variables like reactor geometry, physical properties of reactants, flow rate, etc., and approach to plug-flow conditions.

In the earlier sections, theory pertaining to non-isothermal cases and tubular reactors with recycle was developed. As can be seen, the RTD model can be used with greater ease than classical reactor dynamics methods in these cases. In the case of a reactor with recycle, the response for a concentration upset comes out in the form of steps. It has been established theoretically that as the recycle ratio is increased, the steady state attained finally is lowered. It is recommended that further studies be conducted to test the versatility of the RTD model, with both first-order and second-order non-isothermal systems. It is advisable to study systems without much dispersion so that the effect due to non-isothermal conditions can be obtained explicitly. Another region of interest would be to study the response of a tubular reactor system with recycle.

Even though the reactions discussed in this dissertation

were irreversible, the RTD model can be easily used for reversible reactions as well.

The RTD model can also be extended to tubular reactors with compressible fluids; since the appropriate batch and tubular equations are identical.

Another field where the RTD model can be used is in tubular heat exchanger dynamic studies. The appropriate equations in the case of the tubular heat exchanger are:

$$\text{Batch: } t = \frac{1}{\rho C_p} \frac{dT}{(-r)}$$

$$\text{Plug-flow tubular: } T_r = \frac{V}{F} = \frac{1}{\rho C_p} \frac{dT}{(-r)}$$

where $-r$: Generation term, cal/min °C
 (For constant heat flux, $-r = Q$)
 (For constant wall temperature,

$$-r = \frac{U(T_w - T)}{L})$$

- F : Flow rate, cc/min
- V : Volume of tubular reactor, cc
- T : Temperature, °C
- T_w : Wall temperature, °C
- U : Overall heat transfer coefficient, cal/(sq cm) min °C
- Q : Heat flux at wall, cal/cc min
- L : Length of tubular reactor, cm
- t : Amount of time in batch reactor, min
- ρ : Density of fluid in reactor, g/cc
- C_p : Heat capacity, cal/g °C
- T_r : Residence time, min

In summary, this study has revealed that an isothermal tubular reactor system with a second order reaction shows a

wide variety of responses and that they can be predicted well with the RTD model.

NOMENCLATURE

C_{ai}	Concentration of A @ $x = 0$, mole/liter
C_{al}	Concentration of A @ $x = L$, mole/liter
C_{an}	Concentration of A @ $x = (n/N)L$, mole/liter
C_a	Concentration of A, mole/liter (function of x and t)
C_{bi}	Concentration of B @ $x = 0$, mole/liter
C_{bl}	Concentration of B @ $x = L$, mole/liter
C_{bn}	Concentration of B @ $x = (n/N)L$, mole/liter
C_b	Concentration of B, mole/liter (function of x and t)
C_A	Concentration of sodium hydroxide @ the outlet of the reactor, mole/liter
C_B	Concentration of methyl acetate @ the outlet of the reactor, mole/liter
N	Number of times reactor is divided
k	Reaction rate constant
C_{AI}	Concentration of sodium hydroxide in stream A entering the reactor before upset, mole/liter
C_{BI}	Concentration of methyl acetate in stream B entering the reactor before upset, mole/liter
F_{A0}	Flow rate of stream A (sodium hydroxide) before upset, liter/min
F_{B0}	Flow rate of stream B (methyl acetate) before upset, liter/min
C_{A0}	Concentration of sodium hydroxide at the inlet of the reactor before upset (based upon the mixed stream) mole/liter
C_{B0}	Concentration of methyl acetate at the inlet of the reactor before upset (based upon the mixed stream) mole/liter

T_0	Residence time before upset, min
C_{AS0}	Steady state concentration of A before upset, mole/liter
C_{BS0}	Steady state concentration of B before upset, mole/liter
V	Volume of reactor, liter
C_{AF}	Concentration of sodium hydroxide in stream A entering the reactor after upset, mole/liter
C_{BF}	Concentration of methyl acetate in stream B entering the reactor after upset, mole/liter
F_{A1}	Flow rate of stream A (sodium hydroxide) after upset, liter/min
F_{B1}	Flow rate of stream B (methyl acetate) after upset, liter/min
C_{A1}	Concentration of sodium hydroxide at the inlet of the reactor after upset (based upon the mixed stream) mole/liter
C_{B1}	Concentration of methyl acetate at the inlet of the reactor after upset (based upon the mixed stream) mole/liter
T_1	Residence time after upset, min
C_{AS1}	Steady state concentration of A after upset, mole/liter
C_{BS1}	Steady state concentration of B after upset, mole/liter
n	Positive integer, 1, 2, 3, ...
t_D	Time constant of dispersion curve, min
C_{Ai_n}	Concentration of A at the inlet of the recycle reactor for the time interval $(n-1)T_0 \leq t < n T_0$, mole/liter
C_{Ao_n}	Concentration of A at the outlet of the recycle reactor for the time interval $(n-1)T_1 \leq t < n T_1$, mole/liter

C_{Bi_n}	Concentration of B at the inlet of the recycle reactor for the time interval $(n - 1)T_0 \leq t < n T_0$, mole/liter
C_{Bo_n}	Concentration of B at the outlet of the recycle reactor for the time interval $(n - 1)T_1 \leq t < n T_1$, mole/liter
	$t = 0$ at time of upset
R	Recycle ratio = Recycle flow/Reactor throughput
T	Temperature (function of x and t), °C
x	Length variable, cm
t	Time variable, min
k_0	Frequency factor
ΔE	Activation energy, kcal/mole
R_1	Universal gas constant
ρ	Density of reacting mixture, gm/cc
C_p	Heat capacity of reacting mixture, cal/gm °C
$-\Delta H$	Heat of reaction, kcal/mole
v	Velocity of reactants in reactor, cm/min
T_i	Initial temperature of reacting mixture, °C
$-r_A$	Reaction rate, mole/liter min
$-r$	Heat generation term, cal/min

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APPENDIX I

Experimental Data (Transient Response)

Table 2
Single Flow Upset (methyl acetate)

Run No. 1 A		Run No. 1 B	
$C_{AI} = 0.2486$	$C_{AF} = 0.2486$	$C_{AI} = 0.2486$	$C_{AF} = 0.2486$
$C_{BI} = 0.2221$	$C_{BF} = 0.2221$	$C_{BI} = 0.2221$	$C_{BF} = 0.2221$
$F_{A0} = 0.052$	$F_{A1} = 0.052$	$F_{A0} = 0.052$	$F_{A1} = 0.052$
$F_{B0} = 0.079$	$F_{B1} = 0.052$	$F_{B0} = 0.052$	$F_{B1} = 0.079$
Time min.	C_A moles/liter	Time min.	C_A moles/liter
0.0	0.0254	0.0	0.0418
0.1	0.0251	0.1	0.0422
0.2	0.0243	0.2	0.0426
0.3	0.0240	0.3	0.0434
0.4	0.0232	0.4	0.0422
0.5	0.0229	0.5	0.0450
0.6	0.0220	0.6	0.0462
0.7	0.0219	0.7	0.0464
0.8	0.0216	0.8	0.0446
0.9	0.0222	0.9	0.0367
1.0	0.0274	1.0	0.0314
1.1	0.0328	1.1	0.0290
1.2	0.0360	1.2	0.0271
1.3	0.0383	1.3	0.0264
1.4	0.0395	1.4	0.0258
1.5	0.0401	1.5	0.0256
1.6	0.0407	1.6	0.0255
1.7	0.0411	1.7	0.0258
1.9	0.0417	1.9	0.0254
2.1	0.0419		
2.3	0.0419		

Table 3
Simultaneous Flow Upset

Run No. 2 A		Run No. 2 B	
$C_{AI} = 0.1235$	$C_{AF} = 0.1235$	$C_{AI} = 0.1235$	$C_{AF} = 0.1235$
$C_{BI} = 0.1216$	$C_{BF} = 0.1216$	$C_{BI} = 0.1216$	$C_{BF} = 0.1216$
$F_{A0} = 0.052$	$F_{A1} = 0.079$	$F_{A0} = 0.079$	$F_{A1} = 0.052$
$F_{B0} = 0.052$	$F_{B1} = 0.079$	$F_{B0} = 0.079$	$F_{B1} = 0.052$
Time min.	C_A moles/liter	Time min.	C_A moles/liter
0.0	0.02795	0.0	0.03415
0.1	0.02855	0.1	0.03342
0.3	0.02942	0.2	0.03295
0.4	0.03055	0.3	0.03190
0.5	0.03127	0.4	0.03148
0.6	0.03305	0.5	0.03095
0.7	0.03413	0.6	0.03022
0.8	0.03435	0.7	0.02940
		0.8	0.02925
		0.9	0.02885
		1.0	0.02840
		1.1	0.02805
		1.2	0.02790

Table 4
Single Flow Upset (sodium hydroxide)

Run No. 3 A		Run No. 3 B	
$C_{AI} = 0.2486$	$C_{AF} = 0.2486$	$C_{AI} = 0.2486$	$C_{AF} = 0.2486$
$C_{BI} = 0.2221$	$C_{BF} = 0.2221$	$C_{BI} = 0.2221$	$C_{BF} = 0.2221$
$F_{A0} = 0.079$	$F_{A1} = 0.016$	$F_{A0} = 0.016$	$F_{A1} = 0.079$
$F_{B0} = 0.031$	$F_{B1} = 0.031$	$F_{B0} = 0.031$	$F_{B1} = 0.031$

Time min.	C_A moles/liter	Time min.	C_A moles/liter
0.0	0.1208	0.0	0.0018
0.2	0.1201	0.1	0.0019
0.4	0.1181	0.2	0.0021
0.6	0.1176	0.3	0.003
0.8	0.1180	0.4	0.0035
1.0	0.1165	0.5	0.0050
1.2	0.1148	0.6	0.0055
1.4	0.1153	0.7	0.0065
1.6	0.1150	0.8	0.0070
1.8	0.1145	0.9	0.0110
2.0	0.1130	1.0	0.0580
2.2	0.1025	1.1	0.0891
2.4	0.076	1.2	0.0985
2.6	0.055	1.3	0.1022
2.8	0.039	1.4	0.1104
3.0	0.0295	1.5	0.1161
3.2	0.0265	1.6	0.1179
3.4	0.022	1.7	0.1183
3.6	0.018	1.8	0.1195
3.8	0.012	1.9	0.121
4.0	0.0081	2.0	0.1205
4.2	0.0055		
4.4	0.004		
4.6	0.0032		

Table 5
Single Flow Upset (methyl acetate)

Run No. 4 A		Run No. 4 B	
$C_{AI} = 0.2486$	$C_{AF} = 0.2486$	$C_{AI} = 0.2486$	$C_{AF} = 0.2486$
$C_{BI} = 0.1216$	$C_{BF} = 0.1216$	$C_{BI} = 0.1216$	$C_{BF} = 0.1216$
$F_{A0} = 0.031$	$F_{AI} = 0.031$	$F_{A0} = 0.031$	$F_{AI} = 0.031$
$F_{B0} = 0.016$	$F_{BI} = 0.052$	$F_{B0} = 0.052$	$F_{BI} = 0.016$

Time min.	C_A moles/liter	Time min.	C_A moles/liter
0.0	0.1225	0.0	0.0360
0.2	0.1226	0.2	0.0360
0.4	0.1230	0.4	0.0351
0.6	0.1230	0.6	0.0340
0.8	0.1227	0.8	0.0315
1.0	0.1221	1.0	0.0320
1.2	0.1220	1.2	0.0320
1.4	0.091	1.4	0.0310
1.6	0.0655	1.6	0.0301
1.8	0.0510	1.8	0.0295
2.0	0.0475	2.0	0.0300
2.2	0.0405	2.2	0.0495
2.4	0.038	2.4	0.0680
2.6	0.037	2.6	0.0865
2.8	0.0375	2.8	0.0945
3.0	0.036	3.0	0.1015
3.2	0.0375	3.2	0.1072
3.4	0.036	3.4	0.1120
		3.6	0.1152
		3.8	0.1170
		4.0	0.1183
		4.2	0.1189
		4.4	0.1201
		4.6	0.1190
		4.8	0.1209
		5.0	0.1205

Table 6

Simultaneous Upset

(sodium hydroxide concentration, methyl acetate flow)

Run No. 5 A		Run No. 5 B	
$C_{AI} = 0.247$	$C_{AF} = 0.1215$	$C_{AI} = 0.1215$	$C_{AF} = 0.247$
$C_{BI} = 0.2275$	$C_{BF} = 0.2275$	$C_{BI} = 0.2275$	$C_{BF} = 0.2275$
$F_{A0} = 0.068$	$F_{A1} = 0.068$	$F_{A0} = 0.068$	$F_{A1} = 0.068$
$F_{B0} = 0.068$	$F_{B1} = 0.031$	$F_{B0} = 0.031$	$F_{A1} = 0.068$

Time min.	C_A moles/liter	Time min.	C_A moles/liter
0.0	0.0469	0.0	0.0359
0.1	0.0465	0.1	0.0360
0.2	0.0455	0.2	0.0367
0.3	0.0444	0.3	0.0375
0.4	0.0432	0.4	0.0382
0.5	0.0422	0.5	0.0390
0.6	0.0419	0.6	0.0401
0.7	0.0414	0.7	0.0420
0.8	0.0407	0.8	0.0444
0.9	0.0402	0.9	0.0463
1.0	0.0395	1.0	0.0466
1.1	0.0386	1.1	0.0468
1.2	0.0375	1.2	0.0469
1.3	0.0369	1.3	0.0471
1.4	0.0365	1.5	0.0470
1.5	0.0362	1.7	0.0471
1.6	0.0360	1.9	0.0471
1.8	0.0359		
1.9	0.0358		
2.1	0.0358		
2.3	0.0358		

Table 7

Simultaneous Upset

(methyl acetate concentration and sodium hydroxide flow)

Run No. 6 A		Run No. 6 B	
$C_{AI} = 0.1215$	$C_{AF} = 0.1215$	$C_{AI} = 0.1215$	$C_{AF} = 0.1215$
$C_{BI} = 0.1187$	$C_{BF} = 0.2275$	$C_{BI} = 0.2275$	$C_{BF} = 0.1187$
$F_{A0} = 0.068$	$F_{A1} = 0.031$	$F_{A0} = 0.031$	$F_{A1} = 0.068$
$F_{B0} = 0.068$	$F_{B1} = 0.068$	$F_{B0} = 0.068$	$F_{B1} = 0.068$

Time min.	C_A moles/liter	Time min.	C_A moles/liter
0.0	0.032	0.0	0.0026
0.1	0.0319	0.1	0.0026
0.2	0.0313	0.2	0.0026
0.3	0.0306	0.3	0.0029
0.4	0.0298	0.4	0.0032
0.5	0.0298	0.5	0.0033
0.6	0.0293	0.6	0.0035
0.7	0.0289	0.7	0.0040
0.8	0.0286	0.8	0.0054
0.9	0.0283	0.9	0.0194
1.0	0.0281	1.0	0.026
1.2	0.0119	1.2	0.0312
1.4	0.0068	1.4	0.0317
1.6	0.0043	1.6	0.0321
1.8	0.0029	1.8	0.0318
2.0	0.0026	2.0	0.0321

Table 8
Simultaneous Concentration Upset

Run No. 7 A		Run No. 7 B	
$C_{AI} = 0.1258$	$C_{AF} = 0.2486$	$C_{AI} = 0.2486$	$C_{AF} = 0.1258$
$C_{BI} = 0.1216$	$C_{BF} = 0.2221$	$C_{BI} = 0.2221$	$C_{BF} = 0.1216$
$F_{A0} = 0.079$	$F_{A1} = 0.079$	$F_{A0} = 0.079$	$F_{A1} = 0.079$
$F_{B0} = 0.079$	$F_{B1} = 0.079$	$F_{B0} = 0.079$	$F_{B1} = 0.079$
Time min.	C_A moles/liter	Time min.	C_A moles/liter
0.0	0.035	0.0	0.0531
0.1	0.0352	0.1	0.0527
0.2	0.0347	0.2	0.0532
0.3	0.0352	0.3	0.0528
0.4	0.0354	0.4	0.053
0.5	0.0353	0.5	0.053
0.6	0.0357	0.6	0.0525
0.65	0.0397	0.65	0.0495
0.7	0.0455	0.7	0.0417
0.75	0.050	0.75	0.0385
0.8	0.0515	0.8	0.0365
0.9	0.0526	0.9	0.0355
1.0	0.0529	1.0	0.0352
1.1	0.0531	1.1	0.0348
1.2	0.0534	1.2	0.0346
1.3	0.0531	1.3	0.0349
1.4	0.0528	1.4	0.0348
1.5	0.0532	1.5	0.0352
1.6	0.0532	1.6	0.0352

Table 9

Simultaneous Upset (sodium hydroxide concentration and flow)

Run No. 8 A		Run No. 8 B	
$C_{AI} = 0.274$	$C_{AF} = 0.1215$	$C_{AI} = 0.1215$	$C_{AF} = 0.247$
$C_{BI} = 0.2275$	$C_{BF} = 0.2275$	$C_{BI} = 0.2275$	$C_{BF} = 0.2275$
$F_{A0} = 0.068$	$F_{A1} = 0.031$	$F_{A0} = 0.031$	$F_{A1} = 0.068$
$F_{B0} = 0.068$	$F_{B1} = 0.068$	$F_{B0} = 0.068$	$F_{B1} = 0.068$

Time min.	C_A moles/liter	Time min.	C_A moles/liter
0.0	0.047	0.0	0.0026
0.1	0.0464	0.1	0.0022
0.2	0.0454	0.2	0.0024
0.3	0.0436	0.3	0.0033
0.4	0.0430	0.4	0.0036
0.5	0.0420	0.5	0.0044
0.6	0.0412	0.6	0.0046
0.7	0.0405	0.7	0.0060
0.8	0.0400	0.8	0.0224
0.9	0.0384	0.9	0.0336
1.0	0.0353	1.0	0.0404
1.1	0.0298	1.1	0.0444
1.2	0.0208	1.2	0.0464
1.3	0.0138	1.3	0.0464
1.4	0.0100	1.4	0.0468
1.5	0.0090	1.5	0.0468
1.6	0.0064	1.6	0.0472
1.7	0.0048	1.7	0.0472
1.8	0.0037	1.8	0.0470
1.9	0.0032	1.9	0.0470
2.0	0.0029		
2.1	0.0027		
2.2	0.0020		
2.3	0.0025		

Table 10

Simultaneous Upset (methyl acetate concentration and flow)

Run No. 9 A		Run No. 9 B	
$C_{AI} = 0.2486$	$C_{AF} = 0.2486$	$C_{AI} = 0.2486$	$C_{AF} = 0.2486$
$C_{BI} = 0.1216$	$C_{BF} = 0.2221$	$C_{BI} = 0.2221$	$C_{BF} = 0.1216$
$F_{A0} = 0.052$	$F_{A1} = 0.052$	$F_{A0} = 0.052$	$F_{A1} = 0.052$
$F_{B0} = 0.052$	$F_{B1} = 0.079$	$F_{B0} = 0.079$	$F_{B1} = 0.052$

Time min.	C_A moles/liter	Time min.	C_A moles/liter
0.0	0.0741	0.0	0.026
0.1	0.0735	0.1	0.0252
0.2	0.075	0.2	0.0245
0.3	0.0749	0.3	0.0238
0.4	0.0756	0.4	0.0233
0.5	0.076	0.5	0.0222
0.6	0.077	0.6	0.0230
0.7	0.0734	0.7	0.0217
0.8	0.062	0.8	0.0215
0.9	0.0455	0.9	0.0222
1.0	0.0345	1.0	0.0383
1.1	0.0303	1.1	0.0492
1.2	0.0283	1.2	0.0582
1.3	0.0268	1.3	0.0635
1.4	0.0260	1.4	0.0677
1.5	0.0259	1.5	0.0700
1.6	0.0257	1.6	0.0715
1.7	0.0252	1.7	0.0725
1.8	0.0255	1.8	0.0727
1.9	0.0252	1.9	0.0729
		2.0	0.0728

Table 11
Single Concentration Upset (methyl acetate)

Run No. 10 A		Run No. 10 B	
$C_{AI} = 0.2486$	$C_{AF} = 0.2486$	$C_{AI} = 0.2486$	$C_{AF} = 0.2486$
$C_{BI} = 0.2390$	$C_{BF} = 0.1216$	$C_{BI} = 0.1216$	$C_{BF} = 0.2390$
$F_{A0} = 0.024$	$F_{A1} = 0.024$	$F_{A0} = 0.024$	$F_{A1} = 0.024$
$F_{B0} = 0.024$	$F_{B1} = 0.024$	$F_{B0} = 0.024$	$F_{B1} = 0.024$

Time min.	C_A moles/liter	Time min.	C_A moles/liter
0.0	0.0222	0.0	0.065
0.25	0.0213	0.25	0.066
0.50	0.022	0.50	0.0655
0.75	0.022	0.75	0.0652
1.00	0.022	1.00	0.0655
1.25	0.0217	1.25	0.0656
1.50	0.0215	1.50	0.0652
1.75	0.022	1.75	0.0650
2.00	0.023	2.00	0.0640
2.25	0.030	2.25	0.0541
2.50	0.0383	2.50	0.0434
2.75	0.046	2.75	0.0363
3.00	0.053	3.00	0.0318
3.25	0.0565	3.25	0.0282
3.50	0.0592	3.50	0.0271
3.75	0.0616	3.75	0.0255
4.00	0.0628	4.00	0.0242
4.25	0.0640	4.25	0.0235
4.50	0.0632	4.50	0.0225
4.75	0.065	4.75	0.0220
5.00	0.0652		
5.25	0.066		

Table 12

Single Concentration Upset (methyl acetate)

Run No. 11 A		Run No. 11 B	
$C_{AI} = 0.2486$	$C_{AF} = 0.2486$	$C_{AI} = 0.2486$	$C_{AF} = 0.2486$
$C_{BI} = 0.2390$	$C_{BF} = 0.1216$	$C_{BI} = 0.1216$	$C_{BF} = 0.2390$
$F_{A0} = 0.052$	$F_{A1} = 0.052$	$F_{A0} = 0.052$	$F_{A1} = 0.052$
$F_{B0} = 0.052$	$F_{B1} = 0.052$	$F_{B0} = 0.052$	$F_{B1} = 0.052$

Time min.	C_A moles/liter	Time min.	C_A moles/liter
0.0	0.0742	0.0	0.0376
0.2	0.0739	0.2	0.0385
0.4	0.0732	0.4	0.0372
0.6	0.0732	0.6	0.0380
0.8	0.0735	0.8	0.0380
1.0	0.068	1.0	0.0395
1.2	0.0547	1.2	0.0564
1.4	0.0445	1.4	0.066
1.6	0.0406	1.6	0.0695
1.8	0.0385	1.8	0.072
2.0	0.0381	2.0	0.0732
2.2	0.038	2.2	0.0732
2.4	0.0385	2.4	0.0737
2.6	0.038	2.6	0.0735
2.8	0.0375	2.8	0.0738
3.0	0.0375	3.0	0.0738

Table 13

Single Concentration Upset (sodium hydroxide)

Run No. 12 A

Run No. 12 B

$C_{AI} = 0.1235$

$C_{AF} = 0.246$

$C_{AI} = 0.246$

$C_{AF} = 0.1235$

$C_{BI} = 0.1216$

$C_{BF} = 0.1216$

$C_{BI} = 0.1216$

$C_{BF} = 0.1216$

$F_{A0} = 0.052$

$F_{A1} = 0.052$

$F_{A0} = 0.052$

$F_{A1} = 0.052$

$F_{B0} = 0.052$

$F_{B1} = 0.052$

$F_{B0} = 0.052$

$F_{B1} = 0.052$

Time
min. C_A
moles/literTime
min. C_A
moles/liter

0.0

0.0282

0.0

0.0718

0.2

0.0282

0.2

0.0718

0.4

0.0280

0.4

0.0720

0.6

0.0276

0.6

0.0719

0.8

0.0280

0.8

0.0719

1.0

0.0286

1.0

0.0713

1.1

0.0492

1.1

0.0483

1.2

0.0594

1.2

0.0420

1.3

0.0684

1.3

0.0370

1.4

0.0677

1.4

0.0352

1.5

0.0690

1.5

0.0328

1.7

0.0702

1.7

0.0302

1.9

0.0708

1.9

0.0286

2.1

0.0714

2.1

0.0283

2.3

0.0715

2.3

0.0282

2.5

0.0717

2.5

0.0275

2.7

0.0715

2.7

0.0281

2.9

0.0718

2.9

0.0277

3.1

0.0717

3.1

0.0282

3.3

0.0718

3.3

0.0283

3.5

0.0718

3.5

0.0282

Table 14
Simultaneous Concentration Upset

Run No. 13 A		Run No. 13 B	
$C_{AI} = 0.2486$	$C_{AF} = 0.1258$	$C_{AI} = 0.1258$	$C_{AF} = 0.2486$
$C_{BI} = 0.1216$	$C_{BF} = 0.2390$	$C_{BI} = 0.2390$	$C_{BF} = 0.1216$
$F_{A0} = 0.031$	$F_{A1} = 0.031$	$F_{A0} = 0.037$	$F_{A1} = 0.031$
$F_{B0} = 0.031$	$F_{B1} = 0.031$	$F_{B0} = 0.031$	$F_{B1} = 0.031$
Time min.	C_A moles/liter	Time min.	C_A moles/liter
0.0	0.0675	0.0	0.005
0.2	0.0675	0.2	0.0055
0.4	0.067	0.4	0.005
0.6	0.0673	0.6	0.0045
0.8	0.0674	0.8	0.0050
1.0	0.0670	1.0	0.0045
1.2	0.0672	1.2	0.0045
1.4	0.0672	1.4	0.0045
1.6	0.0665	1.6	0.0050
1.7	0.0585	1.7	0.010
1.8	0.0475	1.8	0.0225
1.9	0.0349	1.9	0.0335
2.0	0.0290	2.0	0.0402
2.2	0.0225	2.1	0.0465
2.4	0.020	2.3	0.0525
2.7	0.015	2.5	0.0554
2.9	0.0105	2.7	0.0600
3.1	0.0084	2.9	0.0627
3.3	0.0067	3.1	0.064
3.5	0.0057	3.3	0.0652
3.7	0.0052	3.5	0.0657
3.9	0.0045	3.7	0.0668
4.1	0.005	3.9	0.0665
4.3	0.0043	4.1	0.0675
4.5	0.0044	4.3	0.0668
		4.5	0.0672

Table 15
Simultaneous Concentration Upset

Run No. 14 A		Run No. 14 B	
$C_{AI} = 0.1258$	$C_{AF} = 0.2486$	$C_{AI} = 0.2486$	$C_{AF} = 0.1258$
$C_{BI} = 0.1216$	$C_{BF} = 0.2390$	$C_{BI} = 0.2390$	$C_{BF} = 0.1216$
$F_{A0} = 0.044$	$F_{A1} = 0.044$	$F_{A0} = 0.044$	$F_{A1} = 0.044$
$F_{B0} = 0.044$	$F_{B1} = 0.044$	$F_{B0} = 0.044$	$F_{B1} = 0.044$

Time min.	C_A moles/liter	Time min.	C_A moles/liter
0.0	0.0262	0.0	0.0337
0.2	0.0262	0.2	0.0338
0.4	0.0261	0.4	0.0338
0.6	0.0262	0.6	0.0338
0.8	0.0262	0.8	0.0338
1.0	0.0262	1.0	0.0337
1.1	0.0269	1.1	0.0334
1.2	0.0289	1.2	0.0305
1.3	0.0308	1.3	0.0285
1.4	0.0317	1.4	0.0277
1.5	0.0327	1.5	0.0273
1.7	0.0332	1.7	0.0269
1.9	0.0334	1.9	0.0265
2.1	0.0336	2.1	0.0263
2.3	0.0337	2.3	0.0262
2.5	0.0337	2.5	0.0262
2.7	0.0338	2.7	0.0261
2.9	0.0337	2.9	0.0262

Table 16

Single Concentration Upset (sodium hydroxide)

Run No. 15 A		Run No. 15 B	
$C_{AI} = 0.1235$	$C_{AF} = 0.246$	$C_{AI} = 0.246$	$C_{AF} = 0.1235$
$C_{BI} = 0.1216$	$C_{BF} = 0.1216$	$C_{BI} = 0.1216$	$C_{BF} = 0.1216$
$F_{A0} = 0.024$	$F_{A1} = 0.024$	$F_{A0} = 0.024$	$F_{A1} = 0.024$
$F_{B0} = 0.024$	$F_{B1} = 0.024$	$F_{B0} = 0.024$	$F_{B1} = 0.024$
Time min.	C_A moles/liter	Time min.	C_A moles/liter
0.0	0.0185	0.0	0.0647
0.5	0.018	0.5	0.0638
1.0	0.0182	1.0	0.0645
1.5	0.018	1.5	0.0645
2.0	0.0202	2.0	0.0631
2.1	0.0267	2.1	0.0566
2.2	0.0326	2.2	0.0515
2.3	0.0375	2.3	0.0455
2.4	0.0420	2.4	0.0420
2.6	0.0472	2.6	0.0355
2.8	0.0532	2.8	0.033
3.0	0.0560	3.0	0.0305
3.0	0.0585	3.2	0.0271
3.4	0.0587	3.4	0.0235
3.6	0.0606	3.6	0.022
3.8	0.0617	3.8	0.0203
4.0	0.0629	4.0	0.0196
4.2	0.0632	4.2	0.0198
4.4	0.0631	4.4	0.0186
4.6	0.0635	4.6	0.0185
4.8	0.0638	4.8	0.0180

APPENDIX II

Electrode Response Data

Table 17
Response Data

Run RES 1		Run RES 2		Run RES 3	
$C_1 = 0.032$ mole/liter		$C_1 = 0.065$ mole/liter		$C_1 = 0.25$ mole/liter	
$C_2 = 0.125$ mole/liter		$C_2 = 0.25$ mole/liter		$C_2 = 0.065$ mole/liter	
<u>Time</u> <u>sec</u>	<u>% Change</u>	<u>Time</u> <u>sec</u>	<u>% Change</u>	<u>Time</u> <u>sec</u>	<u>% Change</u>
0.0	00.00	0.0	0.0	0.0	0.0
0.75	48.2	0.75	43.2	0.75	50.4
2.25	72.0	1.50	61.4	1.50	61.8
3.75	80.4	2.25	69.0	3.0	71.5
5.25	84.9	3.75	78.8	4.5	78.0
6.75	88.6	5.25	84.2	6.0	83.0
8.25	90.1	6.75	87.0	7.5	85.4
9.75	91.6	9.00	89.5	9.0	87.8
11.25	93.2	10.50	91.0	10.5	89.4
12.75	94.0	13.50	92.6	16.50	91.0
14.25	94.7	16.50	94.1	19.50	92.6
20.25	96.2	19.50	95.7	21.50	94.3
21.75	97.0				
29.25	98.2				

APPENDIX III

Kinetic Data

Table 18
Kinetic Data

Temperature °C	Rate Constant liter/(mole) (min)
25.5	11.57
31.0	14.15
35.0	18.79
36.5	20.71

Activation energy = $\Delta E = 7.90$ kcal/mole

Frequency factor = $k_0 = (6.35)10^6$

APPENDIX IV

Computer Programs

Lumped Parameter Model

$$N = 8$$

#LIST
#FORTRAN LISTING 5703 RAMASWAMY

```
C PROGRAMME NO. T - 3 - REVISED
C PROGRAMMED BY RAMASWAMY
C 8 AXIAL DIVISIONS
C RUNGE-GUTTA METHOD
50 READ25,FA1,FB1,FA2,FB2,CA0,CB0
   IF(FA1)80,80,45
35 FORMAT(1H1,/6X,3HFA1,7X,3HFB1,5X,3HFA2,5X,3HFB2,7X,3HCA0,7X,3HCB0/
   1)
45 PRINT 35
25 FORMAT(6F10.8)
   PRINT25,FA1,FB1,FA2,FB2,CA0,CB0
   LEN=497.0
   CAI=(FA1/(FA1+FB1))*CA0
   CBI=(FB1/(FA1+FB1))*CB0
   FO=(FA2+FB2)*1000.
95 FORMAT(/5X,3HCAI,10X,3HCBI/)
   PRINT 95
105 FORMAT(2F16.8)
   PRINT 105,CAI,CBI
   RES=110.0/FO
110 FORMAT(/2X,14HRESIDENCE TIME/)
   PRINT 110
115 FORMAT(1F16.8)
   PRINT 115,RES
55 FORMAT(///5X,4HTIME,8X,3HCA2,9X,3HCA4,9X,3HCA6,9X,3HCA8/)
   PRINT 55
   FA0=0.031
   FB0=0.016
   T=110.0/((FA0+FB0)*1000.)
   CAS=(FA0/(FA0+FB0))*CA0
   CBS=(FB0/(FA0+FB0))*CB0
   K=19.5
   CA1=(CBS-CAS)/((CBS/CAS)*EXPF(K*(T/8.)*(CBS-CAS))-1.)
   CB1=(CBS-CAS)+CA1
   CA2=(CBS-CAS)/((CBS/CAS)*EXPF(K*(T/4.)*(CBS-CAS))-1.)
   CB2=(CBS-CAS)+CA2
   CA3=(CBS-CAS)/((CBS/CAS)*EXPF(K*(3.*T/8.)*(CBS-CAS))-1.)
   CB3=(CBS-CAS)+CA3
   CA4=(CBS-CAS)/((CBS/CAS)*EXPF(K*(T/2.)*(CBS-CAS))-1.)
   CB4=(CBS-CAS)+CA4
   CA5=(CBS-CAS)/((CBS/CAS)*EXPF(K*(5.*T/8.)*(CBS-CAS))-1.)
   CB5=(CBS-CAS)+CA5
   CA6=(CBS-CAS)/((CBS/CAS)*EXPF(K*(6.*T/8.)*(CBS-CAS))-1.)
   CB6=(CBS-CAS)+CA6
   CA7=(CBS-CAS)/((CBS/CAS)*EXPF(K*(7.*T/8.)*(CBS-CAS))-1.)
   CB7=(CBS-CAS)+CA7
   CA8=(CBS-CAS)/((CBS/CAS)*EXPF(K*T*(CBS-CAS))-1.)
   CB8=(CBS-CAS)+CA8
   Y0=0.0
   Y=0.0
   DELY=0.01
   YL=3.*RES
42 IF(Y-Y0)41,40,40
40 PRINT70,Y,CA2,CA4,CA6,CA8
   Y0=Y0+0.05
41 R11=K*((CA1+CAI)/2.)*((CB1+CBI)/2.)
   AK11=DELY*((FO*(CAI-CA1))/(0.1828*LEN/8.)-R11)
   BK11=DELY*((FO*(CBI-CB1))/(0.1828*LEN/8.)-R11)
```

$R12 = K * ((CA1 + (AK11/2.) + CA1)/2.) * ((CB1 + (BK11/2.) + CB1)/2.)$
 $AK12 = DELY * ((FO * (CA1 - CA1 - (AK11/2.))) / (0.1828 * LEN/8.) - R12)$
 $BK12 = DELY * ((FO * (CB1 - CB1 - (BK11/2.))) / (0.1828 * LEN/8.) - R12)$
 $R13 = K * ((CA1 + (AK12/2.) + CA1)/2.) * ((CB1 + (BK12/2.) + CB1)/2.)$
 $AK13 = DELY * ((FO * (CA1 - CA1 - (AK12/2.))) / (0.1828 * LEN/8.) - R13)$
 $BK13 = DELY * ((FO * (CB1 - CB1 - (BK12/2.))) / (0.1828 * LEN/8.) - R13)$
 $R14 = K * ((CA1 + AK13 + CA1)/2.) * ((CB1 + BK13 + CB1)/2.)$
 $AK14 = DELY * ((FO * (CA1 - CA1 - (AK13))) / (0.1828 * LEN/8.) - R14)$
 $BK14 = DELY * ((FO * (CB1 - CB1 - (BK13))) / (0.1828 * LEN/8.) - R14)$
 $CA1 = CA1 + (AK11 + (2. * AK12) + (2. * AK13) + AK14) / 6.$
 $CB1 = CB1 + (BK11 + (2. * BK12) + (2. * BK13) + BK14) / 6.$
 $R21 = K * ((CA2 + CA1)/2.) * ((CB2 + CB1)/2.)$
 $AK21 = DELY * ((FO * (CA1 - CA2)) / (0.1828 * LEN/8.) - R21)$
 $BK21 = DELY * ((FO * (CB1 - CB2)) / (0.1828 * LEN/8.) - R21)$
 $R22 = K * ((CA2 + (AK21/2.) + CA1)/2.) * ((CB2 + (BK21/2.) + CB1)/2.)$
 $AK22 = DELY * ((FO * (CA1 - CA2 - (AK21/2.))) / (0.1828 * LEN/8.) - R22)$
 $BK22 = DELY * ((FO * (CB1 - CB2 - (BK21/2.))) / (0.1828 * LEN/8.) - R22)$
 $R23 = K * ((CA2 + (AK22/2.) + CA1)/2.) * ((CB2 + (BK22/2.) + CB1)/2.)$
 $AK23 = DELY * ((FO * (CA1 - CA2 - (AK22/2.))) / (0.1828 * LEN/8.) - R23)$
 $BK23 = DELY * ((FO * (CB1 - CB2 - (BK22/2.))) / (0.1828 * LEN/8.) - R23)$
 $R24 = K * ((CA1 + AK23 + CA2)/2.) * ((CB1 + BK23 + CB2)/2.)$
 $AK24 = DELY * ((FO * (CA1 - CA2 - AK23)) / (0.1828 * LEN/8.) - R24)$
 $BK24 = DELY * ((FO * (CB1 - CB2 - BK23)) / (0.1828 * LEN/8.) - R24)$
 $CA2 = CA2 + (AK21 + (2. * AK22) + (2. * AK23) + AK24) / 6.$
 $CB2 = CB2 + (BK21 + (2. * BK22) + (2. * BK23) + BK24) / 6.$
 $R31 = K * ((CA3 + CA2)/2.) * ((CB3 + CB2)/2.)$
 $AK31 = DELY * ((FO * (CA2 - CA3)) / (0.1828 * LEN/8.) - R31)$
 $BK31 = DELY * ((FO * (CB2 - CB3)) / (0.1828 * LEN/8.) - R31)$
 $R32 = K * ((CA3 + (AK31/2.) + CA2)/2.) * ((CB3 + (BK31/2.) + CB2)/2.)$
 $AK32 = DELY * ((FO * (CA2 - CA3 - (AK31/2.))) / (0.1828 * LEN/8.) - R32)$
 $BK32 = DELY * ((FO * (CB2 - CB3 - (BK31/2.))) / (0.1828 * LEN/8.) - R32)$
 $R33 = K * ((CA3 + (AK32/2.) + CA2)/2.) * ((CB3 + (BK32/2.) + CB2)/2.)$
 $AK33 = DELY * ((FO * (CA2 - CA3 - (AK32/2.))) / (0.1828 * LEN/8.) - R33)$
 $BK33 = DELY * ((FO * (CB2 - CB3 - (BK32/2.))) / (0.1828 * LEN/8.) - R33)$
 $R34 = K * ((CA3 + AK33 + CA2)/2.) * ((CB3 + BK33 + CB2)/2.)$
 $AK34 = DELY * ((FO * (CA2 - CA3 - AK33)) / (0.1828 * LEN/8.) - R34)$
 $BK34 = DELY * ((FO * (CB2 - CB3 - BK33)) / (0.1828 * LEN/8.) - R34)$
 $CA3 = CA3 + (AK31 + (2. * AK32) + (2. * AK33) + AK34) / 6.$
 $CB3 = CB3 + (BK31 + (2. * BK32) + (2. * BK33) + BK34) / 6.$
 $R41 = K * ((CA4 + CA3)/2.) * ((CB4 + CB3)/2.)$
 $AK41 = DELY * ((FO * (CA3 - CA4)) / (0.1828 * LEN/8.) - R41)$
 $BK41 = DELY * ((FO * (CB3 - CB4)) / (0.1828 * LEN/8.) - R41)$
 $R42 = K * ((CA4 + (AK41/2.) + CA3)/2.) * ((CB4 + (BK41/2.) + CB3)/2.)$
 $AK42 = DELY * ((FO * (CA3 - CA4 - (AK41/2.))) / (0.1828 * LEN/8.) - R42)$
 $BK42 = DELY * ((FO * (CB3 - CB4 - (BK41/2.))) / (0.1828 * LEN/8.) - R42)$
 $R43 = K * ((CA4 + (AK42/2.) + CA3)/2.) * ((CB4 + (BK42/2.) + CB3)/2.)$
 $AK43 = DELY * ((FO * (CA3 - CA4 - (AK42/2.))) / (0.1828 * LEN/8.) - R43)$
 $BK43 = DELY * ((FO * (CB3 - CB4 - (BK42/2.))) / (0.1828 * LEN/8.) - R43)$
 $R44 = K * ((CA4 + AK43 + CA3)/2.) * ((CB4 + BK43 + CB3)/2.)$
 $AK44 = DELY * ((FO * (CA3 - CA4 - AK43)) / (0.1828 * LEN/8.) - R44)$
 $BK44 = DELY * ((FO * (CB3 - CB4 - BK43)) / (0.1828 * LEN/8.) - R44)$
 $CA4 = CA4 + (AK41 + (2. * AK42) + (2. * AK43) + AK44) / 6.$
 $CB4 = CB4 + (BK41 + (2. * BK42) + (2. * BK43) + BK44) / 6.$
 $R51 = K * ((CA5 - CA4)/2.) * ((CB5 - CB4)/2.)$
 $AK51 = DELY * ((FO * (CA4 - CA5)) / (0.1828 * LEN/8.) - R51)$
 $BK51 = DELY * ((FO * (CB4 - CB5)) / (0.1828 * LEN/8.) - R51)$
 $R52 = K * ((CA5 + (AK51/2.) + CA4)/2.) * ((CB5 + (BK51/2.) + CB4)/2.)$
 $AK52 = DELY * ((FO * (CA4 - CA5 - (AK51/2.))) / (0.1828 * LEN/8.) - R52)$
 $BK52 = DELY * ((FO * (CB4 - CB5 - (BK51/2.))) / (0.1828 * LEN/8.) - R52)$
 $R53 = K * ((CA5 + (AK52/2.) + CA4)/2.) * ((CB5 + (BK52/2.) + CB4)/2.)$

```

AK53=DELY*((FO*(CA4-CA5-(AK52/2.)))/(0.1828*LEN/8.))-R53)
BK53=DELY*((FO*(CB4-CB5-(BK52/2.)))/(0.1828*LEN/8.))-R53)
R54=K*((CA5+AK53+CA4)/2.)*((CB5+BK53+CB4)/2.)
AK54=DELY*((FO*(CA4-CA5-AK53))/(0.1828*LEN/8.))-R54)
BK54=DELY*((FO*(CB4-CB5-BK53))/(0.1828*LEN/8.))-R54)
CA5=CA5+(AK51+(2.*AK52)+(2.*AK53)+AK54)/6.
CB5=CB5+(BK51+(2.*BK52)+(2.*BK53)+BK54)/6.
R61=K*((CA6+CA5)/2.)*((CB6+CB5)/2.)
AK61=DELY*((FO*(CA5-CA6))/(0.1828*LEN/8.))-R61)
BK61=DELY*((FO*(CB5-CB6))/(0.1828*LEN/8.))-R61)
R62=K*((CA6+(AK61/2.)+CA5)/2.)*((CB6+(BK61/2.)+CB5)/2.)
AK62=DELY*((FO*(CA5-CA6-(AK61/2.)))/(0.1828*LEN/8.))-R62)
BK62=DELY*((FO*(CB5-CB6-(BK61/2.)))/(0.1828*LEN/8.))-R62)
R63=K*((CA6+(AK62/2.)+CA5)/2.)*((CB6+(BK62/2.)+CB5)/2.)
AK63=DELY*((FO*(CA5-CA6-(AK62/2.)))/(0.1828*LEN/8.))-R63)
BK63=DELY*((FO*(CB5-CB6-(BK62/2.)))/(0.1828*LEN/8.))-R63)
R64=K*((CA6+AK63+CA5)/2.)*((CB6+BK63+CB5)/2.)
AK64=DELY*((FO*(CA5-CA6-AK63))/(0.1828*LEN/8.))-R64)
BK64=DELY*((FO*(CB5-CB6-BK63))/(0.1828*LEN/8.))-R64)
CA6=CA6+(AK61+(2.*AK62)+(2.*AK63)+AK64)/6.
CB6=CB6+(BK61+(2.*BK62)+(2.*BK63)+BK64)/6.
R71=K*((CA7+CA6)/2.)*((CB7+CB6)/2.)
AK71=DELY*((FO*(CA6-CA7))/(0.1828*LEN/8.))-R71)
BK71=DELY*((FO*(CB6-CB7))/(0.1828*LEN/8.))-R71)
R72=K*((CA7+(AK71/2.)+CA6)/2.)*((CB7+(BK71/2.)+CB6)/2.)
AK72=DELY*((FO*(CA6-CA7-(AK71/2.)))/(0.1828*LEN/8.))-R72)
BK72=DELY*((FO*(CB6-CB7-(BK71/2.)))/(0.1828*LEN/8.))-R72)
R73=K*((CA7+(AK72/2.)+CA6)/2.)*((CB7+(BK72/2.)+CB6)/2.)
AK73=DELY*((FO*(CA6-CA7-(AK72/2.)))/(0.1828*LEN/8.))-R73)
BK73=DELY*((FO*(CB6-CB7-(BK72/2.)))/(0.1828*LEN/8.))-R73)
R74=K*((CA7+AK73+CA6)/2.)*((CB7+BK73+CB6)/2.)
AK74=DELY*((FO*(CA6-CA7-AK73))/(0.1828*LEN/8.))-R74)
BK74=DELY*((FO*(CB6-CB7-BK73))/(0.1828*LEN/8.))-R74)
CA7=CA7+(AK71+(2.*AK72)+(2.*AK73)+AK74)/6.
CB7=CB7+(BK71+(2.*BK72)+(2.*BK73)+BK74)/6.
R81=K*((CA8+CA7)/2.)*((CB8+CB7)/2.)
AK81=DELY*((FO*(CA7-CA8))/(0.1828*LEN/8.))-R81)
BK81=DELY*((FO*(CB7-CB8))/(0.1828*LEN/8.))-R81)
R82=K*((CA8+(AK81/2.)+CA7)/2.)*((CB8+(BK81/2.)+CB7)/2.)
AK82=DELY*((FO*(CA7-CA8-(AK81/2.)))/(0.1828*LEN/8.))-R82)
BK82=DELY*((FO*(CB7-CB8-(BK81/2.)))/(0.1828*LEN/8.))-R82)
R83=K*((CA8+(AK82/2.)+CA7)/2.)*((CB8+(BK82/2.)+CB7)/2.)
AK83=DELY*((FO*(CA7-CA8-(AK82/2.)))/(0.1828*LEN/8.))-R83)
BK83=DELY*((FO*(CB7-CB8-(BK82/2.)))/(0.1828*LEN/8.))-R83)
R84=K*((CA8+AK83+CA7)/2.)*((CB8+BK83+CB7)/2.)
AK84=DELY*((FO*(CA7-CA8-AK83))/(0.1828*LEN/8.))-R84)
BK84=DELY*((FO*(CB7-CB8-BK83))/(0.1828*LEN/8.))-R84)
CA8=CA8+(AK81+(2.*AK82)+(2.*AK83)+AK84)/6.
CB8=CB8+(BK81+(2.*BK82)+(2.*BK83)+BK84)/6.
Y=Y+DELY
70 FORMAT(5F12.6)
85 IF(Y-YL)42,42,50
80 I=XEXITF(0)
END

```

Residence Time Distribution Model

*LIST
*FORTRAN LISTING 5703 RAMASWAMY

```
C PROGRAMMED BY RAMASWAMY  
C RESIDENCE TIME DISTRIBUTION MODEL  
100 READ50,CAI,CBI,FA0,FB0,CAF,CBF,FA1,FB1  
IF(CAI)115,115,55  
50 FORMAT(8F10.8)  
10 FORMAT(1H1,/11X,18HINITIAL CONDITIONS)  
55 PRINT 10  
20 FORMAT(/4X,3HCAI,8X,3HCBI,8X,3HFA0,8X,3HFB0)  
PRINT 20  
PRINT40,CAI,CBI,FA0,FB0  
40 FORMAT(4F10.8)  
30 FORMAT(/,/11X,16HFINAL CONDITIONS)  
PRINT 30  
60 FORMAT(/4X,3HCAF,8X,3HCBF,8X,3HFA1,8X,3HFB1)  
PRINT 60  
PRINT40,CAF,CBF,FA1,FB1  
LEN=497.0  
CA0=(FA0/(FA0+FB0))*CAI  
CB0=(FB0/(FA0+FB0))*CBI  
CA1=(FA1/(FA1+FB1))*CAF  
CB1=(FB1/(FA1+FB1))*CBF  
K=19.5  
TB=91.0/((FA1+FB1)*1000.)  
T0=110.0/((FA0+FB0)*1000.)  
T1=110.0/((FA1+FB1)*1000.)  
CAS0=(CB0-CA0)/((CB0/CA0)*EXPF(K*T0*(CB0-CA0))-1.0)  
CAS1=(CB1-CA1)/((CB1/CA1)*EXPF(K*T1*(CB1-CA1))-1.0)  
80 FORMAT(/8X,4HCAS0,10X,4HCAS1)  
PRINT 80  
PRINT 85,CAS0,CAS1  
85 FORMAT(2F16.8)  
301 FORMAT(/10X,2HT0,12X,2HT1)  
PRINT 301  
PRINT 85,T0,T1  
304 FORMAT(1F16.8)  
302 FORMAT(/10X,11HBREAK POINT)  
PRINT 302  
PRINT 304,TB  
70 FORMAT(/13X,4HTIME,8X,2HCA/)  
PRINT 70  
DIV=0.0  
IF(T0-T1)90,105,90  
90 TL=20.0  
T=(DIV/TL)*T1  
TOT=((1.-(DIV/TL))*T0)+((DIV/TL)*T1)  
CA=(CB0-CA0)/((CB0/CA0)*EXPF(K*TOT*(CB0-CA0))-1.)  
PRINT 15,TL,T,CA  
15 FORMAT(3F10.7)  
DIV=DIV+1.  
IF(ABS(DIV-TL)-0.000025)105,105,90  
105 TNEW=1.83*EXPF(-17.78*(FA1+FB1))  
CA2=(CB0-CA0)/((CB0/CA0)*EXPF(K*TB*(CB0-CA0))-1.)  
DELT=0.1  
205 T=TB+DELT  
CA=CA2+((CAS1-CA2)*(1.-EXPF(-DELT/TNEW)))  
PRINT 15,TL,T,CA  
DELT=DELT+0.1  
IF(ABS(DELT-3.)-0.000025)210,210,205
```

```
210 GO TO 100  
115 I=XEXITF(0)  
END
```