

INCOMPLETE MIXING IN A  
CONTINUOUS STIRRED TANK REACTOR

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Engineering (Chemical Engineering)

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## ABSTRACT

In a Continuous Stirred Tank Reactor (CSTR), deviations from perfect mixing can occur both on the macro and micro scales. The macro scale deviations are covered by the deviation of the residence time distribution (RTD) from a well stirred residence time distribution (WS RTD). A number of models for incomplete mixing in a CSTR have been suggested to cover the micro mixing deviations from maximum mixedness. The Rippin-Ng random mixing model and Weinstein's Consecutive Reactor model are deemed to be the most suitable models for incomplete mixing in a single CSTR.

The Rippin-Ng model has been extended to cover complex kinetics for homogeneous isothermal reaction. The effects of the reactants entering through different feed nozzles have been formalised and quantified. Some estimates of the Rippin-Ng mixing parameter ( $RT$ ) have been obtained for dilute aqueous solutions.

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## CHAPTER I

### INTRODUCTION

Mixing is one of the most widely used chemical engineering operations, and is employed for processing an extremely diverse range of materials. The objective of mixing is homogenisation, manifesting itself in a reduction of concentration or temperature gradients or of both simultaneously. The systems to<sup>be</sup> mixed may consist of fluids or particulate solids or both. This present work will be restricted to the mixing of completely miscible low viscosity fluids of the same density, and all future statements will be assumed valid only for such fluid - fluid systems. In such systems two types of motion may occur:

- a) Spontaneous
- b) Forced

Spontaneous motion is effected by the motion of fluid particles due to the influence of molecular diffusion, mass transfer by free convection. Although this is the only mechanism for motion on the molecular scale, it is not of great importance for the movement within liquids on the larger scale, as it proceeds far too slowly. Forced convection may result either by the handling and treatment of fluids e.g. pumping, <sup>h</sup> heating, cooling etc., or by stirring with an impeller. All future comments will be restricted to homogeneous liquid systems only.

I.

The initial research in this field was directed towards the solution of practical engineering problems. Most of the early workers concentrated on finding the mixing time (33) and power requirements (31, 32) for a wide range of impeller types, impeller and tank sizes and geometry, liquid properties and other operating conditions. These empirical studies solved some of the then existing problems, but contributed little to the understanding of the mechanism of mixing.

One of the branches of chemical engineering affected by mixing is chemical reaction engineering. In the earlier stages of its development, the batch type of reactor was widely employed. With an increase in product demand and higher labour costs, it was found possible to operate continuous reactors with much greater economy than the corresponding batch systems. In the batch reactor, the reaction time and stirrer speed could be varied relatively easily to compensate for the inconsistencies in the mixing. However, with continuous reactors, the conversion is determined by a number of operating conditions, and the interaction between these conditions is generally more complicated than for the corresponding batch system. In view of this and the larger capital investment in a continuous system, incentive was provided to understand more about reactor design and operation.

Homogeneous industrial chemical reactions are performed chiefly in two types of continuous reactors:-

- (I) Plug flow reactors.
- (2) Continuous Stirred Tank Reactors (CSTRs)

In a plug flow reactor no attempt is made to induce mixing in the direction of flow, whereas for a CSTR a definite attempt is made to mix the fluids, generally by means of stirring with an impeller.

A perfect plug flow reactor is defined as one having perfect mixing in the radial direction and zero mixing in the axial direction, whereas the contents of a perfect CSTR are homogeneous at all points within the reactor ie. perfectly mixed.

In practice these conditions do not occur, and both types of reactors will deviate by varying amounts from the idealized form. In a non-ideal CSTR, deviations from perfect mixing may occur in two forms:-

- I) Macro mixing deviations
- 2) Micro mixing deviations

Macro mixing is the large scale mixing phenomenon, and as determined by the residence time distribution (R.T.D.), is in general, a complicated function of the geometry of the system, the physical properties of the fluid, and the rate of flow of the fluid. The RTD

frequency function for a perfect CSTR is given by

$$f(t) = \frac{1}{\tau} \exp(-t/\tau)$$

where  $\tau$  is the mean residence time of all molecules

leaving the system at any instant -(I.I)

If the RTD frequency function of the CSTR is different from this, deviation on the macro scale occurs from the perfect mixing required for the ideal CSTR.

The micro mixing is the small scale phenomenon and often has a lesser effect on the conversion. Whereas the macro mixing determines the time of residence of a molecule in the flow system, the micro mixing determines the environment or concentration history this molecule experiences during that time. This concept may be further illustrated by considering a "point" of fluid. Danckwerts (4) defined a "point" of fluid as being a very small volume, but still large enough to contain many molecules. When a point enters the system, it consists of molecules of the same age, but in the general case of different life expectations (see Chapter 2.2 for definition). When a point leaves the system, it consists of molecules of the same life expectation, but in general of different ages. If the entering point does have a distribution of residence times associated with it, then somewhere in the system there is a transition from a grouping of molecules by identical ages to one of identical life expectations. If, for a well stirred system i.e. one having a RTD frequency

function given by equation (I.1), this transition occurs immediately on entry, perfect micro mixing results. In all other cases a deviation from perfect micro mixing occurs.

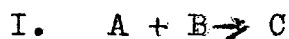
At first, CSTRs were assumed ideal, and an empirical safety factor used for design purposes (5). Kramers applied the mixing time to the concept of RTD (12). It was shown that for a non-first order reaction, a knowledge of the micro mixing is necessary to predict conversion (34). Danckwerts (4) showed it possible to determine an upper and lower limit of conversion, and calculated the limiting conversions for a well stirred RTD. The upper limit of conversion is achieved with complete segregation, when the order of reaction is greater than one. Perfect mixing (for a well stirred RTD) results in the lower limit of conversion. For reactions of the first order, these limits coincide, while the reverse occurs for reactions of order less than one.

Zwietering (30) extended these ideas to cover the case for any arbitrary RTD, and showed that perfect molecular mixing cannot occur unless the RTD corresponds to that for a well stirred system. He defined a state of maximum micro mixing compatible with any arbitrary RTD as being the state of maximum mixedness (Chapter 2.2.).

Complete segregation is theoretically possible with any arbitrary RTD.

Weinstein (26) developed the Consecutive Reactor model for mixing in a CSTR. Rippin and Ng (16) defined a mixing parameter, the knowledge of which would make it possible to predict exactly the conversion with any arbitrary RTD, and Ng (18) evaluated the equations for the case of a second order reaction with premixed feeds. This work is applicable to isothermal homogeneous reaction between two fluids of the same viscosity and density which are also completely miscible.

The aim of this work is to extend the Rippin - Ng model to cover more complicated kinetics, and also to quantify the behaviour of systems when the feed streams enter through two separate feed nozzles i.e. unpremixed feeds, in addition to the normal case for premixed feeds. The same constraints as for the work of Rippin and Ng, will apply to the density, viscosity and miscibility of the system. An attempt will be made to find reliable values for the mixing parameter. The theoretical work will cover the following kinetics:

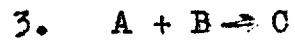


Irreversible Second Order Reaction

(Unpremixed)

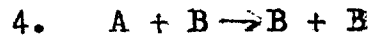


Consecutive Premixed Reaction.



Consecutive Parallel Reaction

(Premixed and Unpremixed)



Autocatalytic Reaction

(Premixed and Unpremixed).

## CHAPTER 2

### LITERATURE SURVEY

#### 2.1. Application of RTD to Mixing in Flow Systems

Danckwerts (3) developed the application of the RTD to the analysis of mixing in a flow system, and showed that the conversion for a second order reaction with a well stirred RTD (WSRTD) i.e. a frequency function of  $\frac{1}{\tau} \exp(-t/\tau)$  would be higher for complete segregation than with perfect mixing (4). To describe the degree of mixing in a fluid, he used the concepts of "concentration at a point" and "age of fluid at a point". A "point" has been defined in Chapter I.

The age  $\alpha$  of a molecule is defined as the time which has elapsed since the molecule entered the flow system, and the variance of the ages of all molecules in the flow system is given by

$$\text{Var } \alpha = \frac{\sum (\alpha - \bar{\alpha})^2}{N} \quad (2.1)$$

where  $\bar{\alpha}$  is the mean age of all molecules which are in the flow system at some particular instant. The mean age at a point  $\alpha_p$  is defined as the mean age of all molecules forming the point at any instant, and the variance between the mean ages of the points is given by

$$\text{Var } \alpha_p = \frac{\sum (\alpha_p - \bar{\alpha})^2}{N} \quad (2.2)$$

Danckwerts (4) defined a new parameter called the degree

of segregation  $J$  as

$$J = \frac{\text{Var } \alpha_p}{\text{Var } \alpha} = \frac{(\alpha_p - \bar{\alpha})^2}{(\alpha - \bar{\alpha})^2} - (2.3)$$

He also showed that when the RTD frequency function is given by  $f(t) = \frac{1}{\tau} \exp(-t/\tau)$  i.e. I CSTRs RTD, with  $J = 0$  perfect mixing results, while  $J = 1$  represents the state of complete segregation.

This process of analysis was further developed by Zwietering (30), who showed that whereas complete segregation and the corresponding value of  $J = 1$  could in theory occur with any arbitrary RTD, that when the RTD is different from a I CSTRs RTD i.e. when the RTD frequency function  $\neq \frac{1}{\tau} \exp(-t/\tau)$ , the value of  $J$  cannot be zero, and perfect mixing cannot occur. He calculated the minimum value of  $J$  for various RTDs, and defined the state of mixing when  $J$  is a minimum for any given RTD, as the state of maximum mixedness (Section 2.2). This state represents the least amount of segregation compatible with the RTD.

## 2.2. Maximum Mixedness

Zwietering (30) defined the life expectation of a molecule at a given instant as the further time the molecule will spend in the flow system. If the total residence time of the molecule in the flow system is  $t$ , and the age at any instant  $\theta$  is  $\alpha \theta$ , then  $\lambda$  is defined by

$$t = \lambda \theta + \alpha \theta - (2.3)$$

The life expectation frequency function is defined as  $\psi(\lambda)$  and at any given instant  $\psi(\lambda) d\lambda$  is the fraction of molecules in the system that have a life expectation between  $\lambda$  and  $\lambda+d\lambda$ . The cumulative life expectation distribution  $\Psi(\lambda)$ , associated with

$\psi(\lambda)$ , is the fraction of molecules in the system that have a life expectation less than  $\lambda$ . The age frequency and life expectation frequency functions of a point  $p$  are  $\phi_p(\alpha)$  and  $\psi_p(\lambda)$  respectively, with  $\Phi_p(\alpha)$  and  $\Psi_p(\lambda)$  being the corresponding cumulative distribution functions.

Using these definitions, two conditions which precisely define maximum mixedness in a steady flow system may be stated (30):-

I. For each point, the molecules within it will leave the system at the same moment

$$\text{i.e. } \psi_p(\lambda) = \begin{cases} 0 & \text{for } \lambda \leq \lambda_p \\ 1 & \text{for } \lambda > \lambda_p \end{cases} \quad (2.4)$$

that is, the cumulative life expectation distribution function at each point is a step function.

2. Points with equal life expectations are mixed, or at least have identical age distributions

$$\Phi_p(\lambda) = \Phi(\lambda_p, \lambda) \quad - (2.5)$$

It has been shown (30) that the degree of segregation  $J$  is a minimum when these two conditions are fulfilled.

## II

### 2.3. Maximum Mixedness Conversion

Zwietering (30) designed two reactor models to show that complete segregation and maximum mixedness are complementary phenomena. The first was the perfect plug flow reactor for complete segregation, with side exits of negligible volume. The flow rates through the exits are regulated such that the resulting RTD conforms to the required form. The maximum mixedness reactor consists of a perfect plug flow reactor with side entrances of negligible volume. In both cases radial mixing is assumed perfect at all cross sections. The second reactor is the same as for the completely segregated case except that the flow is exactly reversed, and hence RTD is the same in the two cases. It can be shown that this maximum mixedness reactor fulfills the two conditions in Section 2.2.

By a material balance around an isothermal maximum mixedness reactor, the following equation for concentration may be obtained

$$\frac{dA}{d\lambda} = f(A(\lambda)) + \frac{f(\lambda)}{1-F(\lambda)} [A - A_0] \quad (2.6)$$

where  $f[A(\lambda)]$  is the batch chemical rate expression as a function of  $\lambda$ . The boundary condition for the integration of equation (2.6) is  $dA/d\lambda = 0$  at  $\lambda = \infty$ . This follows from the fact that at  $\lambda = \infty$  i.e. at the entrance to the reactor, the concentration of A is bounded and positive. However, the very small fraction

of molecules at high residence time do not affect the conversion to a significant extent. For the purposes of numerical integration it is sufficient to assume  $dA/d\lambda = 0$  at  $\lambda = 4\tau$ . The value of A at  $\lambda = 4\tau$  may be obtained if the limit  $f(\lambda)/(1 - F(\lambda))$  at  $\lambda = \infty$  can be evaluated.

Zwietering (30) integrated equation (2.6) for the case of simple first and second order reactions with the RTD of 2 and 3 CSTRs, for various values of the dimensionless rate constant K I. He also showed that with a 1 CSTRs RTD, the concentration is constant at all points in the maximum mixedness reactor.

#### 2.4. The Generalised Micro - Mixing Model

Weinstein (26) conceived a generalised micro mixing model, which is based upon Zwietering's model for segregated flow, and obtained from it by rearrangement. Two further conditions were added:-

1. The fluid is in a segregated state when it enters the reactor, since all molecules have an age zero at this stage.
2. The fluid is in a state of maximum mixedness when it leaves the reactor, since all molecules have a life expectation of zero.

The rearrangement of Zwietering's model is done as follows. Each portion of the flow which exits through

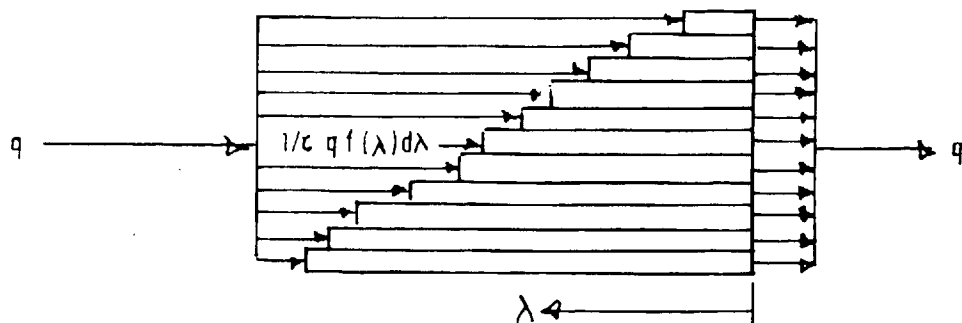


FIGURE 2-1  
SEGREGATED FLOW MODEL

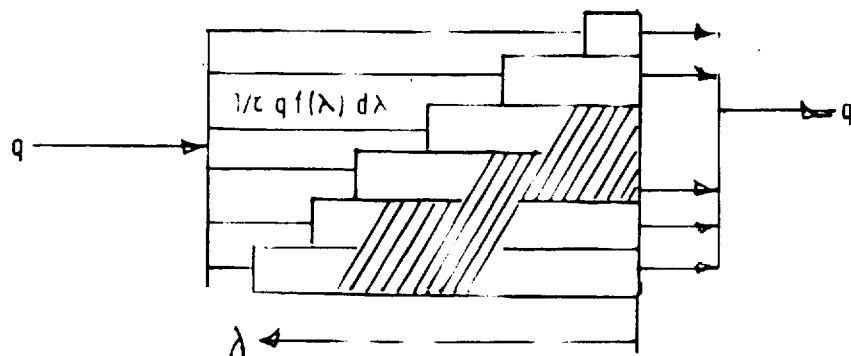


FIGURE 2-2  
PARTIAL MICRO-MIXING MODEL

a side tube is in fact placed in a separate reactor.

All these reactors are then placed next to each other on a life expectation scale, as represented in Figure 2.1.

The chemical conversion from this arrangement is given by

$$Y_t = \frac{1}{\tau} \int_0^{\infty} Y(\lambda) f(\lambda) d\lambda \quad - (2.7a)$$

where  $Y$  is the dimensionless concentration of the desired product. This is exactly the same as obtained from Zwietering's segregated flow model. The model for maximum mixedness is obtained by removing the horizontal lines between the separate reactors, and allowing transverse mixing of all molecules with the same life expectation, but no longitudinal mixing.

Any intermediate degree of mixing is readily represented by allowing for transverse mixing between some of the reactors, for values of  $\lambda$  greater than zero, as represented in Figure 2.2. This mixing may either continue between the reactors until the exit at  $\lambda = \infty$ , or some of the reactors may be closed off from the main area after mixing over a limited region of  $\lambda$ .

Another method of depicting this general model is shown in Figure 2.3.

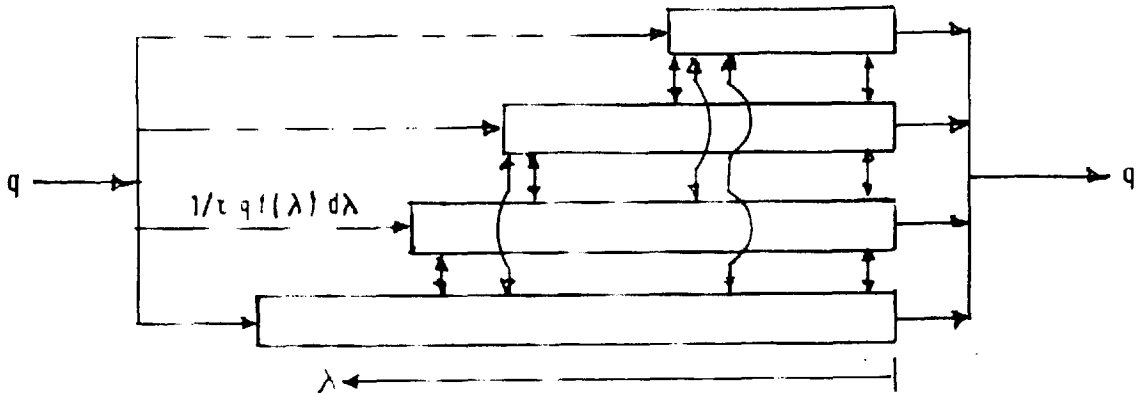


FIGURE 2 3  
ALTERNATE PARTIAL MICRO-MIXING MODEL

The two-headed arrows indicate mixing between two reactors which produces the following conditions:-

1. The concentration in both reactors becomes the same at the axial position of the arrow, the flow rates remaining unchanged.
2. The mixing may occur through any reactor wall, but may never affect a feed stream before it enters the reactor.

This model is a general representation of the micro mixing phenomenon, and there is no state of micro-mixing which cannot be represented by it. Unfortunately there is no single parameter that

characterises the resulting mixing, There are a large number of parameters associated with each separate reactor, and there are in fact an infinity of parameters for the whole model. Weinstein (26) made no attempt to derive the equations associated with this general model, but proceeded to define two parameters from each of which an approximate model of the mixing is obtained. These are

- I. An age which separates the reactor into two parts. One part contains molecules younger than this age in a segregated condition. The other part contains molecules older than this age in a state of maximum mixedness. This leads to the Consecutive Reactor model.
2. An age which separates the entering fluid into two parts. One part has a residence time greater than this age and is always in a maximum mixedness condition. The other has a residence time less than this age and is always in a segregated condition. This leads to the Parallel Reactor model.

## 2.5. The Consecutive Reactor Model

In this model, all the flow entering the reactor remains segregated up to a dimensionless age  $\theta^*$ , and then mixes except for those molecules which have a dimensionless residence time less than  $\theta^*$ , and go

directly from the segregated state to the exit.

The segregated section of the flow may be illustrated by means of Zwietering's segregated flow reactor.

(Section 2.3.), with the important difference that the reactor is of finite length equal to  $y^*$ , the dimensionless age before mixing.

The fluid that leaves this segregated reactor having  $\lambda > 0$ , must now be distributed in such a manner that all fluid with  $\lambda = 0$  leaves together. This is achieved with Zwietering's maximum mixedness reactor (Section 2.3.), with the following alterations:-

1. The side tubes bring in fluid of concentration  $Y(y^*)$  instead of the fresh reactants.

2. The scale of  $\lambda$  is rearranged such that the fluid leaves the reactor at  $\lambda = y^* \tau$ .

This is due to the fact that the fluid has already spent a time  $y^* \tau$  in the segregated flow reactor.

The resulting model is depicted in Figure 2.4.

Weinstein (26) showed that

$$Y_{\text{FINAL}} = \int_0^{y^*} Y(y) f(y) dy + Y_m(y^*) \int_{y^*}^{\infty} H(y) dy \quad (2.7)$$

where  $Y_m(y^*)$  is obtained by integrating the maximum mixedness equation from

$y=4$  to  $y=y^*$ .

This model concurs with the intuitive reasoning that fluid which passes through the reactor rapidly i.e. has relatively a very small residence time, will be mixed very little, while that having a large residence time will be well mixed.

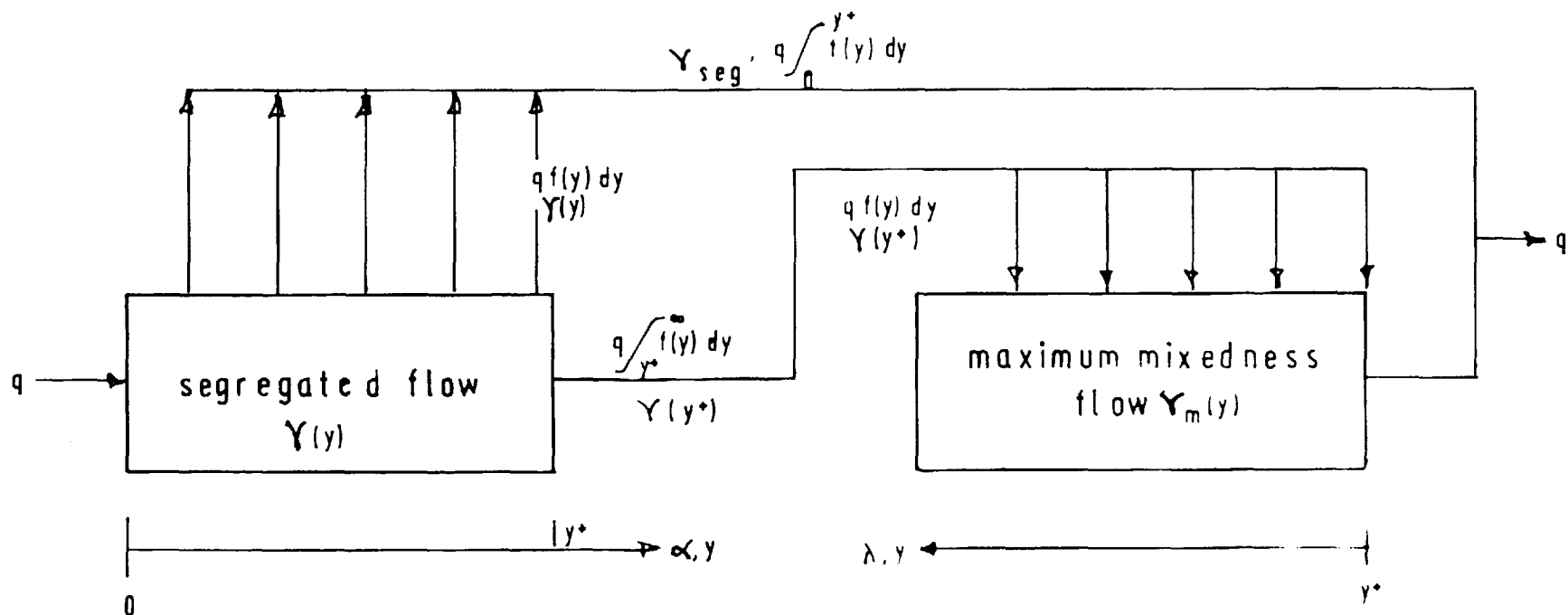


FIGURE 2.4  
CONSECUTIVE REACTOR MODEL

A comparison between this model and the Rippin-Ng model (Section 2.8) will be made in Chapter 3.2.

## 2.6. The Parallel Reactor Model

In this model, (see figure 2.5.) the entering fluid is divided into two sections. The first section consisting of molecules with a residence time less than  $y^* \tau$  is led into segregated flow reactor,

while the second section consisting of the remainder of the flow is led into a maximum mixedness reactor.

The volume of fluid entering into the segregated flow reactor per unit time is  $q \int_0^{y^*} f(y) dy$ , and emerges with the average concentration

$$Y_{seg} = \int_0^{y^*} Y(y) f(y) dy \quad - (2.8)$$

The volume of fluid flowing into the maximum mixedness reactor is

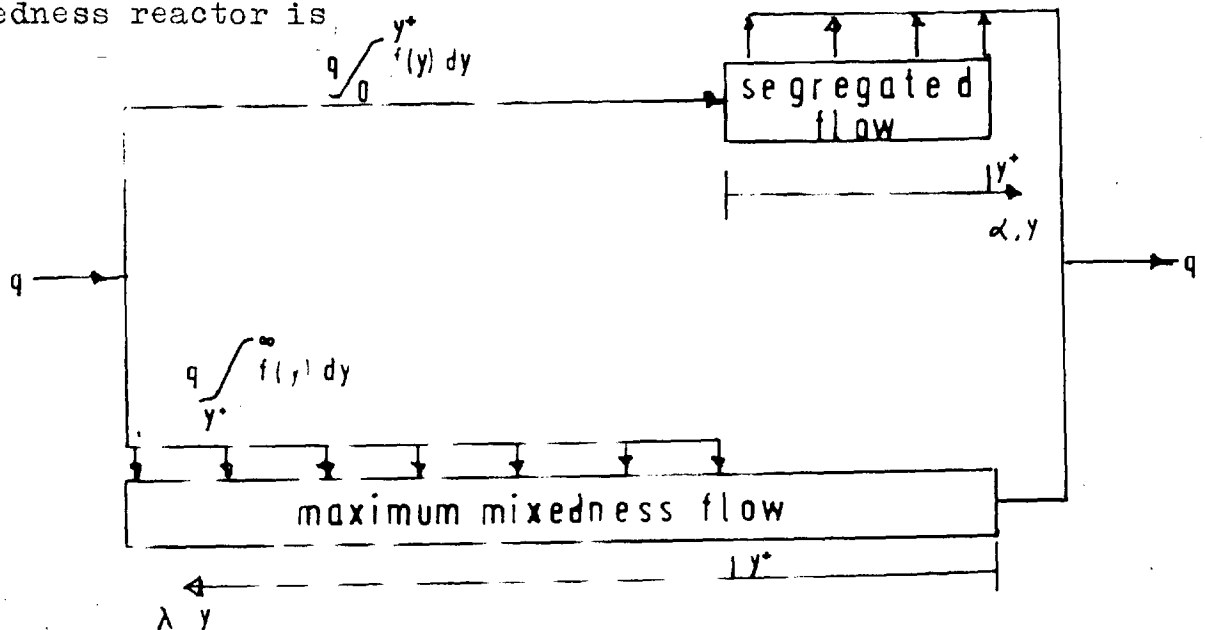


FIGURE 2-5  
PARALLEL REACTOR MODEL

$q \int_{y_x}^{\infty} f(y) dy$  per unit time and emerges with a concentration  $Y_m(0)$  because it spends the whole of its residence time in this reactor. The final concentration is given by

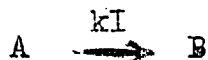
$$Y_{final} = \int_0^{y_x} Y(y) f(y) dy + Y_m(0) \int_{y_x}^{\infty} f(y) dy \quad - (2.9)$$

Weinstein (26) states that the Consecutive Reactor model represents the actual conditions of micro-mixing better, because in it all of the entering fluid remains segregated for at least a very brief interval of time. A more detailed comparison is drawn between these two models in Chapter 3.2.

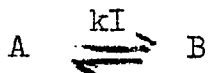
## 2.7. Weinstein's Results.

Weinstein (26) studied the effect of the RTD and micro mixing on the following types of reaction:-

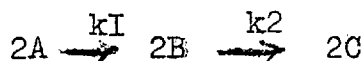
- 1) Isothermal Irreversible Reaction



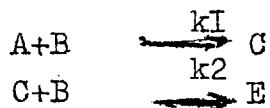
- 2) Isothermal Reversible Reaction



- 3) Isothermal Consecutive Reaction



- 4) Isothermal Consecutive Parallel Reaction



- 5) Adiabatic Irreversible Reaction

He showed that the impulse RTD is the most favourable for both Isothermal Irreversible and reversible reactions independently of the micro mixing, and that a narrowing of the RTD will favour conversion. This also applies for most cases for Consecutive and Consecutive Parallel reactions, but the situation becomes more complex with Adiabatic reactions. For Adiabatic reactions, the micro mixing can have the same order of magnitude effect as the RTD under certain circumstances. Programs were devised to integrate the mixing equations for all five types of reaction with 1, 2 and 5 CSTRs RTD, for both the Consecutive and Parallel Reactor models. The following general conclusions were arrived at:-

1. For complex reactions where side reactions destroy the product at an appreciable rate, early micro mixing is detrimental to reactor performance.
2. Late micro mixing may prove beneficial to reactor performance with complex reactions.

## 2.8. Rippin - Ng Model

Rippin and Ng (16) defined two environments experienced by a molecule during its life span in the reactor. The first is the entering environment, in which complete segregation occurs, and the molecule is always in the neighbourhood of molecules with which it entered the system i.e. other molecules having the same age. The second is the leaving environment, in which

a molecule is in the neighbourhood of other molecules with the same life expectation  $\lambda$  , and in this environment all molecules are in the state of maximum mixedness.

Zwietering's two models (Section 2.3) each correspond to the case where a molecule spends the whole of its life span in one of these two environments, and hence always experiences either complete segregation or maximum mixedness during the whole of its residence time in the system.

Ripplin and Ng (16) showed that intermediate stages of mixing could be attained by having the molecule spend a part of its time in each of the two environments. The molecule enters the system in the entering environment, and is then transferred at an earlier or later stage into the leaving environment. However, molecules of life expectation  $\lambda = 0$  in the entering environment will go directly to the exit without passing through the leaving environment. The earlier the transfer occurs, the greater the micro mixing in the system.

The feasibility of this model may be illustrated by considering a CSTR with a well mixed region around the impeller. Material entering the reactor may remain in the entering environment for a period, but as time progresses, some or all of this material will be drawn into

the impeller region, which forms the region from which it will eventually leave the reactor.

A number of models suggest themselves for the division of the residence time between these two environments e.g.

- A) Every 'point' spends the same fraction of its residence time between the two environments.
- B) The rate of transfer of material from the entering to the leaving environment is proportional to the amount of material remaining in the entering environment.
- C) The rate of transfer of material from the entering to the leaving environment is proportional to the concentration difference between the two environments.

Model (B) corresponds to a quasi-turbulent mixing process, in which all material still in the entering environment has an equal chance of being drawn into the leaving environment.

Model (C) corresponds to the situation where diffusional transfer of material predominates over the random mixing of Model (B). This could be regarded as a quasi-laminar mixing process, and would be suitable for the case of spontaneous mixing. Mixing of low

viscosity liquids is generally performed in the turbulent region of fluid mixing for which Model (B) appears to be the most suitable model.

### 2.8.1 Model B

The age distribution of the molecules in the outlet stream from the reactor is fixed by the RTD. Of the molecules which reach the outlet at the same instant, some will have spent the whole of their residence time in the entering environment, while others will have been transferred at an earlier or later stage to the leaving environment, and only at the outlet from the reactor, will these molecules be mixed with those which have spent the whole of their life time in the entering environment. The constant of proportionality for transfer between the two environments is the Rippin - Ng mixing parameter  $R$ . This mixing parameter has been assumed independent of the concentration of reagents and reaction rate constant, and should be constant for fixed hydrodynamic conditions in a given system i.e. constant flow rates and stirring speed. The knowledge of the value of  $R$  will make it possible to evaluate the conversion exactly for a system of known RTD and kinetics. The Rippin - Ng model is depicted in Figure 2.6.

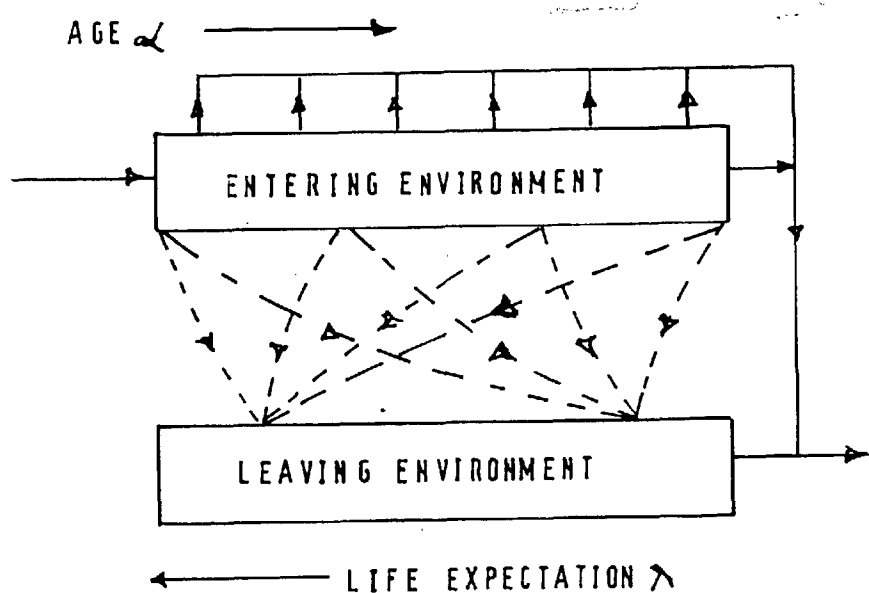


FIGURE 2-6

### RIPPIN-NG MIXING MODEL

#### 2.8.2 General Equations for the Rippin-Ng Model

Let  $m =$  the amount of a particular material  
in the reaction time  $t$

$$\frac{-dm}{dt} = Rm$$

$$m = m_0 \exp(-Rt) \quad - (2.10)$$

where  $m_0 =$  value of  $m$  at  $t = 0$

Zwietering (30) has shown that if  $f(\alpha)d\alpha$  is the volume fraction of material in the outlet stream having an age between  $\alpha$  and  $\alpha + d\alpha$ , then

$$g(\alpha, \lambda) d\alpha d\lambda = \frac{1}{\tau} f(\alpha + \lambda) d\alpha d\lambda \quad - (2.11)$$

is the volume fraction of material in the reactor having an age between  $\alpha$  and  $\alpha + d\alpha$ , and life expectation between  $\lambda$  and  $\lambda + d\lambda$ .

The fraction of material of age  $\alpha$  remaining in the entering environment is  $\exp(-R\alpha)$  from equation (2.10). Thus the fraction in the leaving environment is  $[1 - \exp(-R\alpha)]$ . In order to determine the concentration (a) in the outlet stream, the following quantities are required:-

(a) Total volume of material with life expectation  $\lambda$  to  $\lambda + d\lambda$

$$= V d\lambda \int_0^{\infty} g(\alpha, \lambda) d\alpha = \frac{V d\lambda}{\tau} \int_0^{\infty} f(\alpha + \lambda) d\alpha$$

$$= \text{I} \cdot V d\lambda \quad - (2.12)$$

where  $V$  is the total volume of the reactor contents.

(b) Volume of material in the leaving environment with life expectation  $\lambda$  to  $\lambda + d\lambda$

$$= V \frac{d\lambda}{\tau} \int_0^{\infty} [1 - \exp(-R\alpha)] f(\alpha + \lambda) d\alpha$$

$$= \text{II} \cdot V d\lambda \quad - (2.13)$$

(c) Rate at which material of life expectation  $\lambda$  to  $\lambda + d\lambda$  is transferred from the entering to the leaving environment =  $R$  (Volume of material of life expectation  $\lambda$  to  $\lambda + d\lambda$  in the entering environment)

$$= \frac{V R d\lambda}{\tau} \int_0^{\infty} \exp(-R\alpha) f(\alpha + \lambda) d\alpha$$

$$= \text{III} \cdot R V d\lambda \quad - (2.14)$$

(d) The rate at which reactant of life expectation  $\lambda$  to  $\lambda + d\lambda$  is transferred from the entering to the leaving environment

$$\begin{aligned}
 &= V \frac{R}{\tau} \frac{d\lambda}{d\lambda} \int_0^{\infty} \frac{26}{a(\alpha)} \exp(-R\lambda) f(\lambda + \lambda) d\lambda \\
 &= \frac{IV}{IV} a_0 V R d\lambda \quad \quad \quad -(2.15)
 \end{aligned}$$

The mean concentration at the outlet is that obtained by mixing together, as specified by the RTD, the material in the leaving environment of zero life expectation, and the material still in the entering environment with zero life expectation.

The concentration in the leaving environment is determined as a function of the life expectation by solving the material balance equation:-

$$\begin{aligned}
 \text{rate of change of} & \quad \quad \quad = \text{rate of supply from} \\
 \text{quantity of reactant} & \quad \quad \quad \text{entering environment} \\
 \text{in the leaving environment} & \quad - \text{rate of disappearance} \\
 & \quad \quad \quad \text{by reaction.} \\
 & \quad \quad \quad -(2.16)
 \end{aligned}$$

If  $a_L$  is the concentration in the leaving environment and  $f(a_L)$  the rate of batch disappearance of A per unit volume, since  $\lambda$  increases in the opposite direction to real time, we have

$$\begin{aligned}
 - \frac{d[II a_L]}{d\lambda} &= a_0 R IV - II f(a_L) \\
 \text{or } \frac{da_L}{d\lambda} &= f(a_L) + \frac{R[III a_L - IV a_0]}{II} \quad \quad \quad (2.17)
 \end{aligned}$$

where II, III and IV are as defined by equations (2.12 to 2.15)

When  $R = \infty$ , this equation is reduced to that for Zwietering's maximum mixedness case (Section 2.3), where the leaving environment comprises the whole reactor. The boundary condition for equation (2.17) is the same as that used by Zwietering i.e.  $da_L/d\lambda = 0$  at  $\lambda = \infty$  (c.f. equation 2.6).

The concentration at the exit from the reactor may be evaluated from

$$a_{exit} = \tau [\text{II} a_L + \text{IV} a_0]_{\lambda=0} \quad (2.18)$$

It may be observed by examining the forms of II and IV that at the extreme values  $R = 0$  and  $R = \infty$ , the expression for  $a_{exit}$  corresponds to that for a completely segregated and maximum mixedness reactor respectively.

### 2.8.3 Simple Second Order Irreversible Reaction

Ng (12) investigated the specific case of a second order irreversible reaction with any arbitrary RTD and premixed feeds. Computer programs were developed to find the exit concentration for a given value of  $R\tau$ , and also to find the value of  $R\tau$  corresponding to a given experimental conversion.

An experimental investigation using the hydrolysis of ethyl acetate by Na OH in dilute aqueous solution was carried out, and some values of  $R\tau$  obtained.

This experimental work is discussed in greater detail in Chapter 6.

## 2.9. Other Studies

### 2.9.1 Mixing and Segregation

Worrel (27) studied mixing and segregation in a CSTR using the second order reaction between sodium thiosulphate and hydrogen peroxide. Conversions at various stirrer speeds were measured. At low speeds of stirring substantial segregation was reported. In some comparisons of the experimental conversion with the two limiting conversions, the values of the limiting conversions were obtained using the experimentally measured RTD. The conversion data was also correlated against horse power input, terminal mixing time and recycle ratio.

La Rosa and Manning (14) measured segregation in a CSTR using second order hydrolysis reactions. The reaction conversion was measured at various stirrer speeds, and the increase in conversion at low stirrer speeds attributed to segregation. However, since the experimental RTD was not used in the calculations, the conclusions drawn were incorrect. These results were partially corrected (17), and the recalculated results indicate little segregation under these experimental conditions.

Wu (28) used the hydrolysis of ethyl formate in his study of mixing in a CSTR, and restricted the work to runs with a stirrer speed greater than 100 rpm. The data obtained was compared with a special circulation model as well as six other models. Most of the results agree with the corresponding maximum mixedness conversions.

Gillespie and Carberry (2,36) have put forward a recycle reactor in which part of the effluent from a plug flow reactor is returned to be mixed with fresh feed before re-entering the reactor. It has been shown that at the extremes of zero and infinitely large recycle, this reactor becomes a plug flow reactor and a CSTR respectively. For many cases the calculation of the conversion or yield for the recycle reactor is relatively straightforward in comparison with the calculations required for the plug flow reactor with axial dispersion or the tanks in series model. Rippin (15) has shown that the recycle reactor is always a maximum mixedness reactor, and hence unsuitable for the study of incomplete micro mixing.

### 2.9.2 Standard Reactor

Work in the field of mixing has been performed on a large number of combinations of tank geometry, impeller type, size and location within the tank, making comparison between the data of various workers difficult. In practice, no arrangement is equally suitable for all applications. In order to facilitate

the comparison of data obtained in the future, Voncken et al (25) have suggested a 'Standard Reactor' with the following characteristics:-

1. The tank is a flat bottomed cylinder.
2. The impeller shaft is coincidental with the tank axis.
3. The liquid depth is equal to the tank diameter.
4. Equal amounts of the fluid are found above and below the impeller.
5. The tank is fully baffled i.e. there are four vertical baffles each having a width 0.1 times the tank diameter D.
6. The impeller is a six bladed disc turbine of turbine diameter : blade length: blade height in the ratio 20:5:4; the turbine diameter is  $D/3$ .

This is a suitable type of vessel to study incomplete mixing, as such reactors are widely used in practice. However, for many applications a more suitable position for the impeller would be  $D/3$  from the bottom of the tank. It would appear that Voncken partly chose this position of the impeller to simplify the flow pattern for his mixing model (23).

### 2.9.3 Dispersion and Circulation Time

As a part of an investigation into the nature of imperfect mixing, a study was made of convective flow in turbine-stirred baffled vessels, by measuring the response to a pulse of an ionic tracer. The pulse was injected into the impeller zone and the response measured by a conductivity cell placed near the impeller. The circulation time was obtained from these response curves. A dimensionless group containing the circulation time, the impeller speed and the ratio of the impeller diameter to the tank diameter was found to correlate well over a large range of variables with the impeller Reynolds number. For predicting chemical conversion in imperfectly mixed CSTRs, Voncken, Holmes and Dekker (25) found that besides the circulation time the dispersion occurring during the circulation is also of importance.

Voncken, Holmes and Hartoog (24) devised a two parameter model to predict the chemical conversion in imperfectly mixed systems. The two parameters in question are the circulation time and the Bodenstein number, which is a dimensionless group characterising the dispersion. This model is restricted in its applications to premixed feeds only.

Voncken, Rotte and ten Houten performed batch and continuous flow experiments, (23) using a 'Standard Reactor'

(see Section 2.9.2), and found that the circulation time of the recirculation flow, the exchange between the upper and lower compartments, the momentum of the incoming feed stream, and the location of the feed inlet are the main factors influencing the pulse response curves.

## THEORETICAL SECTION

### CHAPTER 3

#### THEORY

##### 3.1 Introduction.

Weinstein (26) developed the Consecutive Reactor and Parallel Reactor models for mixing in a CSTR, and Ng (18) developed the Rippin-Ng random mixing model. Various other models have also been suggested (2,23,28, 33), but the abovementioned appear to be the most appropriate to characterise mixing in a single CSTR, and hence will be considered in greater detail.

##### 3.2 Choice of Model

A comparison of the two models put forward by Weinstein (26) would result in a more favourable verdict for the Consecutive Reactor model. The Parallel Reactor model suffers from the disability that in it some of the fluid (i.e. the fraction flowing through the maximum mixedness section) is mixed instantaneously on entering the reactor. It is intuitively felt that all of the fluid should remain in the segregated state for at least a very short period.

The Consecutive Reactor model while fulfilling this condition has the disadvantage that molecules of age greater than  $y^* \tau$  change from the segregated to the

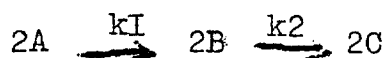
maximum mixedness state in a very abrupt fashion, and no molecule of an age greater than  $y^* \tau$  can be found to be present in the segregated state. Also, not a single molecule of age less than  $y^* \tau$  can be mixed with other molecules within the system, except at the outlet from the reactor.

The Rippin-Ng model is a more sophisticated version of the Consecutive Reactor model, and assumes a random transfer of molecules from the entering to the leaving environment i.e. the number of molecules of a certain species transferred from the entering to the leaving environment is proportional to the number of molecules of that species present in the entering environment. The constant of proportionality  $R$  determines the actual number that do get transferred. This method of transfer between the entering environment (completely segregated) and leaving environment (maximum mixedness state) appears more likely than the wholesale mixing of segregated molecules which occurs in the Consecutive Reactor model, once these have been in the system for a time exceeding  $y^* \tau$ .

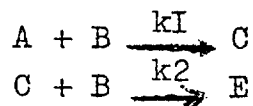
The advantage of the Consecutive Reactor model in its present form lies in its relative simplicity. Should the difference between the two models be small in practice, a case could be made for the Consecutive Reactor model. However, though the Consecutive Reactor model has

already been developed by Weinstein (26) to cover some complicated reaction kinetics, it has yet to be developed in a form whereby it can handle any given arbitrary RTD data in numerical form. Ng (18) has developed the Rippin-  
Ng model to handle any arbitrary numerical RTD for the case of a simple second order reaction. In order to facilitate the comparison between these models, and also to extend the usefulness of the Rippin-  
Ng model, it was decided to extend it to cover the following types of reaction kinetics:-

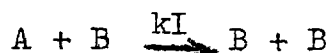
I. Consecutive Reactions



2. Consecutive Parallel Reactions



3. Autocatalytic Reactions



### 3.3 Unpremixed Feeds

Whereas studies of incomplete mixing with chemical reaction in a CSTR, when the feed streams are premixed before entry to the reactor, have been made before, so far no attempt has been made to study incomplete mixing with chemical reaction without this premixing of the feed streams. Ng (18) studied the case of a second order reaction with premixed feeds, and in his experimental work a premixer preceded the entry of the streams into the main reactor. The theoretical studies of Weinstein (26) assumed the

perfect premixing of feeds, but failed to state this assumption explicitly.

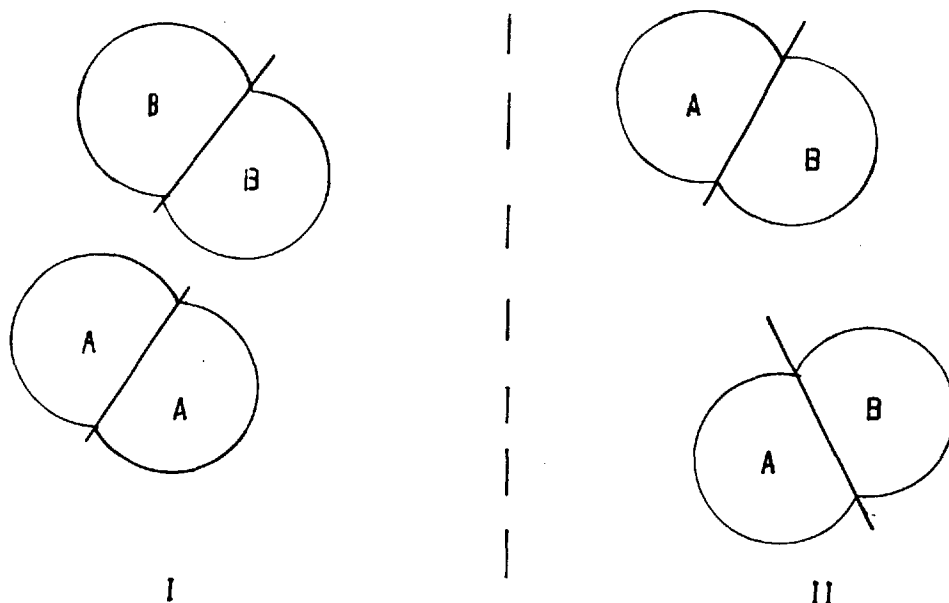


FIGURE 3.1  
UNPREMIXED AND PREMIXED POINTS

In the case of premixed feeds, Figure 3.I -II , the segregated 'point' consists of molecules of both A and B, well mixed in the proportions of the feed concentrations, while with unpremixed feeds Figure 3.I -I the segregated 'point' will consist of either molecules of A or molecules of B, but not of both. When we have a reaction between two molecules of different species, Danckwert's (4) has shown that for a simple reaction of order greater than one, segregation results in greater

conversion than perfect mixing, provided the feeds are premixed. However, with unpremixed feeds and complete segregation, zero conversion will result.

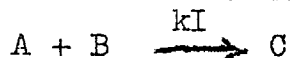
With a simple second order reaction between two molecules of the same species e.g.



unpremixed feeds will still result in greater conversion than the corresponding conversion with premixed feeds, provided the feed streams are of different concentration. When the feed streams are of the same concentration, no difference in conversion will result.

In a cascade of reactors (with no premixer) in which all the fresh reactant enters the first reactor, the first reactor may be treated as having unpremixed feeds, while all subsequent reactors have premixed feeds. Should fresh reactant be introduced at any later stage, a part of the feed will be premixed i.e. that flowing from the previous reactor, and the remainder unpremixed, producing a more complicated situation.

The effect of unpremixed feeds on the measurement of segregation is discussed in Chapter 7.I.

3.4 to 3.7Derivation of Isothermal MixingEquations for the Rippin-Ng Model.3.4. Second Order Irreversible Unpremixed Reaction

In order to determine the average concentration in the outlet stream from the CSTR, the following quantities are required

(a) the total volume of material with life expectation between  $\lambda$  and  $\lambda + d\lambda$

$$= \frac{1}{\tau} V d\lambda \int_0^{\infty} f(\alpha + \lambda) d\alpha$$

$$= I \cdot V d\lambda \quad (3.1)$$

(b) the volume of material in the leaving environment with life expectation between  $\lambda$  and  $\lambda + d\lambda$

$$= \frac{1}{\tau} V d\lambda \int_0^{\infty} [1 - \exp(-R\alpha)] f(\alpha + \lambda) d\alpha$$

$$= II \cdot V d\lambda \quad (3.2)$$

(c) the rate at which material of life expectation  $\lambda$  to  $\lambda + d\lambda$  is transferred from the entering to the leaving environment

$$= R \left[ \frac{1}{\tau} V d\lambda \int_0^{\infty} \exp(-R\alpha) f(\alpha + \lambda) d\alpha \right]$$

$$= R V III d\lambda \quad (3.3.)$$

(d) the rate at which reactant of life expectation  $\lambda$  to  $\lambda + d\lambda$  is transferred from the entering to the leaving environment

$$= V R a_0 III d\lambda \quad (3.4)$$

This is due to the fact that with unpremixed feeds,

no reaction can occur in the entering environment (Section 3.3). The quantity of reactant of life expectation  $\lambda$  to  $\lambda + d\lambda$  in the entering environment is given by

$$III \text{ ao } V d\lambda \quad (3.5)$$

The concentration of reactant in the leaving environment ( $a_1$ ) is determined as a function of the life expectation by solving the material balance equation:

$$\frac{dAL}{dz} = KI AL [Bo - I + AL] - \frac{R_{III}}{II} [I - AL]$$

where  $AL = a_1/a_0$        $Bo = b_0/a_0$       and  $Z = \lambda/\tau$       (3.6)

The boundary condition for equation (3.6) is  $dAL/dz = 0$  at  $z = \infty$ . For numerical integration it has been shown by Zwietering (30) that the mixing equation is relatively insensitive to the starting value of  $AL$ , and that a starting value of  $Z = 4$  is sufficient to perform this numerical integration.

The outlet concentration is obtained by mixing the stream from the leaving environment with the stream going directly from the entering environment to the exit (i.e. molecules having zero life expectation ( $\lambda$ ) but still in the entering environment), in proportions compatible with the RTD, and is given by

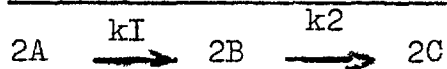
$$A_{EXIT} = \left[ \frac{II AL + III}{\tau} \right]_{z=0} \quad (3.7)$$

It may be pointed out that the second term of the numerator of (3.7) takes this form due to the fact that no reaction occurs in the entering environment. In the general case  $Bo \neq I$ , and  $B_{EXIT}$  is given by

$$B_{EXIT} = \left[ \frac{II.BL + III Bo}{I} \right]_{z=0} \quad (3.8)$$

It is not possible to integrate these and the other mixing equations analytically, and the numerical integration of all the mixing equations will be discussed in Chapter 4, except equation (3.6) which is used in the unpremixed feeds experimental work, and is discussed in Chapter 7.

### 3.5. Consecutive Premixed Reaction



where B is the desired product.

Assuming that the initial concentrations are known, the knowledge of any two concentrations will permit the third to be obtained by a simple mass balance. This system has been tackled for the case of premixed feeds only. Since it involves a second order reaction between two molecules of the same species, the difference in conversion between premixed and unpremixed feeds is much smaller, than would be the case for a system involving two reacting molecules of different species. In this case, reaction will still occur in the entering environment with unpremixed feeds. (see Section 3.3)

The batch kinetics may be represented as

$$\begin{aligned} \frac{da}{dt} &= k_1 a^2 \\ \frac{db}{dt} &= k_1 a^2 - k_2 b^2 \end{aligned} \quad (3.9)$$

$$\text{from which } A = \frac{\frac{4I}{I+KI y}}{I}$$

$$\text{and } \frac{db}{dy} = \frac{KI}{(I+KI y)} - K_2 B^2 \quad (3.10)$$

where  $B = b/a_0$ ,  $y = t/\tau$

$$KI = k_1 a_0 \tau, \quad K_2 = k_2 a_0 \tau$$

$$\text{b.c. at } y = 0 \quad B = 0$$

The boundary condition assumes that  $B_0 = 0$  i.e. in all cases we start with pure A.

The mixing equations for the Rippin-Ng model take the form:

$$\begin{aligned} \frac{dAL}{dz} &= KI A_L^2 + \frac{R\tau}{II} (III AL - IV(A)) \\ \frac{dBL}{dz} &= -KI A_L^2 + K_2 B_L^2 + \frac{R\tau}{II} (III BL - IV(B)) \end{aligned} \quad (3.11)$$

where II and III are defined by equations (3.2 & 3.3)

$$\begin{aligned} IV(A) &= \int_0^\infty \frac{\exp(-R\tau y) f(y+z)}{1 + KI y} dy \\ IV(B) &= \int_0^\infty B(y) \exp(-R\tau y) f(y+z) dy \end{aligned} \quad (3.12)$$

where  $B(y)$  is that value of  $B$  obtained by the integration of equation (3.10) from  $y=0$  to  $y=y$ . For programming purposes, the following substitutions were made in equations (3.11)

$$R \overline{L} \text{ III/II} = (\overline{n} 5)$$

$$R \overline{L} \text{ IV(A)/II} = (\overline{n} 6)$$

$$R \overline{L} \text{ IV(B)/II} = (\overline{n} 7)$$

to give

$$\frac{dAL}{dz} = KI A_L^2 + (\overline{n} 5)AL - (\overline{n} 6)$$

$$\frac{dBL}{dz} = -KI A_L^2 + K2 BL^2 + (\overline{n} 5)BL - (\overline{n} 7) \quad (3.13)$$

The boundary conditions are obtained by putting  $dAL/dz=0$ ,  $dBL/dz=0$  at  $z=4$  Zwietering's boundary conditions , and solving the resulting simple simultaneous equations, and are given by

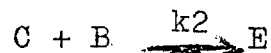
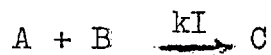
$$\begin{aligned} AL &= \left[ \frac{-(\overline{n} 5) + \sqrt{[(\overline{n} 5)^2 + 4 (\overline{n} 6) KI]}}{2KI} \right]_{Z=4} \\ BL &= \left[ \frac{-(\overline{n} 5) + \sqrt{[(\overline{n} 5)^2 + 4 (\overline{n} 7) K2]}}{2K2} \right]_{Z=4} \end{aligned} \quad (3.14)$$

The mixing equations (3.12) are now integrated simultaneously, using the boundary conditions (3.14), from  $z=4$  to  $z=0$ , whence the concentrations at the outlet from the leaving environment are obtained. The concentrations at the exit from the reactor are given by

$$\begin{aligned} A \text{ EXIT} &= \left[ \frac{II.A_L + IV (A)}{\mp} \right]_{Z=0} \\ B \text{ EXIT} &= \left[ \frac{II BL + IV (B)}{\mp} \right]_{Z=0} \end{aligned} \quad (3.15)$$

where B EXIT is the desired conversion.

### 3.6 Consecutive Parallel Reaction



where C is the desired product.

In the general case, assuming the initial concentrations are given, the knowledge of the concentrations of any two of the four substances will permit the other two concentrations to be obtained from a simple mass balance. It has been assumed that  $C_0$ ,  $E_0$  are both zero for all cases. The cases of premixed and unpremixed feeds will be treated separately, and these yield significantly different results.

#### 3.6.I Batch Kinetics

The kinetics for batch reaction are given by (10):

$$\frac{da}{dt} = -k_1 ab$$

$$\frac{db}{dt} = -k_1 ab - k_2 bc$$

$$\frac{dc}{dt} = k_1 ab - k_2 bc$$

$$a_0 = a + c + e$$

$$b_0 = b + c + 2e$$

$$b - 2a - c = b_0 - 2a_0 = -b_0 \quad (3.16)$$

Since we wish to tabulate the values for A only, and obtain the other batch concentrations by substitution (see Chapter 4.6), we will now proceed to obtain a

relationship between A and B, from which all concentrations may be obtained using an equation involving A and a time parameter only.

Substituting  $Lo = lo/ao$ ,  $\bar{K} = k2/kI$ ,  $B = b/ao$  and  $T = kI aot$  in equations (3.16)

$$\frac{dA}{dT} = -AB$$

$$\frac{dB}{dT} = AB (2\bar{K} - 1) - \bar{K} (B^2 + Lo B)$$

$$\frac{dB}{dA} = - \frac{(2\bar{K} - 1) + \bar{K} (Lo + B)}{A} \quad (3.17)$$

Substituting  $Lo + B = U$  we obtain

$$\frac{dU}{dA} - \frac{\bar{K} U}{A} = - (2\bar{K} - 1) \quad (3.18)$$

Using the integrating factor  $A^{-\bar{K}}$  to integrate equation (3.18) we obtain

$$B = - \frac{(2\bar{K} - 1)}{(1 - \bar{K})} A - Lo + CI A^{\bar{K}} \quad (3.19)$$

where CI the constant of integration =  $I/(1 - \bar{K})$

By substitutions in equation (3.16) the following relationship between A and  $y$  is obtained

$$\frac{dA}{dy} = KI \left[ \frac{(2\bar{K} - 1)}{(1 - \bar{K})} A^2 - \frac{(Bo - 2)A - \frac{A^{\bar{K}}}{1 - \bar{K}} + I}{1 - \bar{K}} \right]$$

where  $y = t/\tau$

$$\text{b.c. } A = I \text{ at } y = 0 \quad (3.20)$$

The other concentrations are obtained by substituting the value of A in equations (3.16 and 3.19).

### 3.6.2 Consecutive Parallel Premixed Reaction

The mixing equations for Consecutive Parallel premixed reaction take the form:

$$\frac{dAL}{dz} = KI AL BL + \frac{RT}{II} \{ III AL - IV(A) \}$$

$$\frac{dBL}{dz} = KI AL BL + K2 BL CL + \frac{RT}{II} \{ III BL - IV(B) \}$$

$$\frac{dCL}{dz} = - KI AL BL + K2 BL CL + \frac{RT}{II} \{ III CL - IV(C) \}$$

(3.21)

where II and III are as defined by equations (3.2 and 3.3)

$$\begin{aligned} IV(A) &= \int_0^{\infty} \exp(-RTy) A(y) f(y+z) dy \\ IV(B) &= \int_0^{\infty} \exp(-RTy) B(y) f(y+z) dy \\ IV(C) &= \int_0^{\infty} \exp(-RTy) C(y) f(y+z) dy \end{aligned}$$

(3.21 A)

where A(y) the batch dimensionless concentration of Y obtained from equation (3.20)

The following substitutions were made for programming purposes:

$$\begin{aligned} RT \overline{III} / \overline{II} &= (\pi 5) \\ RT \overline{IV}(A) / \overline{II} &= (\pi 6) \\ RT \overline{IV}(B) / \overline{II} &= (\pi 7) \\ RT \overline{IV}(C) / \overline{II} &= (\pi 8) \end{aligned}$$

to give

$$\begin{aligned}\frac{dAL}{dz} &= K_1 AL BL + (\pi_5) AL - (\pi_6) \\ \frac{dBL}{dz} &= K_1 AL BL + K_2 BL CL + \pi_5 BL - \pi_7 \\ \frac{dCL}{dz} &= -K_1 AL BL + K_2 BL CL + \pi_5 CL - \pi_8\end{aligned}\quad (3.22)$$

Applying Zwietering's boundary conditions and rearranging the resulting simultaneous equations, the following cubic in BL is obtained:

$$\begin{aligned}& BL^3 [-\pi_5 K_1 K_2] \\ & + BL^2 [ - (\pi_5)^2 (K_1 + K_2) + (\pi_7 - \pi_5) K_1 K_2 \\ & \quad - 2 \pi_6 K_1 K_2 ] \\ & + BL [ - (\pi_5)^3 + (\pi_7)(\pi_5)(K_1 + K_2) - (\pi_5) \pi_8 K_2 \\ & \quad - (\pi_5)(\pi_6) K_1 ] \\ & + (\pi_7)(\pi_5)^2 = 0\end{aligned}\quad (3.23)$$

where all terms are evaluated at  $z=4$ . Equation (3.23) may now be solved by the Newton iterative method, and the other two initial values obtained from

$$\begin{aligned}A_L &= \left[ \frac{\pi_6}{\pi_5 + K_1 BL} \right]_{z=4} \\ C_L &= \left[ \frac{\pi_7 + \pi_8 - \pi_5 BL}{\pi_5 + 2 K_2 BL} \right]_{z=4}\end{aligned}\quad (3.24)$$

The mixing equations (3.22) may now be integrated from  $z=4$  to  $z=0$ , to obtain the concentrations at the exit from the leaving environment.

The average concentrations at the outlet from the reactor are given by

$$\begin{aligned}
 A \text{ EXIT} &= \left[ \frac{II.AL + (\bar{V} 6)}{\bar{V}} \right]_{Z=0} \\
 B \text{ EXIT} &= \left[ \frac{II.BL + (\bar{V} 7)}{\bar{V}} \right]_{Z=0} \\
 C \text{ EXIT} &= \left[ \frac{II.CL + (\bar{V} 8)}{\bar{V}} \right]_{Z=0} \quad (3.25)
 \end{aligned}$$

where C EXIT is the desired conversion.

### 3.6.3 Consecutive Parallel Unpremixed Reaction

The mixing equations with unpremixed feeds take the form:

$$\begin{aligned}
 \frac{dAL}{dz} &= KI AL BL + \frac{R \text{ III } (AL-I)}{II} \\
 \frac{dBL}{dz} &= KI AL BL + K2 BL CL + \frac{R \text{ III } (BL-B_0)}{II} \\
 \frac{dCL}{dz} &= -KI AL BL + K2 BL CL + \frac{R \text{ III } CL}{II}
 \end{aligned}$$

where II and III are as defined by equations (3.2 and 3.3) (3.26)

It may be noted that since the entering environment is in a segregated state, no reaction occurs between A and B, and the concentration of C is zero in it. This accounts for the absence of C in the stream being transferred from the entering to the leaving environment.

Applying Zwietering's boundary conditions, the following cubic for the initial value of BL is obtained:

$$\begin{aligned}
 & BL^3 \left[ -(\pi I) KI K2 \right] \\
 & + BL^2 \left[ -(\pi I)^2 KI - (\pi I)^2 K2 + (\pi I) KI K2 Bo \right. \\
 & \quad \left. - 2 (\pi I) KI K2 \right] \\
 & + BL \left[ -(\pi I)^3 + (\pi I)^2 KI Bo + (\pi I)^2 K2 Bo \right. \\
 & \quad \left. - (\pi I)^2 KI \right] \\
 & + (\pi I)^3 Bo = 0
 \end{aligned}$$

$$\text{where } \pi I = R_{TIII}/II \quad (3.27)$$

and all terms are evaluated at  $z=4$ .

The other initial conditions are obtained from

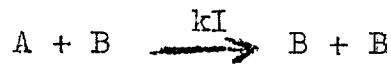
$$\begin{aligned}
 AL &= \left[ \frac{\pi I}{\pi I + KI BL} \right]_{Z=4} \\
 CL &= \left[ \frac{\pi I Bo - \pi I BL}{\pi I + 2K2 BL} \right]_{Z=4} \quad (3.28)
 \end{aligned}$$

After integrating equations (3.26) from  $z=4$  to  $z=0$ , the concentrations at the exit from the reactor may be obtained from

$$\begin{aligned}
 A \text{ EXIT} &= \left[ \frac{II AL + III}{\mp} \right]_{Z=0} \\
 B \text{ EXIT} &= \left[ \frac{II BL + III Bo}{\mp} \right]_{Z=0} \\
 C \text{ EXIT} &= \left[ \frac{II CL}{\mp} \right]_{Z=0} \quad (3.29)
 \end{aligned}$$

### 3.7 Autocatalytic Reaction

### 3.7.1 Batch Kinetics



The second order Autocatalytic reaction is of particular interest because it has yet to be studied under conditions of incomplete mixing. The batch kinetics may be represented as

$$\begin{aligned} \frac{da}{dt} &= -kI ab \\ &= -KIa (a_0 + b_0 - a) \end{aligned}$$

Substituting  $y = t/\tau$

$$\frac{da}{dy} = -KI A [I + B_0 - A]$$

$$\text{or } A(y) = \frac{I + B_0}{I + B_0 \exp [KI (I + B_0)]}$$

$$\text{i.e. rate constant } (r) = C_I A^2 - C_2 A \quad (3.30)$$

### 3.7.2 Mixing in a Batch Reactor

By differentiating the reaction rate vs A equation (3.30), the behaviour of the curve may be predicted

$$\frac{dr}{dA} = 2 C_I A - C_2$$

$$\frac{d^2 r}{dA^2} = 2 C_I \quad (3.31)$$

Since  $C_I$  is always positive, the second derivative of the reaction rate curve is always positive (equation 3.31), and hence the curve of  $r$  vs  $A$  will always be convex downwards. Ng (18) has shown graphically that by considering the total conversion from two lumps of fluid

of different concentrations reacting with and without mixing, that when the curve is convex downwards, greater conversion is always obtained by mixing the lumps.

The reverse applies when the curve is concave downwards, while the two conversions are identical for a straight line. Hence, for premixed and unpremixed Autocatalytic reaction, we have a reaction of order greater than one, in which the conversion for maximum mixedness always exceeds the complete segregation conversion.

### 3.7.3 Autocatalytic Premixed Reaction

The mixing equation takes the form:

$$\frac{dAL}{dz} = -K_I AL^2 + AL K_I (I + B_0) + R \tau \left[ \frac{III AL - IV}{II} \right]$$

II and III are defined by equations (3.2 and 3.3)

$$IV = \int_0^\infty \frac{(1+B_0) \exp[-R \tau y] (y+z) dy}{1 + B_0 \exp[K_I \tau (1+B_0) y]} \quad (3.32)$$

This may be integrated in the usual manner, and the concentration at the exit from the reactor obtained from A EXIT =  $\left[ \frac{II AL + IV}{I} \right]_{z=0}$  (3.33)

### 3.7.4 Autocatalytic Unpremixed Reaction

The mixing equation for the case of unpremixed feeds is

5I

$$\frac{dAL}{dz} = -KI A_L^2 + AL KI (I + B_0) + \frac{R \text{III} (AL-I)}{II}$$

II

(3.34)

where II and III are defined by equations (3.2 and 3.3)

The concentration at the exit from the reactor is given by

$$A_{EXIT} = \left[ \frac{II AL + III}{\pm} \right]_{Z=0} \quad (3.35)$$

---

## CHAPTER 4

### Computer Programs

Since an important section of this work consists of the development of the Rippin-Ng model to cover Autocatalytic, Consecutive Parallel and Consecutive reactions, and also the solution of the problems arising when the reactants enter the reactor through two separate feed nozzles i.e. the case of unpremixed feeds, we will now proceed to discuss the associated computer programs.

#### 4.1 Computer and Programming Language

The programs were developed to be run on the University of London 'Atlas' computer, and were written in the EXCHLF programming language, as developed by the University of London Computer Unit for this machine. All earlier programs in Mercury Autocode (18) were modified wherever necessary to be compatible with the new compiler, which is about three times as efficient as the Autocode Compiler. It was decided to continue to work with 5-hole tape, in spite of the greater technical advantages of 7 hole tape and the associated flexowriters, because it was deemed that the effort required to convert the original programs from 5-hole to 7-hole tape was too large. This may be looked upon as an error, but it may be pointed out that the computer was adapted to 7-hole tape after the commencement of the project. The possibility of converting

the programs for use with the IBM 7090 Computer employing Fortran 4 was also considered, but rejected on the following grounds:

1. The initial programs were written in Autocode (18, 20)
2. Due to the large size of the individual programs, it was felt that the greater speed of 'Atlas' would be a valuable asset.

It is hoped that the future developemnt of the compiler compiler will remove these drawbacks, and make it possible to transfer the programs from one compiler to another, using a new intermediate meta language.

This decision did have one major unforeseen effect on the programs developed. In the EXCHLF system, the integration of differential equations is performed by the instruction INTSTEP (N), which integrates the differential equations in label (N). It was later discovered that when it became necessary to evaluate the batch conversion numerically in the case of Consecutive and Consecutive Parallel premixed reactions, it was not possible to use the first INTSTEP (N), and then proceed to integrate the second set of differential equations, employing the instruction INTSTEP ( N<sup>f</sup> ), where ( N<sup>f</sup> ) contains the batch kinetics equations. The incomplete comprehension of this procedure caused many difficulties, and it was eventually discovered

that the INTSTEP (N) built-in sub-routine uses certain backing store facilities, which are also used by INTSTEP (N'), and hence overwritten in spite of the use of the PRESERVE instruction. Hence, an INTSTEP instruction cannot be executed within the loop of another INTSTEP instruction. The solution of this problem is discussed in Section 4.6.

## 4.2 Lay-out and Cross Checking Procedures

### 4.2.I General

The computer programs associated with the theoretical study may be grouped as

- a) Consecutive Parallel Reactions
- b) Consecutive Reactions
- c) Autocatalytic Reactions

There are eight programs associated with Consecutive Parallel reactions, four with Consecutive reactions and seven with Autocatalytic reactions, making a total of nineteen programs. A gist of the contents of the programs along with the identifying codes are given in Tables II. I to II.3. In general, the programs were developed for the specific cases of 1 and 2 CSTRs RTD, and two programs were developed to deal with any known arbitrary RTD (available in numerical form) for the two regions when  $\infty > R\tau \geq 2$  and  $2 > R\tau > 0$ . The reasons for this division of the  $R\tau$  range between two general RTD programs

are discussed in Section 4.3. The equations from which the general RTD programs have been devised were discussed in Chapter 3, while those relating to the specific cases for 1 and 2 CSTRs RTD are given in Appendix I.

#### 4.2.2 Choice of Programs

It was decided to develop programs which were capable of dealing with any general RTD, even though the results derived have been limited to the specific cases of 1, 2 and 5 CSTRs RTD, which could have been more easily obtained using specific programs. This is due to the fact, that though the RTD for many single CSTRs does not differ greatly from that of a well-stirred system

i.e.  $f(t) = \frac{1}{\tau} \exp(-t/\tau)$ , fallacious conclusions may easily be arrived at if the measured RTD is not employed in the calculations. Manning (I4) calculated the segregation in a system assuming a well-stirred RTD. Rippin and Ng (I7) showed that the results derived were inaccurate, and that very different results would have been obtained if the measured RTD had been employed in the calculations. Hence, general RTD programs were developed, and all results for 5 CSTRs RTD were obtained using these programs, even though marginally more accurate results could have been obtained using specific programs for 5 CSTRs RTD. These general RTD programs are suitable for any numerical RTD input, except that of a ICSTR RTD, and hence programs for the specific case of a ICSTR RTD were also developed (I8).

In order to cross check the general RTD programs, programs for the specific case of 2 CSTRs RTD were also developed, and the cross checking procedures will be discussed in Section 4.2.3. With these three types of programs, the results could be cross checked, and a comparison between the Rippin-Ng and Weinstein's Consecutive Reactor model be drawn.

#### 4.2.3 Cross Checking of Programs

A system of 2 CSTRs RTD has a frequency function  $f(t) = 4t/2 \exp(-2t)$  and that of 5 CSTRs RTD a  $f(t) = \frac{130.15}{\tau^6} \exp(-5t/\tau)$ . Since the general programs can only be fed with the RTD in numerical form, two small programs were devised by which the computer generated these functions accurate to seven significant figures, and punched out the values at the appropriate intervals, (so as to be compatible with Routine 'A' of Section 4.5), onto five hole tape. These programs ensured accuracy, and saved a great deal of tedious work.

The specific programs for 2 CSTRs RTD were obtained in working order, and the extreme values checked against the values obtained by Weinstein. The complete segregation conversion with a 2 CSTRs RTD was also obtained using a specific program to cover this case for each type of reaction kinetics, and cross checked with the conversion at very high  $Re$  obtained with the general RTD program. The general RTD programs were now fed with the RTD data for

2 CSTRs, and conversions evaluated at the same values of  $RT$  as for the 2 CSTRs RTD specific programs. The specific programs are much simpler than the corresponding programs for the general RTD, and hence it is easier to obtain them in functioning order. The programs for 1 CSTR RTD at very high  $RT$  were checked against the conversion for the corresponding perfectly mixed system, for which the equations occur in a simplified form, and may often be obtained by hand computation.

#### 4.3. Inaccuracy of the General RTD Programs at Low $RT$

It had been assumed that the method employed by Ng (18) to check the programs was a suitable one. Essentially this entails halving the step-length employed to integrate the mixing equations, and when this results in no change in the computed conversion to four places of decimals, it is assumed that the program is correct. This value was cross checked with the conversion obtained using the specific 2 CSTRs RTD program.

An important sub-routine is employed to evaluate I, II, III, IV. On examination, these take the form:

$$I. = \int_0^{\infty} f(y+z) dy$$

$$II. = \int_0^{\infty} [1 - \exp(-RTy)] f(y+z) dy$$

$$III. = \int_0^{\infty} \exp(-RTy) f(y+z) dy$$

$$IV. = \int_0^{\infty} \delta(y) \exp(-RTy) f(y+z) dy$$

I was evaluated using Gauss' Arbitrary Interval Formula (I), which may be expressed as

$$\int_a^b f(u) du = \frac{b-a}{2} \sum_{i=1}^n w_i f(u_i) + R_n$$

where  $U_i = \pm \frac{(b-a)}{2} y_i + \frac{b+a}{2}$

$R_n$  = remainder

$W_i$  = Gaussian weighting factor (4.1)

A sixteen point Gaussian Quadrature i.e. with  $n = 8$ , and a value of  $b = 20$ , were found to make the remainder negligible, and be more accurate than the use of Simpson's rule with many times the number of points.

II, III and IV were transformed into the form:

$$\int_0^{\infty} \exp(-x) f(x) dx \quad (4.2)$$

and then evaluated using the abscissas and weight factors for Laguerre integration, whereby

$$\int_0^{\infty} \exp(-x) f(x) dx = \sum_{i=1}^n w_i f(x_i) + R_n \quad (4.3)$$

Ng (18) employed a ten point formula, and he accepted the results as being accurate over the whole range of  $R\tau$ , to four significant figures. This is explained by assuming that he cross checked the general RTD conversions at high  $R\tau$  only. However, the Laguerre integration does not give suitable results at low  $R\tau$ . This is best explained by examining the integration of III. By the substitution

of  $u = R\tau y$  in equation (3.2IA), III is transformed into

$$III = \frac{1}{R\tau} \int_0^{\infty} \exp(-u) f(u/R\tau + z) du \quad (4.4)$$

The value for the abscissas in case when  $n = 10$  for the Laguerre integration are given in Table 4.I.

TABLE 4.I

| n  | $x_i$       |
|----|-------------|
| 1  | 0.1377 9347 |
| 2  | 0.72945454  |
| 3  | 1.80834290  |
| 4  | 3.40143369  |
| 5  | 5.5524961   |
| 6  | 8.33015274  |
| 7  | 11.84378583 |
| 8  | 16.27925783 |
| 9  | 21.99658580 |
| 10 | 29.92069701 |

When measuring the RTD of any real system, it is impractical to work for a time period greater than  $5-6\tau$ . Not only is this due to the fact that with  $\tau$  equal to thirty minutes this would make the measurement of RTD very drawn out, but also that after such a time period, the concentration of the output pulse would be very close to the base line, and extremely sensitive instruments would be required for the results to be at all meaningful.

Taking the case when  $R\tau = 1$ , and recalling that  $Z$  will assume values between 0 and 3.999, in the most favourable instance i.e. when  $z = 0$ , only a maximum of four points fall within the measured range of RTD. Our programs will automatically equate the RTD frequency function to zero for the other six points. In the integration of the mixing equations (e.g. equation 3.21), the term  $I_1 - I_2$  occurs in the denominator, and is of small value. Therefore, any errors in the value of  $I_2$  can cause significant errors in the conversion. The integration procedure is not very accurate when only four of the ten points contribute meaningfully in the most favourable case. When  $R\tau < 1$ , it may be seen that still fewer points will fall within the limits of the RTD, and eventually the number of points contributing may fall to one or even zero. The reverse occurs at high  $R\tau$ , and the Laguerre integration formulae are particularly suited to the calculation of conversion at high  $R\tau$ , provided the interpolation routines are accurate.

#### 4.4      Integration of the General RTD Mixing Equations           at Low $R\tau$

It was first attempted to improve the accuracy of the existing programs by increasing the number of points used for the Laguerre Quadrature, and programs were run with  $n = 12$  and  $n = 15$ . A slight improvement in the accuracy at high  $R\tau$  results, but little improvement

is found at low  $R\tau$  . When  $2 > R\tau > 0.5$  , a significant error in the computed conversion was noticed, but for  $R\tau < 0.5$  , the computer in fact rejects the program, usually due to a number overflow. By trial and error, it was eventually realised that the Laguerre Quadrature was unsuitable for  $R\tau < 2$ , and the programs were modified so that II, III and IV were evaluated using the Gaussian Quadrature. It may be pointed out that the Gaussian Quadrature is not normally suited to the integration of functions containing an exponential term, and therefore was not employed initially. In performing the Gaussian Quadrature at high  $R\tau$  , the computer will read the term  $\exp(-R\tau y)$  as zero, causing a large error or even rejecting the program. The programs of the type CP/PM/GEN are suitable when  $R\tau \geq 2$  and those of the type CP/PM/GLRT when  $2 > R\tau > 0$  . There is no essential difference between the two types, other than in the use of both Gaussian and Laguerre Quadratures in the former, and only Gaussian in the latter.

#### 4.5 RTD data - Normalisation and Interpolation

It was decided to use the procedure devised by Ng (I8) to normalise and interpolate the RTD data. For the sake of completeness, a brief outline is indicated here.

The RTD data obtained by measuring the output response to a pulse of ionic tracer at the input is normalised according to the equation

$$f(y) = \frac{\text{Chart deflection (y)}}{\int_0^{\infty} \text{chart deflection (y)} dy} \quad (4.5)$$

The denominator of equation (4.5) is the area under the curve of chart deflection vs y. Since the initial section of the curve is much more significant than the later section for the case of a single CSTR, the data points are taken at intervals of 0.025 in the range y=0 to y=0.30. Beyond Y=0.30, the interval is doubled to 0.05. In Section 4.3 it was decided that it is impractical to measure the RTD for a time period greater than 6 $\tau$ . This process of normalisation is performed in Chapter I of all the general RTD programs.

Since the Gaussian and Laguerre Quadratures use the values of  $f(y+z)$  at uneven intervals, it is necessary to know accurately the values of the RTD frequency function, at points other than those at which measurements have been made. This problem has been overcome by the use of the four point interpolation routine devised by Li (20), which is termed as Routine 'A', and is suited to deal with RTD data measured as indicated above. Except for very minor changes, so as to be compatible with the EXCHLF compiler, both Chapter I and Routine 'A' are in the form used by Ng (18).

#### 4.6 Interpolation of Batch Kinetics - Routine 'B'

One of the important unforeseen side effects

resulting from the choice of the ATLAS computer and associated EXCHLF compiler, is the necessity of tabulating the batch kinetics, and developing a routine to perform accurate interpolation between the tabulated values. This results from the inability of the compiler to execute one INTSTEP instruction within the loop of another INTSTEP instruction (Section 4.I).

For both simple second order reactions and Autocatalytic reactions, the batch kinetics may be obtained analytically. However, both with Consecutive and Consecutive Parallel reactions with premixed feeds, it is necessary to evaluate the batch kinetics numerically. It may be pointed out that in the case of Consecutive unpremixed reactions (a case which has not been tackled), it would also be necessary to evaluate the batch kinetics.

The batch kinetics were to be tabulated for the range  $y = 0$  to  $y = 6.00$ , so as to be in line with the RTD measurements. An examination of the actual values revealed a greater sensitivity at low values of  $y$ , and it was decided that the interval of tabulation should be 0.05 in the range  $y = 0$  to  $y = 1.0$ , while an interval of 0.2 would be adequate for values of  $y$  greater than 1.00. For  $y$  greater than 6.00, it was decided to use the batch concentration at  $y = 6.00$ .

Routine 'B' was developed to be a modified version

of Routine A' (the RTD interpolation routine). It is conceivable that for some values of the involved parameters this procedure could prove to be unsatisfactory, but over a broad range covering most of the important cases, it should prove adequate.

The kinetics for B are tabulated for Consecutive reactions, those for A being available analytically. For Consecutive Parallel reactions, the kinetics for A are tabulated, those for B and C being obtained by substitution in equations (3.16 and 3.19). On examination of equation (3.19), it may be seen that the terms  $\bar{K}-1$ ,  $2 \bar{K}-1$  occur in the denominator. Therefore, the substitution of the value of A in this equation cannot be made when  $\bar{K} = 1, 0.5$ , because of the resulting zero in the denominator. Should it be necessary to derive the results for these values of  $\bar{K}$ , either the equations for each of these parameters, which are special cases of equations (3.21), may be derived and integrated, or equations (3.21) may be integrated directly, and the values of any two of the three concentrations of A, B, C be tabulated and interpolated, the third being obtained from a simple mass balance. However, the latter procedure would considerably increase the backing store requirements, and is not recommended for general use.

One additional difficulty was encountered when only the 45 points in the range  $y = 0$  to  $y = 6.00$  were stored.

This may be described as an "end effect". Routine 'B' uses a four point interpolation formula. Hence, when working in the vicinity of  $y = 6.00$ , use may be made of some of the points beyond the forty fifth. If only the first forty five registers contain a number, the remainder have an effective value zero. The use of zero as one of the points for interpolation can cause an error when the concentration at  $y = 6.00$  is not zero. This end effect was eliminated by placing the concentration at  $y = 6.00$  in five storage registers beyond the previous last one containing the concentration at  $y = 6.00$ .

#### 4.7 General RTD Programs

The Block Diagrams for the following five general RTD programs are given in Figures 4.1 to 4.5:

- a) CP/PM/GEN
- b) CP/UP/GEN
- c) CON/GEN
- d) AC/PM/GEN
- e) AC/UP/GEN

These programs deal with the range  $2 > RE \geq 0$ . The Block Diagrams for the range  $2 > RE > 0$  would be very similar, the main differences between these two types of programs having been explained in Section 4.4. The flow paths for the above mentioned programs will now be discussed in greater detail.

4.7.1 CP/PM/GEN

The Block Diagram for program CP/PM/GEN which integrates the mixing equations (3.21) for Consecutive Parallel premixed reactions, for the case of any arbitrary numerical RTD is given in Figure 4.1. Chapter 0 starts with the input of data, which includes the initial concentrations of A and B,  $R, \tau, \bar{K}, KI$ , the appropriate Gaussian and Laguerre integers, the RTD data and the first guess for the Newton iterative solution of equation (3.23) i.e. the cubic equation from which the boundary conditions for the integration of the mixing equation are obtained. The flow now moves across to Chapter I, where the normalisation and tabulation of the RTD data occurs, (details in Section 4.5), and then returns to Chapter 0. The batch kinetics for A are now evaluated and tabulated, using equations (3.20).

Z is set at 3.999, and the sub routine for the evaluation of I, II, III, IV(A), IV(B), IV(C) executed using Routine 1 (Routine 'A') to interpolate the normalized RTD data, and Routine 2 (Routine 'B') to interpolate the batch kinetics. The boundary conditions for the simultaneous integration of the three mixing equations (3.21) are found by the iterative solution of equation (3.23) for  $B_L$ , and substituting this value in equations (3.24) to obtain  $A_L, C_L$ .

The Runge-Kutta integration of the mixing equations

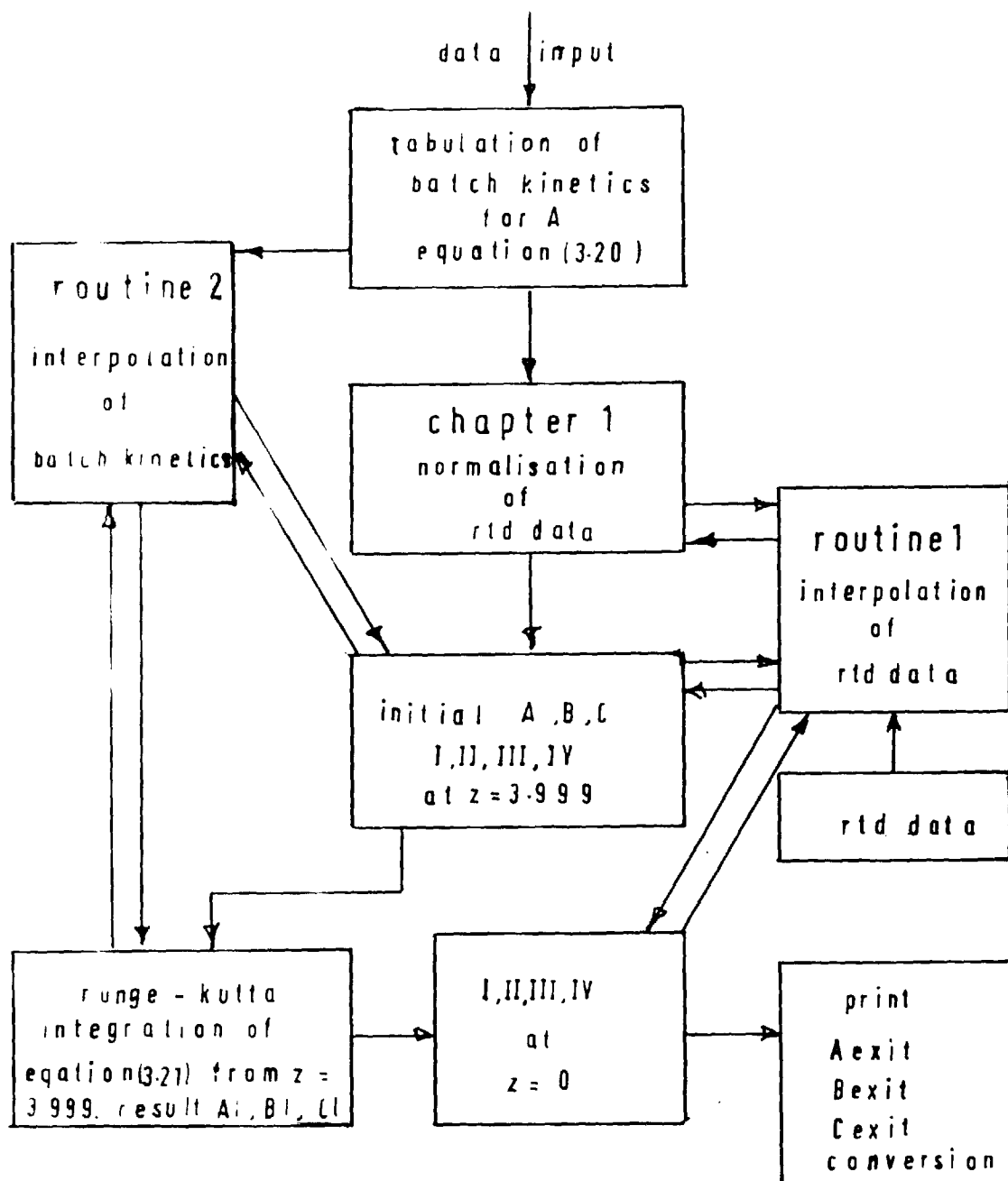


FIGURE 4.1

FLOW DIAGRAM OF PROGRAM CP/PM/GEN

(3.2I) is now performed using a steplength of  $-0.01$ , from  $z = 3.999$  to  $z = 0$ , to obtain the concentrations at the exit from the leaving environment. The value of  $z$  is set to zero, and the sub routine for I, II, III, IV(A), IV(B), IV(C) once again executed, and by substitution in equations (3.25), the concentrations at the exit from the reactor obtained. The conversion may now be calculated, and printed out along with the exit concentrations.

#### 4.7.2 CP/UP/GEN

The Block Diagram for program CP/UP/GEN which integrates the mixing equations (3.26) for Consecutive Parallel unpremixed reactions with any general RTD, is given in Figure 4.2.

Chapter 0 starts with the data input, which is the same as for CP/PM/GEN, and then the flow moves across to Chapter I for the normalisation of the RTD data.

Since no tabulation of the batch kinetics is required, we now proceed to obtain the initial conditions for integrating the mixing equations (3.26).  $z$  is set equal to  $3.999$ , the sub routine for I, II and III executed, and the resulting values used in the solution of equation (3.27) by Newton's iterative method to provide the initial value of  $B_L$  for the integration of equations (3.26). The other initial conditions are found by substituting this value of  $B_L$  in equations (3.28).

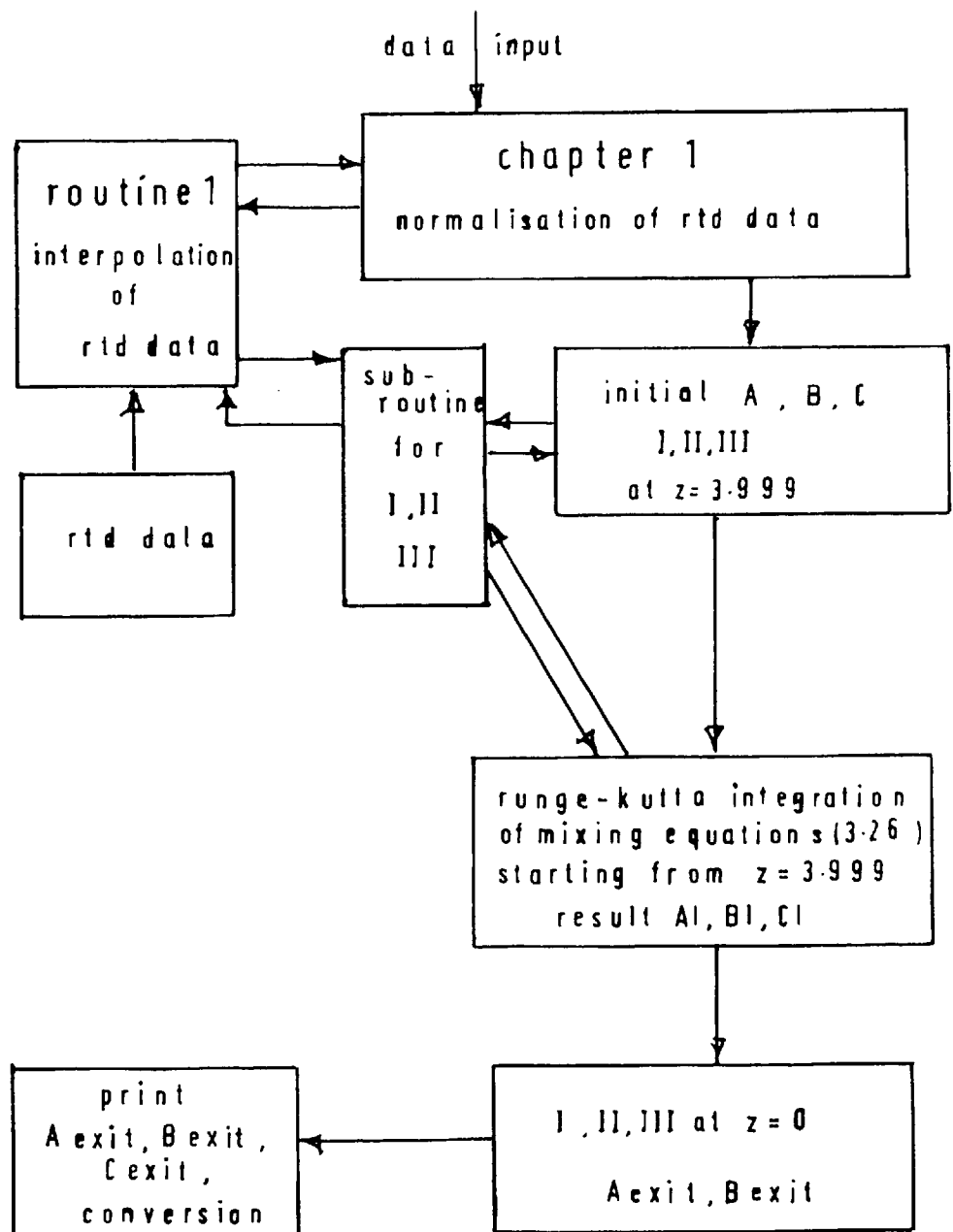


FIGURE 4.2

FLOW DIAGRAM OF PROGRAM CP/UP/GEN

The Runge-Kutta integration of the mixing equations (3.26) is now performed using a step-length of  $-0.01$ . The outlet values of  $A_L$ ,  $B_L$ ,  $C_L$  are substituted in equations (3.29) to obtain the concentrations at the exit from the CSTR.

#### 4.7.3 CON/GEN

The Block Diagram for program CON/GEN which integrates the mixing equations (3.11) for Consecutive premixed reactions for any general RTD is given in Figure 4.3.

Chapter 0 starts with the data input, which includes the initial concentration of A ( $a_0$ ) [the initial concentration of B ( $b_0$ ) is assumed to be zero for all cases],  $R^*$ ,  $\tau$ ,  $\bar{K}$ ,  $KI$ , Gaussian and Laguerre integers and the RTD data. The flow moves across to Chapter I where the RTD data is normalised. On returning to Chapter 0, the kinetics for B are evaluated using equation (3.10) and tabulated, the kinetics for A being obtained analytically from equation (3.9).

Z is set at 3.999, the sub routine for I, II, III, IV(A), IV(B), executed, and the boundary conditions for the integration of equation (3.11) evaluated by substitution in equation (3.14). Since equation (3.13) is a quadratic, no iterative procedure is required in this case.

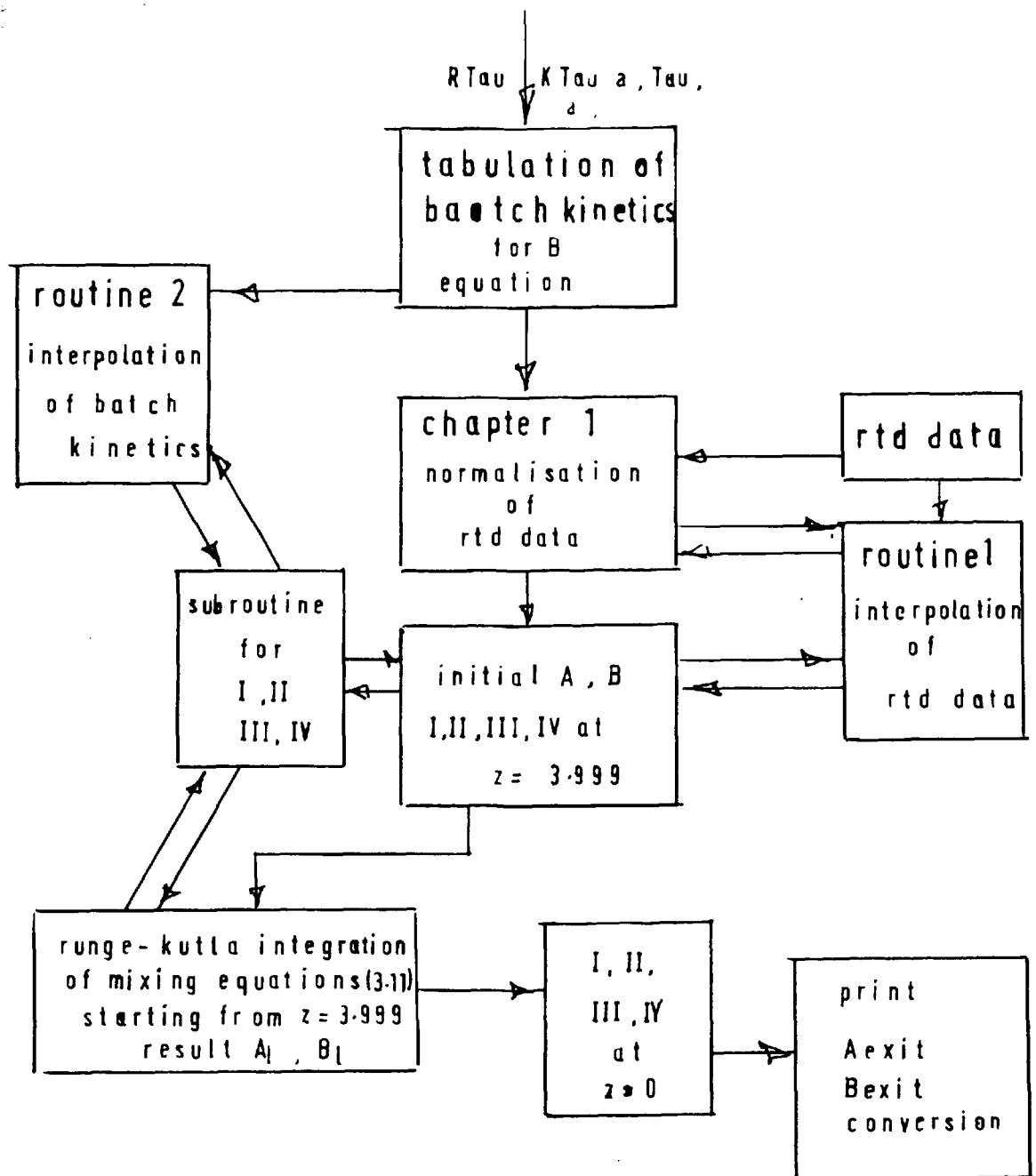


FIGURE 4.3

FLOW DIAGRAM OF PROGRAM  
CON/GEN

The Runge-Kutta integration of the mixing equation (3.II) is now performed using a step-length of - 0.01. Z is set to zero, the sub routine for I, II, III, IV(A), IV(B) re-executed, and the concentrations  $A_L$ ,  $B_L$  at the outlet from the leaving environment substituted in equations (3.I5) from which the concentrations and conversion at the outlet from the reactor are obtained.

#### 4.7.4 AC/PM/GEN

The Block Diagram for program AC/PM/GEN which integrates the mixing equations (3.32) for Autocatalytic premixed reactions with a general RTD are given in Figure 4.4.

Chapter 0 starts with the data ~~input which includes~~  $a_0$ ,  $b_0$ ,  $R, \tau$ , KI, Gaussian and Laguerre integers and the RTD data. The flow moves across to Chapter I, where the RTD data is normalised. The batch kinetics are available in analytical form from equation (3.30), and hence do not require tabulation. Z is set equal to 3.999, and the sub routine to evaluate I, II, III and IV executed. The boundary condition for the integration of equation (3.32) is now obtained by replacing the L.H.S by zero, and solving for  $A_L$ .

The Runge-Kutta integration of equation (3.32) is now performed using a step-length of - 0.01. Z is

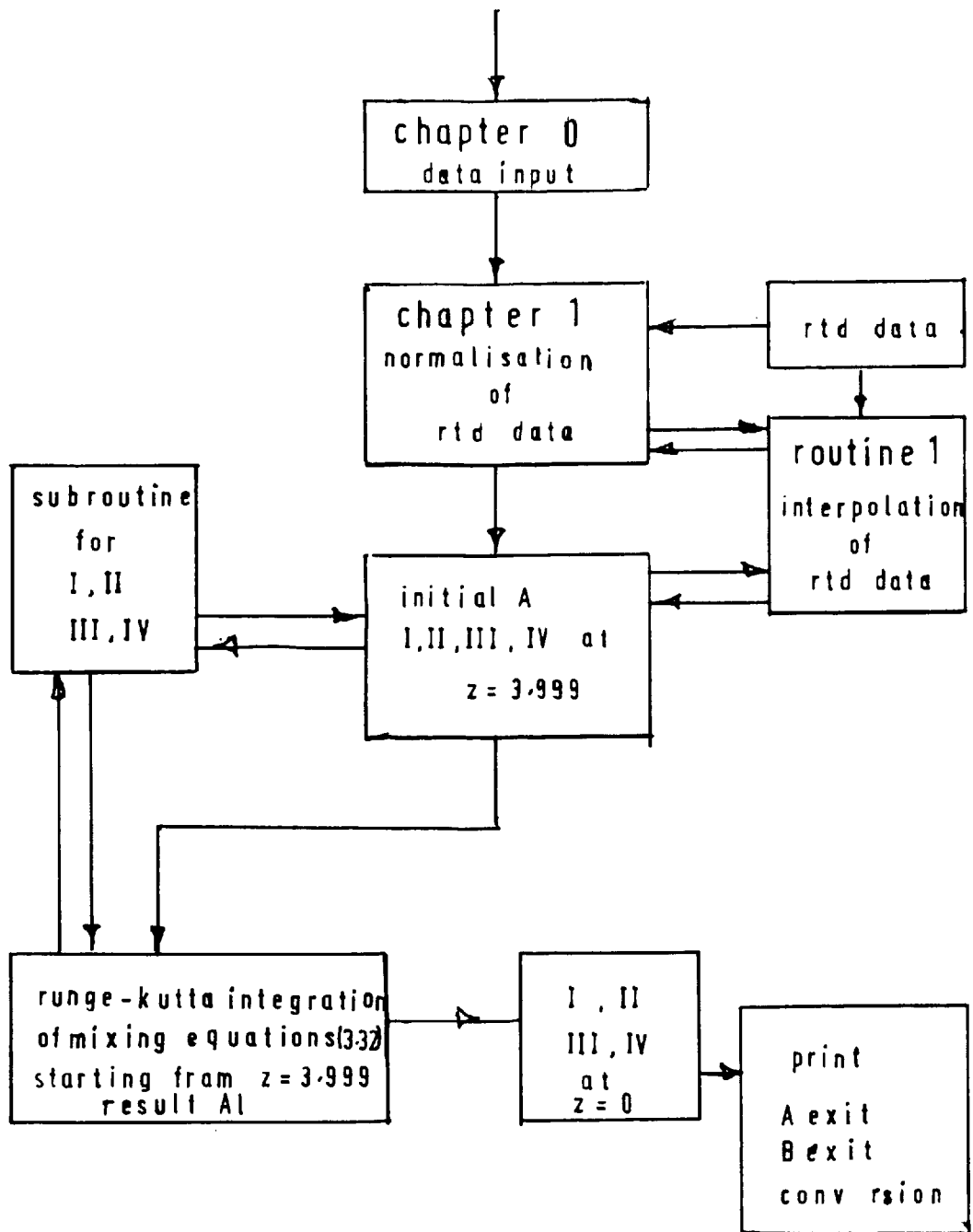


FIGURE 4.4

FLOW DIAGRAM OF PROGRAM  
AC/PM/GEN

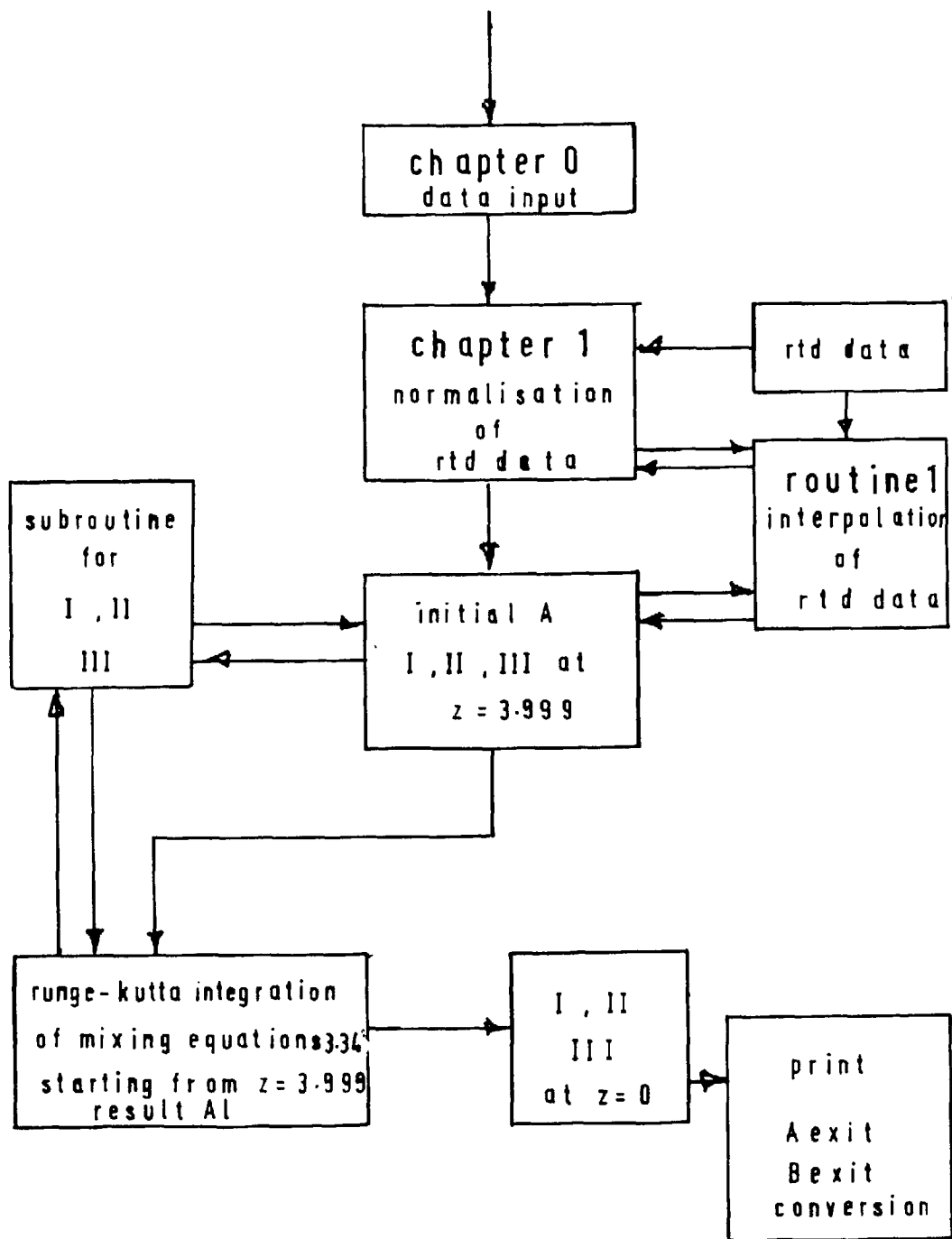


FIGURE 4-5  
FLOW DIAGRAM OF PROGRAM  
AC/UP/GEN

set to zero, and the sub routine for I, II, III, IV re-executed, and the concentrations at the outlet from the reactor obtained by substitution in equation (3.33).

#### 4.7.5 AC/UP/GEN

The Block Diagram for program AC/UP/GEN which integrates the mixing equation (3.34) for Autocatalytic unpremixed reactions with a general RTD is given in Figure 4.5.

Chapter 0 starts with the data input, which is similar to that for AC/PM/GEN. The flow moves across to Chapter I, where the normalisation of the RTD data occurs. Z is set equal to 3.999, I, II, III evaluated, and the boundary conditions for equation (3.34) found in a similar fashion as for the premixed feeds.

The Runge-Kutta integration of the mixing equation (3.34) is now performed. The value of Z is set to zero, the sub routine for I, II, III re-executed, and the concentrations in the stream at the outlet from the reactor obtained from equation (3.35).

CHAPTER 5Results and Discussion5.1 General

Once the computer programs were obtained in functioning order and had been cross checked, it was necessary to decide which results were to be printed out. As discussed in Chapter 4.6, the existing programs are quite suitable for a broad range of parameters, the important exception being for Consecutive Parallel reactions when  $\bar{K}=0.5$  or 1.0. Results for simple second order unpremixed reactions have been omitted from the theoretical section of this work, and are discussed in Chapter 7 of the experimental section.

Weinstein (26) rearranged the batch kinetics equations by replacing the time parameter  $t$  by  $u = KI \text{ as } t$ , and then integrated the equations by a Runge-Kutta method to obtain a relationship between  $\bar{K}$  and the value of  $u$  at which the peak concentration  $\{Y\}$  of the desired product is obtained. When the value of  $KI$  is set equal to the value of  $u$  at the peak  $Y$ , the initial conditions are such that the maximum value of  $Y$  occurs on the batch concentration curve at  $t/\tau = 1$  i.e. when the residence time in the system is equal to the mean residence time  $\tau$ . These equations were solved for the Consecutive and Parallel Reactor models.

These equations were solved for  $\bar{K}$  values of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 15.0, 20.0, 25.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0, 100.0.

It was decided that the results for Consecutive and Consecutive Parallel premixed reactions should be obtained so as to be comparable with those obtained by Weinstein. The results for unpremixed reactions were derived for the same parameters in order to permit comparison between the premixed and unpremixed cases. Since Autocatalytic reactions were not covered by Weinstein, they are treated separately.

In general, the results for 1 and 2 CSTRs RTD come from the specific programs designed to cover these cases, while those for 5 CSTRs RTD are derived from the two general RTD programs which together cover the whole  $RT$  range. The general RTD programs require much more computing time e.g. approximately 25,000 instructions for CP/PM/GEN compared with 11,000 instructions for CP/PM/2CSTRs and 8,000 instructions for CON/2CSTRs. Also, when considering a single CSTR, the case of 5 CSTRs RTD is not in itself of great importance, because the actual RTD in a fairly well-stirred system will not vary a great amount from that for 1 CSTRs RTD, and will often lie between 1 and 2 CSTRs RTD. With this and the length of the individual general RTD programs in mind, some economy in computing time has been achieved by omitting some of the results for 5 CSTRs RTD.

The results are indicated graphically in Figures 5.1 to 5.9, and are tabulated in Tables III.1 to III.9 of Appendix III. The graphs have been plotted on a six cycles logarithmic vs linear scale, so as to cover the wide range of  $R\tau$  desired, and to allow for the fact that the most significant section often lies in the region  $20 \geq R\tau \geq 0.1$ .

## 5.2 Consecutive Parallel Reactions

The results for Consecutive Parallel reactions, for both premixed and unpremixed feeds, have been derived for six values of  $R\tau$  between 0.01 and 1,000. The choice of parameters is the same as made by Weinstein for  $Bo = 1.00$  and  $Bo = 3.00$ , with the exception that  $\bar{K} = 1.0$  was not tackled due to the inability of the programs in their present form to handle this parameter value (Chapter 4.6).

The results for  $R\tau$  greater than 10 were obtained from CP/PM/GEN and CP/UP/GEN, while those for  $R\tau \leq 1$  were obtained using CP/PM/GLRT and CP/UP/GLRT. The results for 2 CSTRs RTD were obtained from the specific programs, both because these programs are marginally more accurate, and also because they require less computing time. The results for 1 and 2 CSTRs were checked against the conversions for complete segregation and maximum mixedness obtained from separate programs, and halving the step-length does not change the conversion to four significant figures. The general RTD programs may be considered accurate to three

significant figures.

### 5.2.1 Consecutive Parallel Premixed Reactions

Figures 5.1 and 5.2 depict Consecutive Parallel premixed reactions with  $Bo = 1$  and  $Bo = 3.00$  respectively. It may be observed that segregation favours an increase in conversion as for the case of the simple irreversible second order reaction. The narrowing of the distribution of residence times also increases the conversion, and the effect of micro mixing decreases with increasing  $Bo$ . This may be expected, since when  $Bo$  becomes very large, the reaction becomes essentially first order for which type of reaction kinetics, the micro mixing does not affect conversion. The curves for 5 CSTRs RTD are considerably flatter than those for 1 CSTR RTD. The maximum effect of  $RT$  on conversion is experienced in the range  $0.3 < RT < 15$ .

### 5.2.2 Consecutive Parallel Unpremixed Reaction

Figures 5.3 and 5.4 depict Consecutive Parallel unpremixed reactions for the same values of the parameters as for the corresponding premixed reactions.

As may be expected, the effect of segregation is larger than with premixed feeds. The curves for premixed and unpremixed feeds are similar when  $RT$  is greater than 20, the conversion being the same at  $RT = \infty$  for both cases, but with the premixed curve bending slightly upwards

# CONSECUTIVE PARALLEL PREMIXED REACTIONS

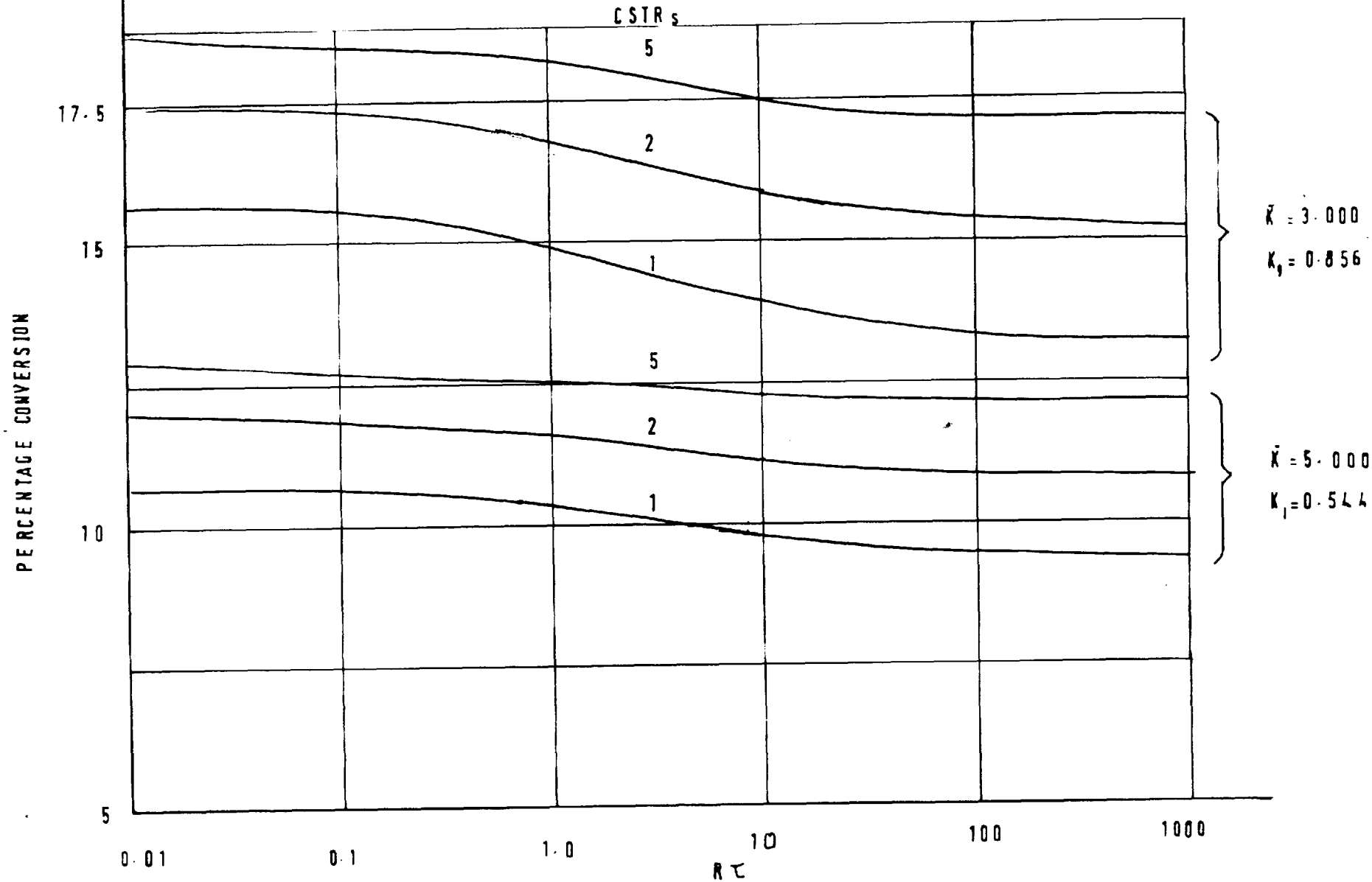


FIGURE 5.1

# CONSECUTIVE PARALLEL PREMIXED REACTIONS-II

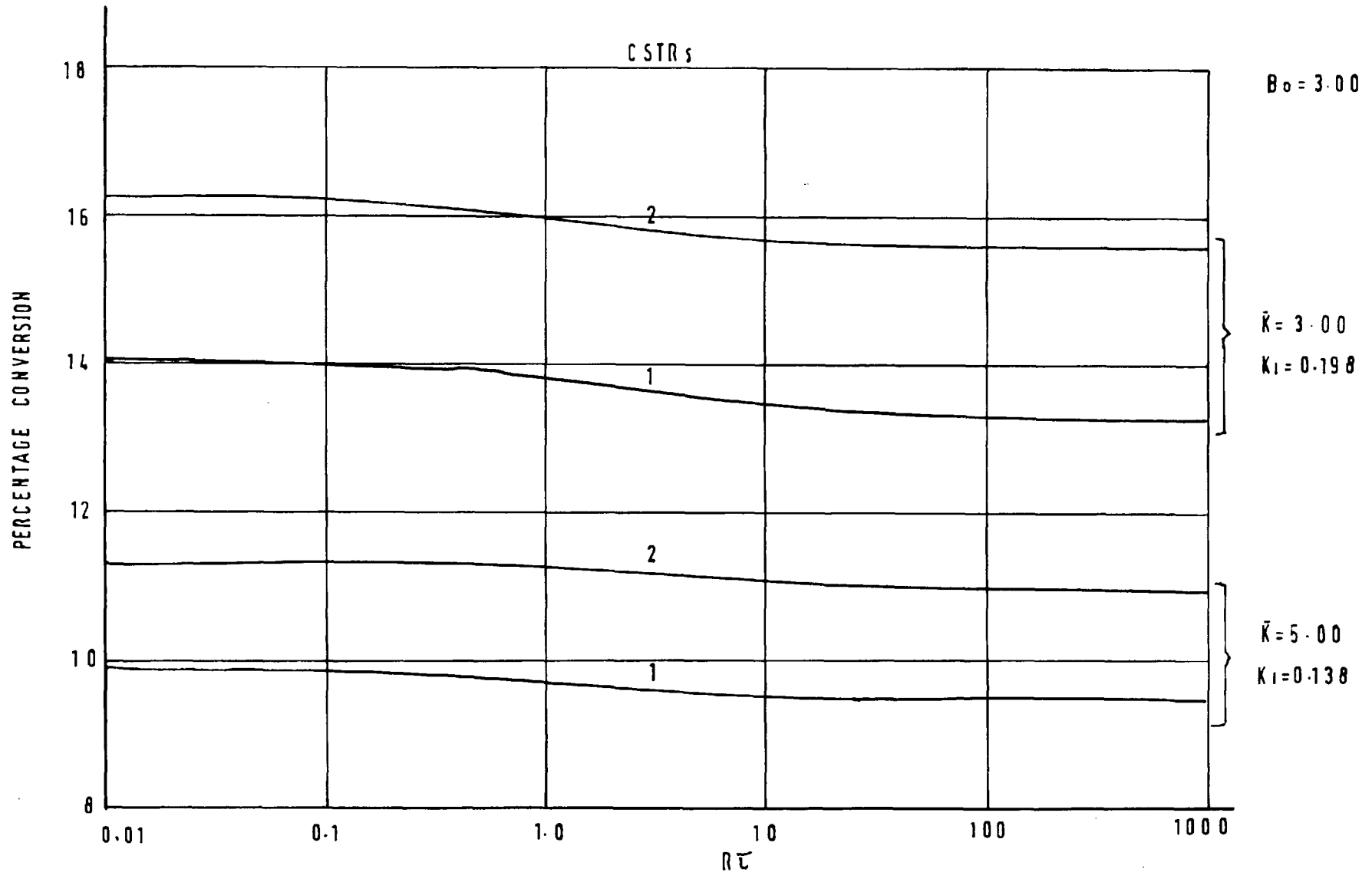


FIGURE 5.2

# CONSECUTIVE PARALLEL UNPREMIXED REACTIONS

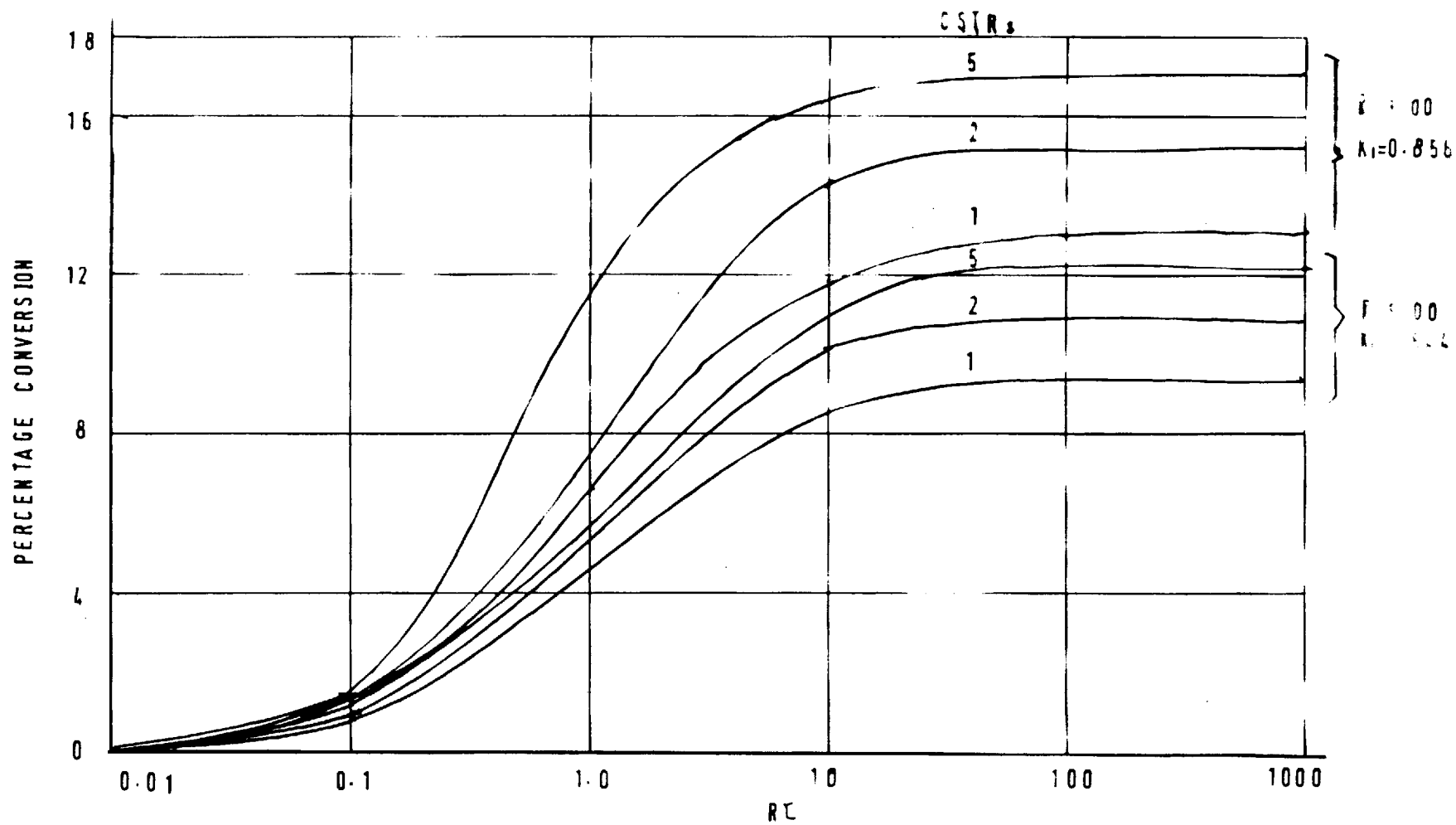


FIGURE 5.3

# CONSECUTIVE PARALLEL UNPREMIXED REACTIONS

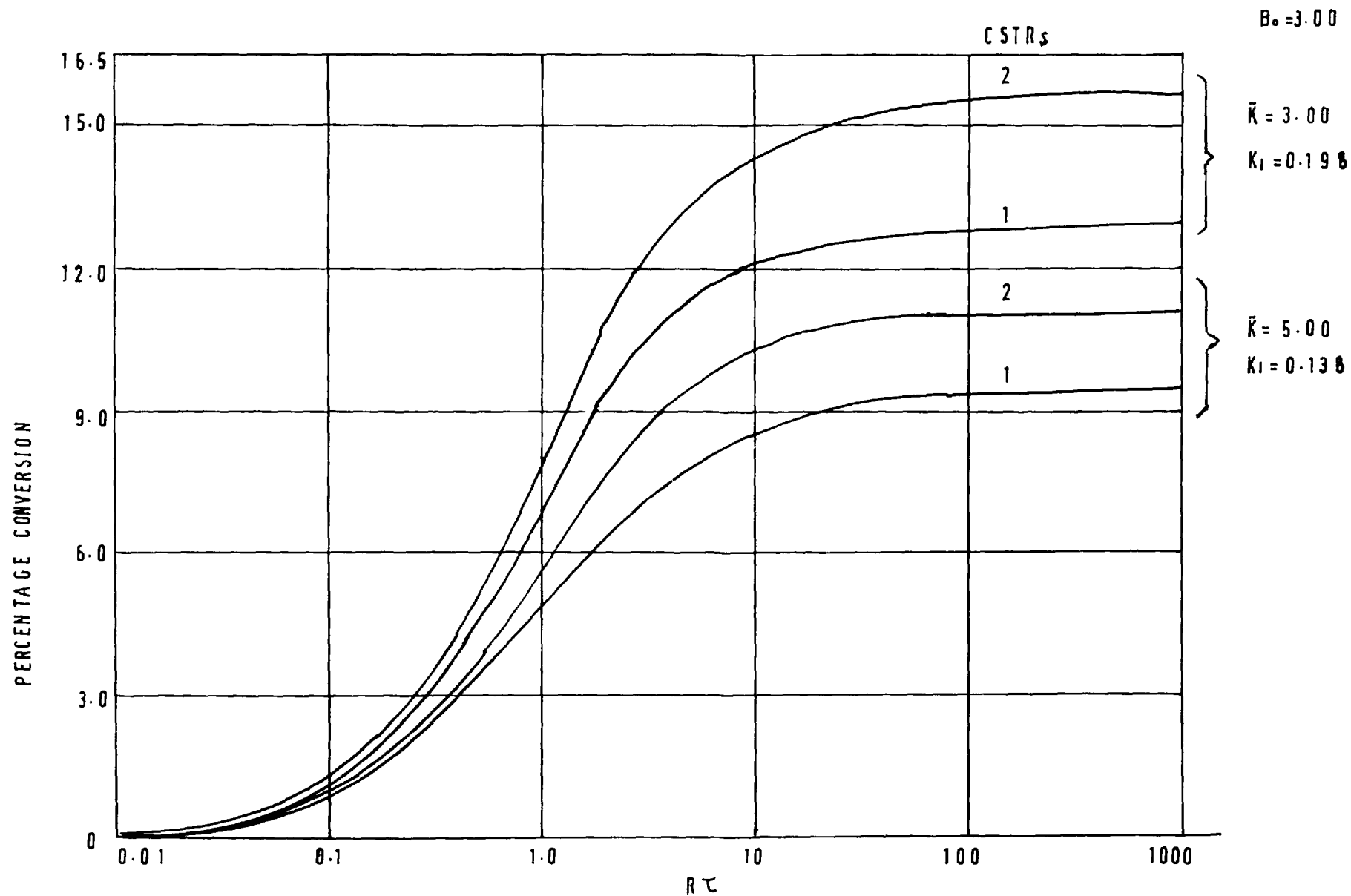


FIGURE 5.4

as  $R\tau$  decreases, while the unpremixed curve slopes a similar amount downwards. However, when  $R\tau$  is less than 20, the effect of  $R\tau$  on conversion is large, and the conversion falls rapidly below the curve for premixed feeds, until  $R\tau = 0.1$  is reached. From here the curve continues to fall, but does so much less rapidly, until it reaches the value zero at  $R\tau$  equal to zero.

### 5.3 Consecutive Premixed Reactions

The results for Consecutive premixed reactions have been calculated for six values of  $R$  between 0.01 and 1,000. The choice of parameters is the same as made by Weinstein, and for all cases it has been assumed that  $Bo=0$ . The accuracy of the results and the programs from which they were derived are the same as for Consecutive Parallel reactions, as discussed in Section 5.2.

The results are indicated graphically in Figures 5.5 to 5.7 and are tabulated in Tables III.5 to III.7. For  $\bar{K} = 0.118$ , i.e. a low value of  $\bar{K}$ , the curves for 1, 2 and 5 CSTRs RTD (figure 5.5) are very similar to those for a simple second order reaction. This is expected, because when  $\bar{K} = 0$ , the system degenerates into a simple second order reaction. For  $\bar{K} = 1.36$  and 3.00, the curves for 5 CSTRs RTD have been omitted in order to economise on computing time (Section 5.1). With  $\bar{K} = 1.36$  (figure 5.6), there are two near plateaus when  $R\tau > 10$  and  $R\tau < 0.1$ ,

# CONSECUTIVE PREMIXED REACTIONS

$$R = 0.118$$

$$K_1 = 3.50$$

$$K_2 = 0.413$$

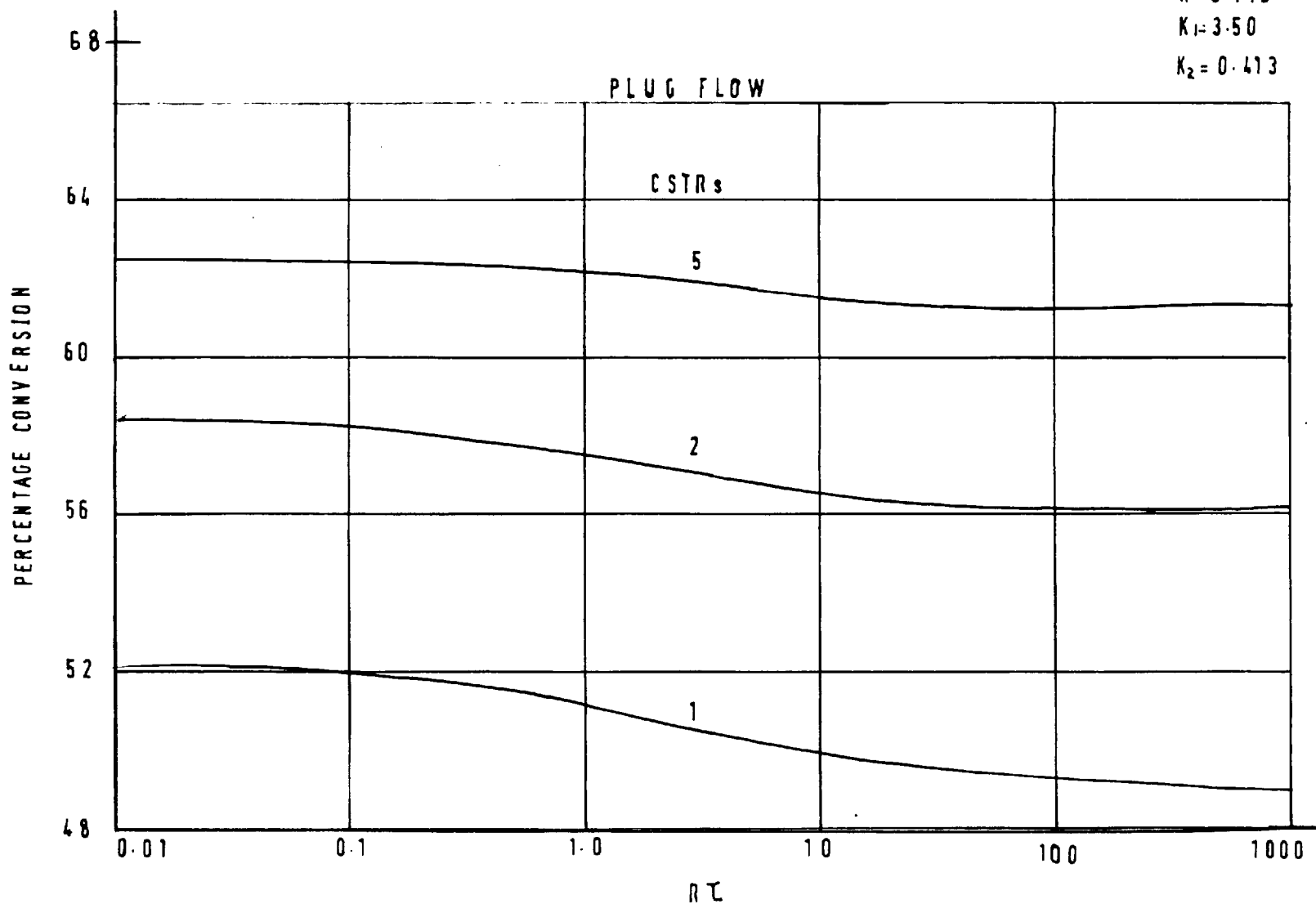


FIGURE 5.5

# CONSECUTIVE PREMIXED REACTIONS

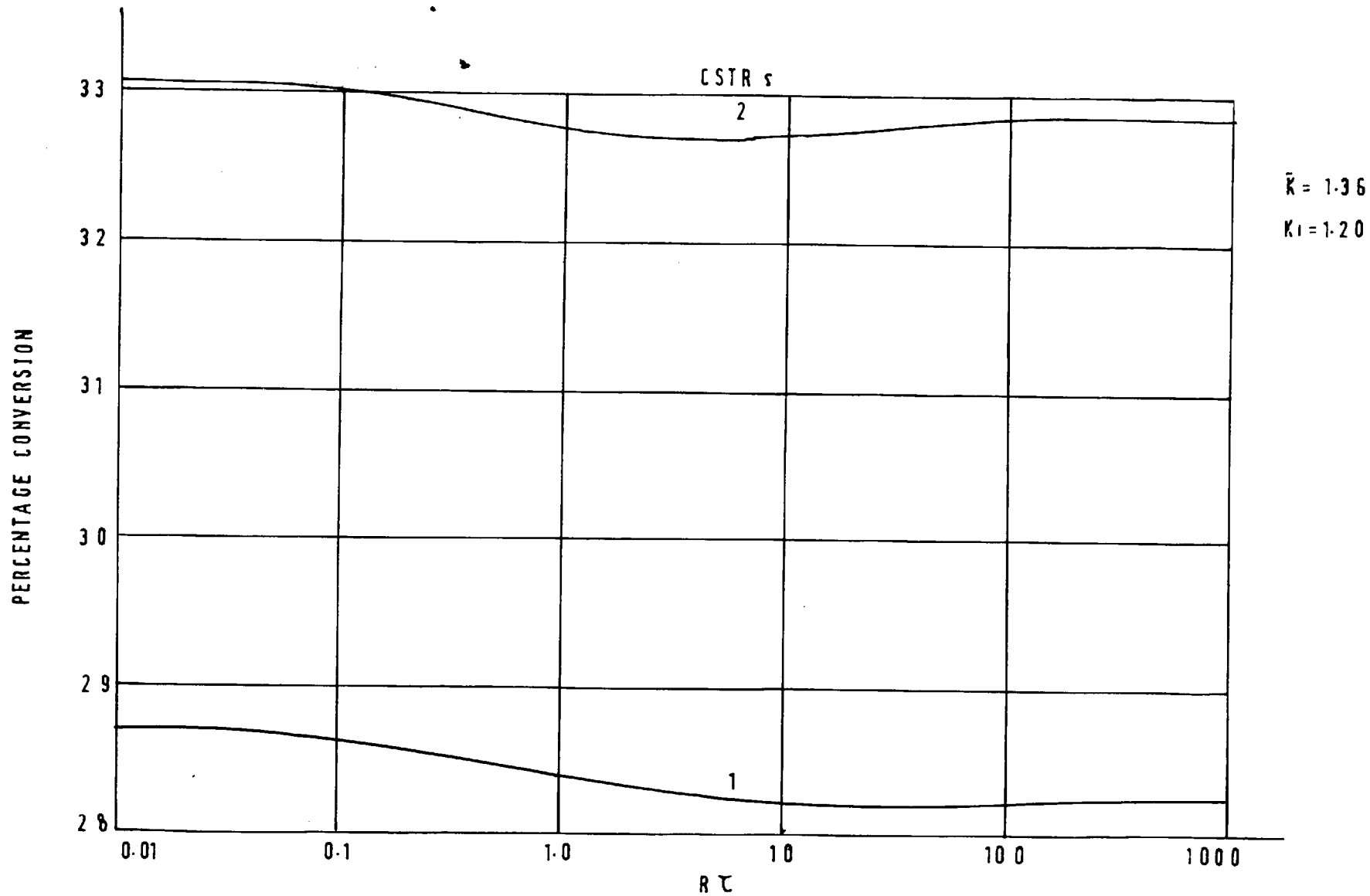


FIGURE 5.6

# CONSEUTIVE PREMIXED REACTIONS

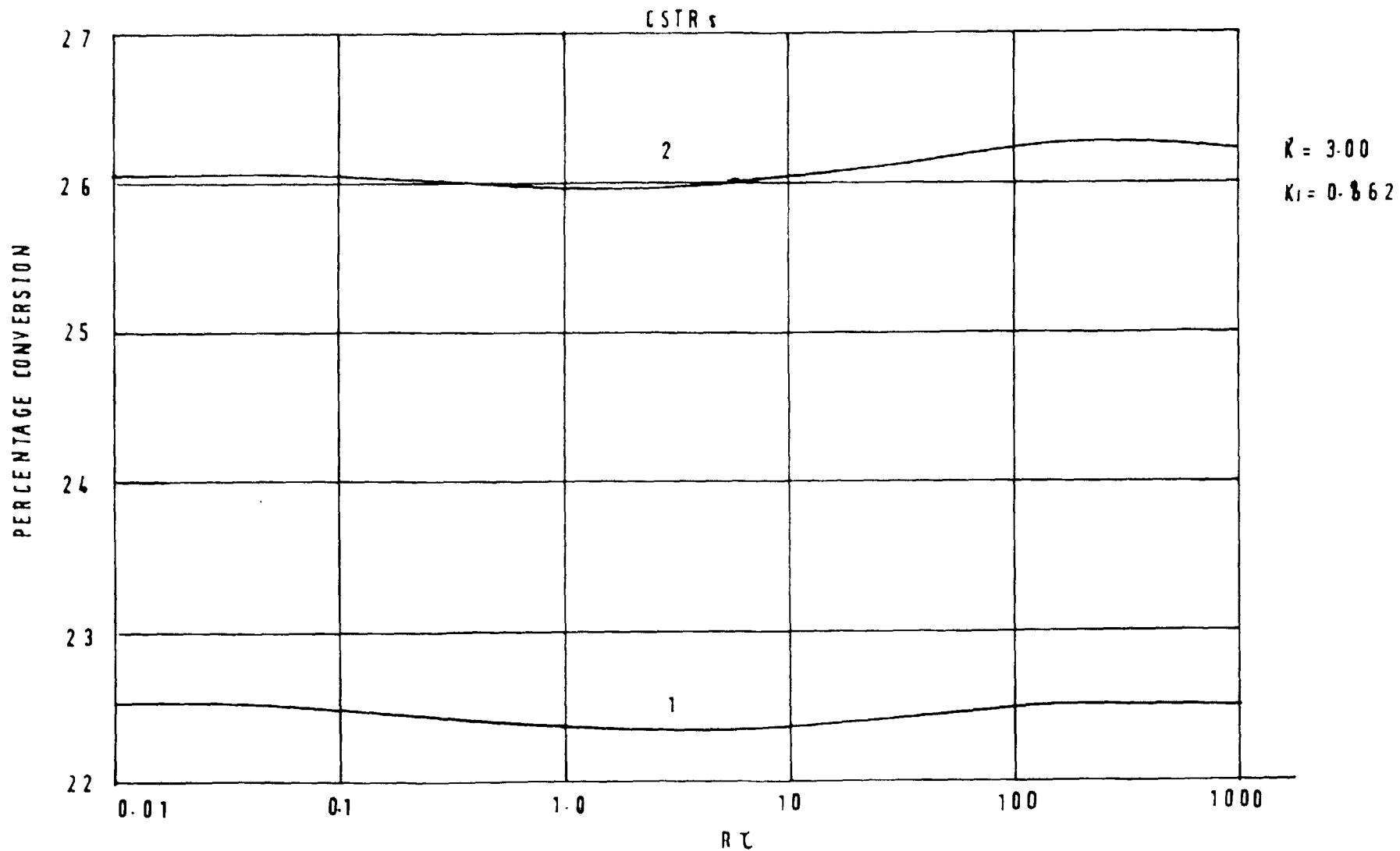


FIGURE 5.7

and good segregation still results in a higher conversion than good micro mixing, but for intermediate values of  $R\tau$ , the conversion falls to minimum, and is lower in value than for either plateau. For  $\bar{K} = 3.00$ , the maximum conversion occurs at high values of  $R\tau$ , and then falls to a minimum at an intermediate value of  $R\tau$ , before climbing up to the plateau at very low  $R\tau$ . In this case the conversion plateau for  $R\tau > 10$  is higher than the rest of the curve.

The following general observations may be made:-

- (1) The effect of the RTD is much more significant than that of the micro mixing.
- (2) Micro mixing decreases the conversion at low  $\bar{K}$  (i.e. less than one) and increases it at high  $\bar{K}$ .
- (3) A minimisation of the distribution of residence times favours conversion, independently of  $R\tau$ .

#### 5.4 Autocatalytic Reactions

The results for Autocatalytic premixed and unpremixed reactions were calculated for five values of  $R\tau$  between 0.05 and 500.  $KI$  was assumed to be 3.3 and  $Bo = 0.1$  for all cases. This choice is arbitrary, and many other values for these parameters would have been equally suitable. The results are indicated graphically in Figures 5.8 and

5.9, and have been tabulated in Tables III.8 and III.9. The general lay out and accuracy is similar to that for Consecutive Parallel reactions.

#### 5.4.1 Autocatalytic Premixed Reactions

These provide an interesting case in so far as they are the only isothermal premixed reactions of order greater than one in which conversion always increases with an improvement of the micro mixing. On examination of Figure 5.8, it may be observed that the curve for 5 CSTRs RTD falls from a conversion of 85.86 per cent at  $R\tau = 500$  to 66.06 per cent at  $R\tau = 0.05$ . This conversion difference of 19.8 per cent is considerably larger than the conversion difference for other premixed reactions. Ng (18) has shown that the maximum difference between the maximum mixedness and complete segregation conversions is approximately 7 per cent for a simple second order premixed reaction, and is generally even smaller for Consecutive and Consecutive Parallel premixed reactions. The decrease in conversion is most rapid in the region  $R\tau = 20$  to  $R\tau = 0.3$ . The behaviour of the curves for 1 and 2 CSTRs RTD follows the same general patterns as for 5 CSTRs RTD.

#### 5.4.2 Autocatalytic Unpremixed Reactions

For unpremixed feeds, the conversion improves with increasing  $R\tau$  for any given RTD. Examining the curve for 5 CSTRs RTD in Figure 5.9, the conversion falls

# AUTOCATALYTIC PREMIXED REACTIONS

$$K = 3.3$$

$$B_0 = 0.1$$

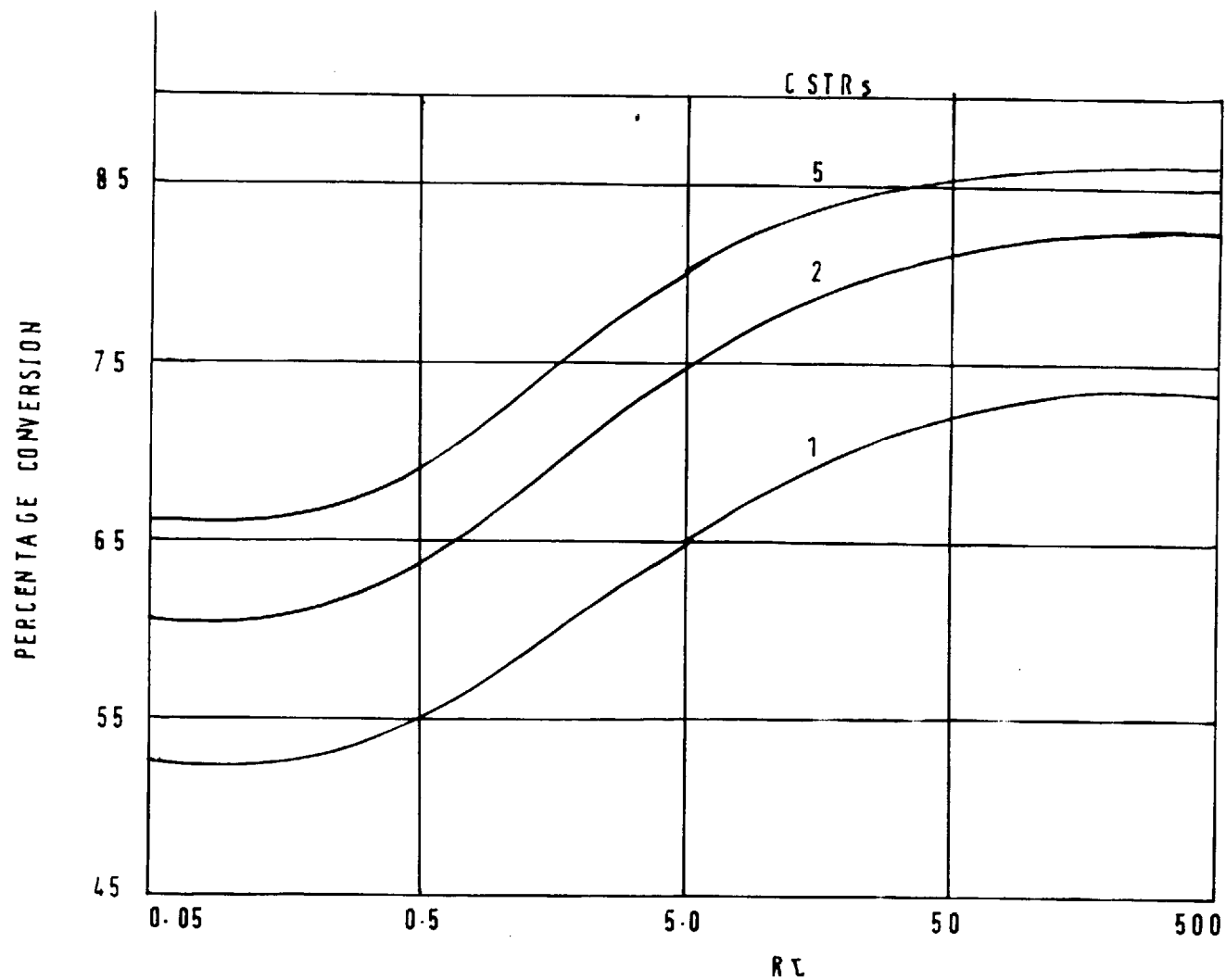


FIGURE 5.6

# AUTOCATALYTIC UNPREMIXED REACTIONS

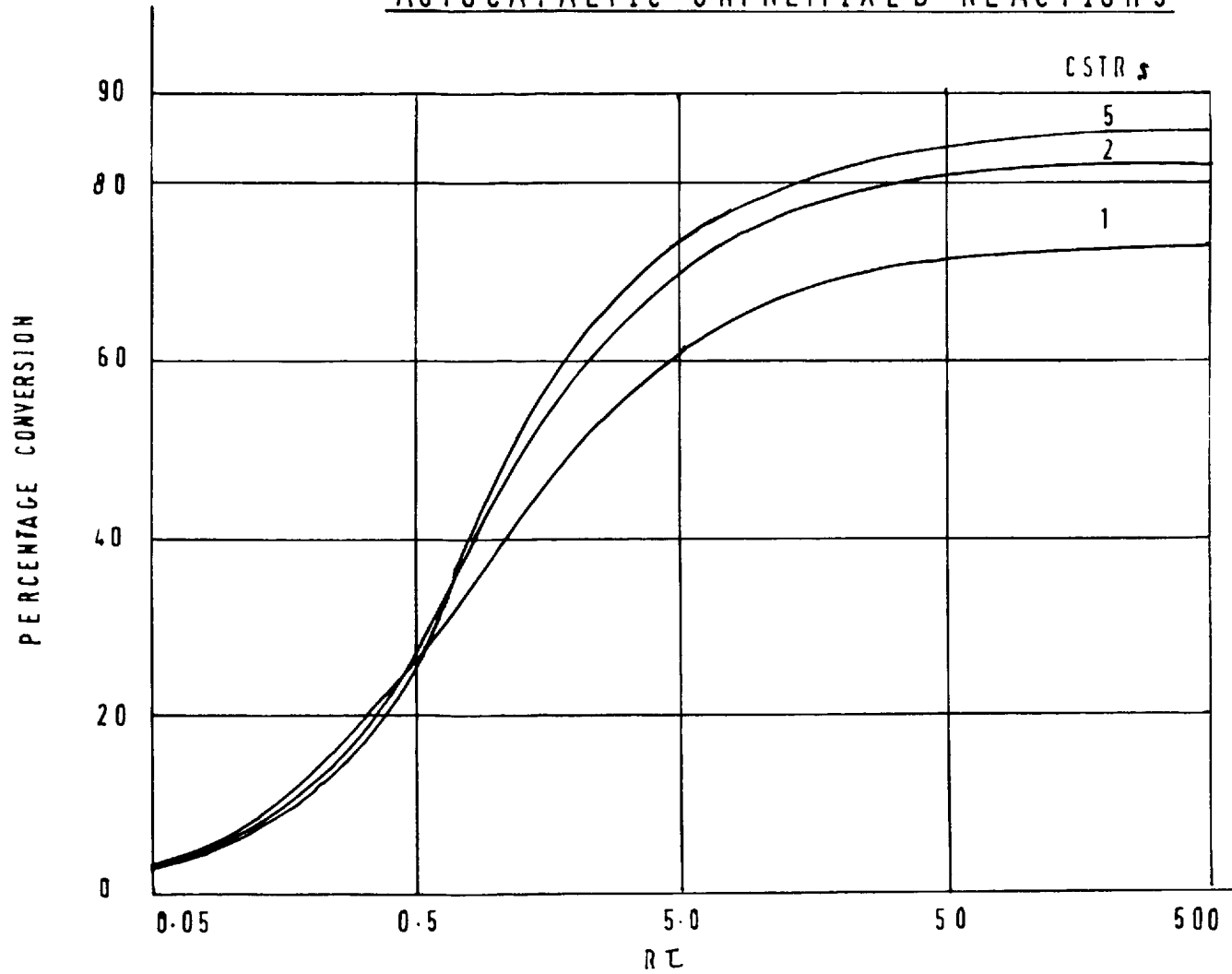


FIGURE 5.9

from 85.75 per cent at  $R\tau = 500$  to 2.85 per cent at  $R\tau = 0.05$ . This is due to the fact that no reaction occurs in the entering environment. The conversion vs  $R\tau$  curve is most sensitive to changes in  $R\tau$  in the region  $20 > R\tau > 0.3$ .

At low  $R\tau$  an unusual phenomenon is observed. The curves for 5 CSTRs RTD and 2 CSTRs RTD cross the curve for 1 CSTR RTD, the conversions at  $R\tau = 0.05$  being 3.5 per cent for 1 CSTR, 3.26 per cent for 2 CSTRs and only 2.85 per cent for 5 CSTRs RTD. For isothermal reaction, this is the only known case for this inversion to occur.

This inversion may be explained qualitatively by the fact that there are two factors at work.

(1) A minimisation of the distribution of residence times which favours a tendency towards plug flow, whereby a RTD of 5 CSTRs is favoured over that of a RTD of 1 CSTRs.

(2) The micro mixing which always improves conversion in the case of Autocatalytic reactions (Chapter 3.7.2). It may be assumed that for the same  $R\tau$ , a system of 1 CSTR RTD is inherently better mixed than one of 5 CSTRs RTD.

Hence, at high  $R\tau$ , when the system is well mixed

on the micro scale, the RTD becomes the dominating factor, while at very low  $Re$  there is so little micro mixing that it becomes much more important than the RTD, causing the above mentioned inversion.

## 5.5 Discussion

We have developed the Rippin-Ng model for incomplete mixing in a single CSTR whereby both premixed and unpremixed feeds may be tackled for any arbitrary RTD with Autocatalytic, Consecutive or Consecutive Parallel reaction. Though this work does not cover all known types of homogeneous isothermal reactions e.g. Consecutive unpremixed reactions have not been studied, with the knowledge and experience derived, it would be relatively easy to extend it to cover most other cases.

Results corresponding to those derived by Weinstein (26) for the Consecutive and Parallel Reactor models for isothermal reaction have been obtained, but no attempt was made to deal with adiabatic or other non-isothermal conditions. The latter, particularly for the case of heat transfer through coils, is of great practical significance. The problems associated with an arbitrary numerical RTD, which is of great importance (Chapter 4.2.2) have been solved. This covers the macro mixing deviations from perfect mixing. The differences between premixed and

unpremixed feeds have been put into the correct perspective, and the effect of incomplete mixing with unpremixed feeds quantified for the first time. It may be pointed out that Weinstein only covered the case of premixed feeds, without expressly stating that the results for unpremixed feeds would in fact be very different.

Qualitatively, the Rippin-Ng model behaves in a fashion similar to the Consecutive Reactor model, and differs from the Parallel Reactor model in a similar fashion to the Consecutive Reactor model. Since the differences between the two latter models have been compiled by Weinstein (26), no comparison between the Rippin-Ng and Parallel Reactor models need be drawn here.

The conversions with complete segregation or maximum mixedness are of course the same for both the Rippin-Ng and Consecutive Reactor models. However, the path the curve follows between these two values, though similar for the two models is by no means identical. A direct comparison between the two models is difficult, as the two parameters  $y^*$  and  $R \tau$  behave in the opposite fashion i.e. at  $y^*=0$  we have maximum mixedness, while with  $R \tau = 0$  complete segregation occurs, while high  $y^*$  denotes a large amount of segregation, while high  $R \tau$  indicates good micro mixing. Therefore it was felt

## RIPPIN-NG AND CONSECUTIVE REACTOR MODELS

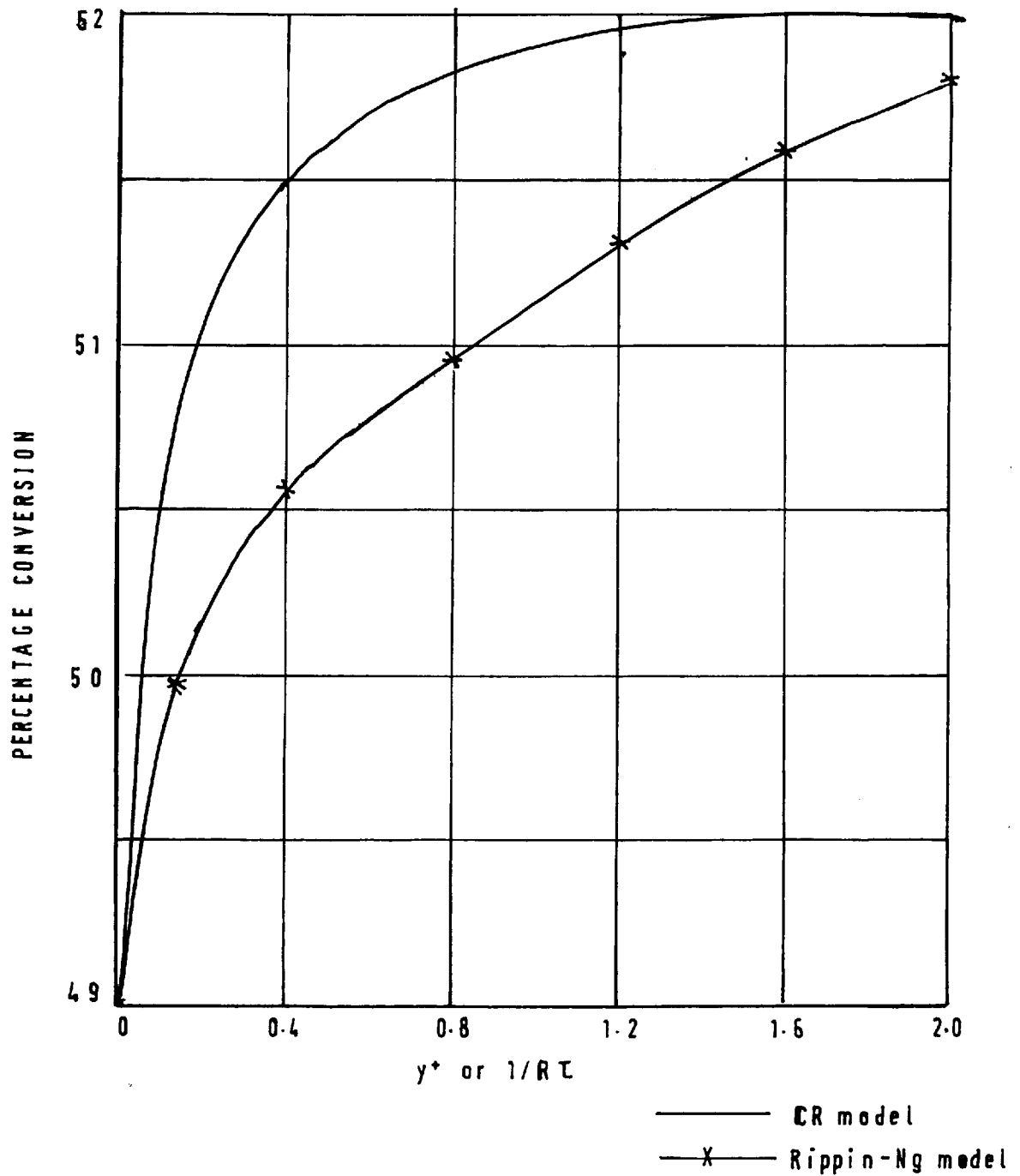


FIGURE 5.10

that  $y^*$  and  $I/R\tau$  may be suitable parameters for a comparison of the two models. Figure 5.10 shows a plot of the percentage conversion vs  $y^*$  or  $I/R\tau$  for the case of a Consecutive premixed reaction with a I CSTR RTD,  $\bar{K} = 0.118$  and  $KI = 3.50$ . The corresponding plot of percentage conversion vs  $R\tau$  is given in Figure 5.5.

It will be observed from Figure 5.10, that the perfect mixing conversion is approximately 3 per cent lower than the conversion with complete segregation. However, the plot of conversion vs  $y^*$  rises more rapidly towards the plateau of the complete segregation conversion, than the corresponding curve for the Rippin-Ng modified parameter  $I/R\tau$ . An examination of Tables III.10 to III.12 will reveal that the curve for  $y^*$  always goes more rapidly to the final value of conversion, than the corresponding curve for  $I/R\tau$ . The actual superiority of one model over the other, as being a more accurate representation of incomplete micro-mixing in a CSTR can only be determined experimentally.

At first sight, it may appear that since there is not too great a difference between the two models, the greater simplicity of the Consecutive Reactor model is a point in its favour. However, this is misleading, because the Consecutive Reactor model programs in their present form, cannot handle numerical RTD data. Once this additional

facility has been introduced, the programs for the two models will be of a similar degree of complexity, and hence the main deciding factor should be the fit of the experimental data.

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## EXPERIMENTAL SECTION

### CHAPTER 6

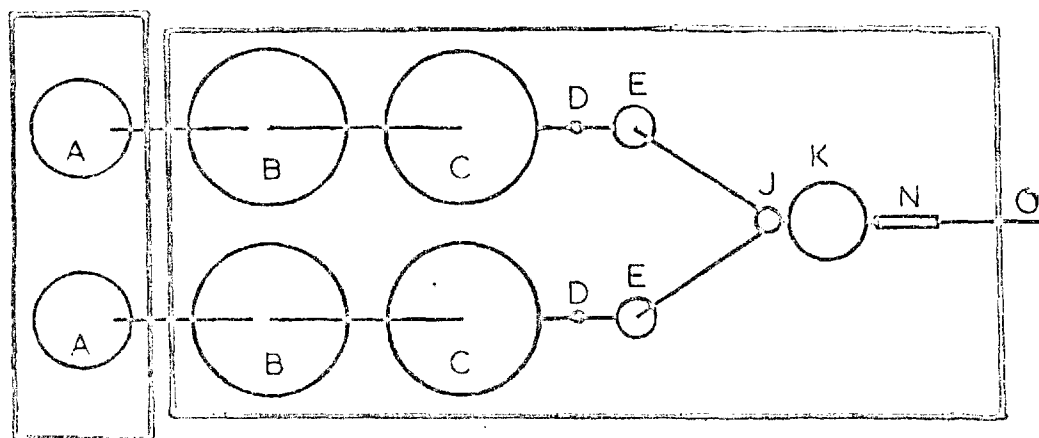
#### PREMIXED FEEDS

##### 6.I Equipment Layout

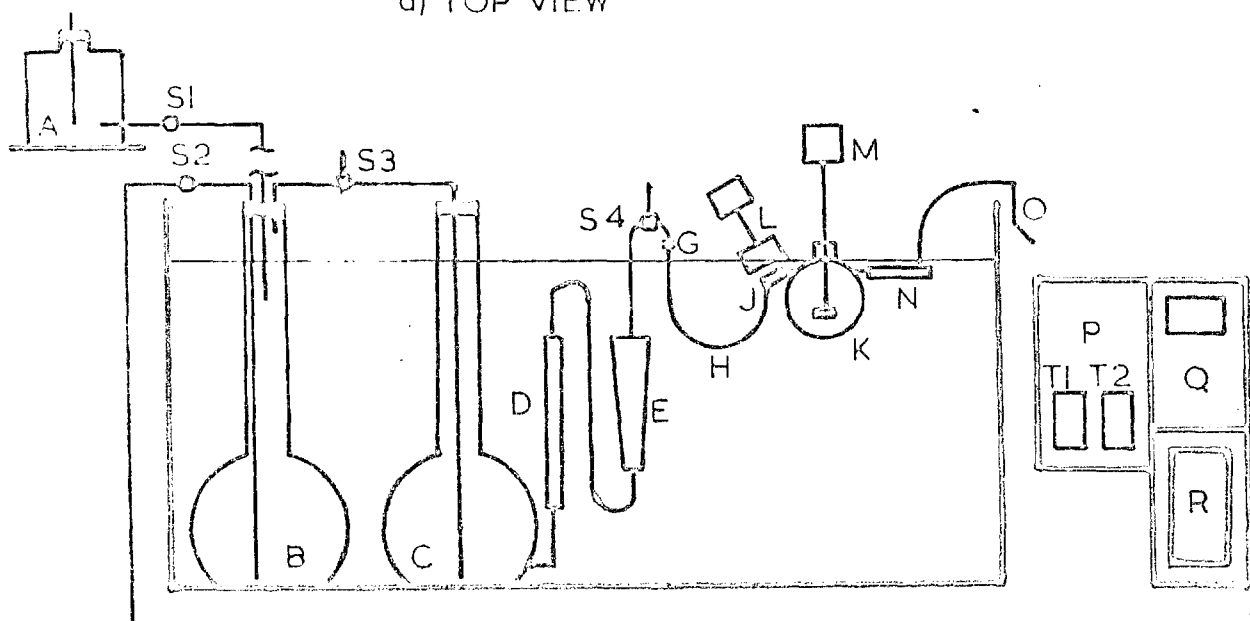
##### 6.I.I Flow System

The flow system for premixed feeds was the same as that employed by Ng (18), with minor modifications of equipment and improvement in technique. The reactor system will be described in greater detail in Section 6.I.2 and the modifications discussed in Section 6.I.3. For the experimental system with unpremixed feeds, the same flow system was used, but the reactor system is described in Chapter 7.I. A brief description of the flow system is given below, the detailed specifications being available from Ng's work (18). The general arrangement of the experimental equipment is shown in the schematic diagrams of Figures 6.I(c) and 6.I(b).

Figure 6.I(b) shows the side view of the equipment and the constant temperature oil bath. The Mariotte bottles (A) containing water were placed on a platform some distance above the bath to give a constant hydrostatic head. The pressurised air in the air bottles (B) was used to drive the reactants in the reagent bottles (C). The flow rate was regulated by the length and size of the capillary tubing (D). The reactants flowed through



a) TOP VIEW



b) FRONT VIEW

- |                        |                           |
|------------------------|---------------------------|
| A MARIOTTE BOTTLE      | L MOTOR & MAGNET          |
| B AIR BOTTLE           | M REACTOR STIRRER MOTOR   |
| C REAGENT BOTTLE       | N CONDUCTIVITY CELL       |
| D GLASS CAPILLARY      | O OUTLET TUBE             |
| E ROTAMETER            | P SWITCH PANEL            |
| F SYPHON               | Q CONDUCTIVITY METER      |
| G SPHERICAL JOINT      | R RECORDER                |
| H POLYTHENE INLET TUBE | S STOPCOCKS               |
| J PREMIXER             | T1 ELECTRONIC RELAY       |
| K REACTOR              | T2 SMOOTH SPEED REGULATOR |

**FIGURE 6-1**  
**FLOW SYSTEM**

the 3-way stop-cocks (S4) into the premixer (J) where they were mixed by a small magnetic stirrer, the motor and magnetic unit (L) turning the stirrer. The stirrer of the main reactor (K) was propelled by the motor (M). The effluent from the reactor flowed into the conductivity cell (N) and out through the polythene tubing connecting the cell and the outlet (O). In addition to the switches and fuses, the electronic relay (TI), the smooth speed regulator (T2) and the dial for the tachometer (T) were all mounted on the control panel (P). The smooth speed regulator controlled the main reactor motor (M). The conductivity meter (Q) and the recorder (R) were mounted next to the control panel. The syphons (F) were employed to empty the air bottles at the end of a run.

Figure 6.1(a) shows the top view of the arrangement of the two identical flow systems in the constant temperature bath.

#### 6.1.2 Premixed Feeds Reactor System

All experimental work with premixed feeds was performed on the reactor system devised by Ng (18), a schematic diagram of which is given in Figure 6.2. A brief description is given below, the photographs and detailed specifications being available in the work by Ng (18).

The reactor (H) consists of a spherical flask with four creases  $90^{\circ}$  apart, which act as baffles. The volume of the reactor was designed to be of the same order of magnitude as the half life of the reaction ( 39 ).

Denbigh, Stead and Page (6) have pointed out the necessity of having a well defined reaction volume. The solutions filled the reactor completely. The boundaries of what will be considered to be the main reactor are indicated by dotted lines at the inlet and outlet in Figure (6.2), and the reactor volume was measured with the stirrer in position.

The stirrer is a simple paddle, and is positioned 6.5cm. from the top of the reactor for all runs. This is approximately one-third of the distance from the reactor bottom. The stainless steel conical joint (K) contained a PTFE seal to prevent any leakage up the stirrer shaft. The conical joint was sealed with picine wax to the B40 glass joint of the reactor. Two different motors were used for the main reactor motor, one each for the high and low range of stirring speeds. The stirrer speed was measured by a continuous reading tachometer, and the dial was connected by a flexible coupling to the top of the motor shaft.

There was a conductivity cell (D) connected to

the outlet of the reactor by polythene tubing. In order to ensure that the feeds were completely premixed before entry to the main reactor, they were fed into a small premixer unit, and well mixed with the aid of a magnetic stirrer. The criteria for a good premixer i.e. that it should be of small volume and only a small fraction of the total conversion should occur in it were satisfied. For some of the later runs, a new premixer was necessary, as the original one disintegrated. This new premixer was of a slightly larger volume, but the general characteristics of the original were maintained.

### 6.1.3 Modification of Equipment and Technique

The equipment was overhauled and rewired because the old electric wiring was considered unsafe, and the control switches mounted on a new and more convenient panel. The top of the motor shaft was modified to accept a flexible coupling from the new continuous tachometer, the dial of which was large enough to allow the measurement of the stirrer speed to  $\pm 1$ rpm. This was a great improvement over the old hand tachometer, as it allowed the instantaneous measurement and control of the stirrer speed. It was observed that the PTFE seal on the stirrer shaft created an uneven stress at different points, causing the stirrer speed to vary at different angles of a single revolution by  $\pm 3$ rpm. This unevenness could not be eliminated in spite of many attempts to rectify it.

A new deionising unit supplied deionised water in a degassed state, eliminating the necessity of boiling water to expel the dissolved gases. This resulted in less deposition of air bubbles in the capillaries. It was decided to cut out the rotameters which served no useful purpose in the flow system, and it was found that the last traces of air in the tube connecting the 3-way stopcocks (S4) to the premixer could best be removed by forcing fluid backwards after filling the reactor. The substitution of Edwards Silicone grease in place of Edwards High Vacuum grease caused less blockage in the capillaries. The other procedures and techniques employed were essentially the same as described by Ng (18).

## 6.2 Previous Experimental Work

### 6.2.1 Ng's Results

Ng (18) studied incomplete mixing with chemical reaction, using the flow system described in Section 6.1.1, employing the reaction between Na OH and ethyl acetate in dilute aqueous solution. The stoichiometry of the reaction may be represented by

$$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{Na}^+ \text{OH}^- \longrightarrow \text{CH}_3\text{COO}^- \text{Na}^+ + \text{C}_2\text{H}_5\text{OH} \quad (6.1)$$

About 36 isothermal reaction runs were made at 25°C, and may be divided into two groups, one having a total flow rate of approximately 16ml/min and the other of 22.5ml/min. The normality of the solutions just after entry to the premixer was approximately 0.075N

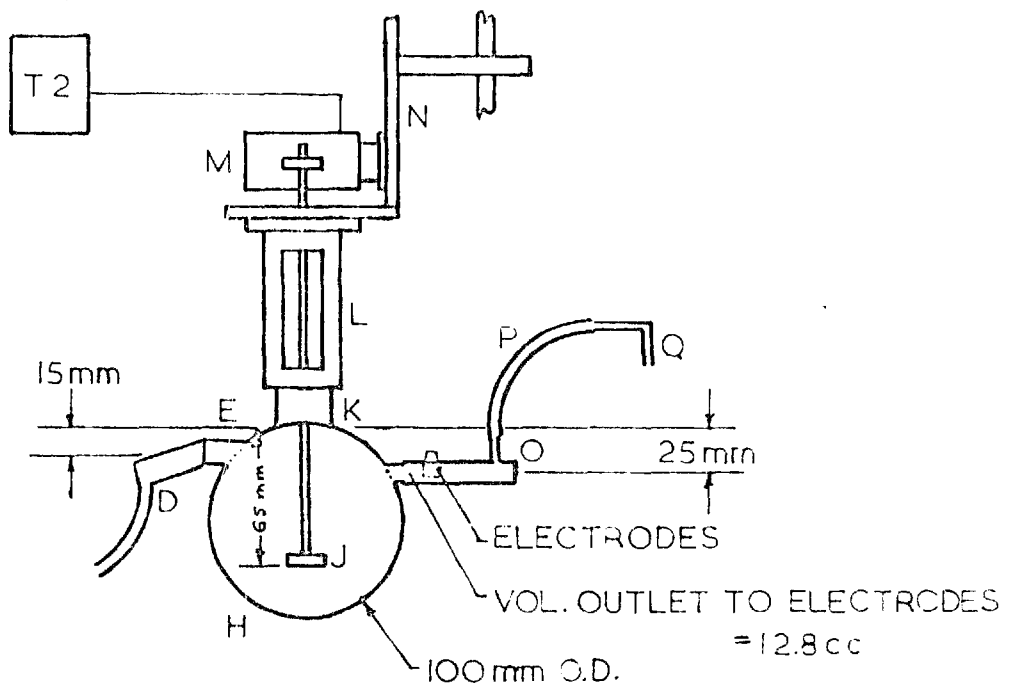


FIGURE 6.2

PREMIXED REACTOR SYSTEM

SPECIFICATIONS

- D- Premixer
- E- Premixer Outlet
- H- Main Reactor- vol=470 ml.
- J- Paddle Stirrer
- K- Conical Joint
- L- Frame
- M- Stirrer Motor
- N- Motor Mount
- O- Conductivity Cell
- P- Polythene Outlet Tube
- Q- Glass Outlet Tube- 7mm I.D.
- T2- Smooth Speed Regulator

for both reactants for all runs. The stirrer speeds varied between 0 and 400 rpm, being constant over the duration of an individual run. A summary of the operating conditions for the reaction runs is given in Table (IV.1) of Appendix IV.

The RTD data for the system was obtained using a pulse input method, the most suitable pulse having been found to consist of 2 ml. of a 4 per cent aqueous KCl solution, with methyl alcohol added to achieve a density correction. Experiments were also conducted using a step change method, but the necessity of differentiating the resulting cumulative distribution curve ruled this out as a suitable method. The required curves for the residence time frequency functions may be obtained directly from the pulse input method. A summary of the relevant RTD runs is given in Table (IV.2).

The experimental conversion, and the conversion assuming a well stirred residence time distribution (WSRTD) for the cases of complete segregation and perfect micro-mixing were calculated by feeding the appropriate data into program P3/Ng. Since mixing in a single CSTR was being studied, allowance was made for the premixer and outlet tube in these calculations. Program PI2/Ng calculates the complete segregation and maximum mixedness conversions for any arbitrary RTD, and was used in

conjunction with the experimental RTD data to calculate the two limiting conversions, and to obtain a first guess for the value of  $R\tau$ . Program P9E/Ng calculates the value of  $R\tau$  by an iterative procedure from the input data consisting of the RTD data, guess value of  $R\tau$  and operating data. These results have been tabulated in Table (IV.3).

The values of  $R\tau$  for the main reactor were found to vary from 0 for run RI5 which is at 30 rpm and a nominal flow rate of 16 ml/min to  $R\tau = \infty$  for runs RI8, RI9, R20 and R35. The runs at 0 rpm were not evaluated because the RTD runs indicated an instability of the flow pattern, and to obtain the RTD in this case it would be necessary to make a number of runs and average the resulting flow patterns i.e. treat the 0 rpm RTD runs as a non-stationary phenomenon.

The results obtained by Ng indicate that under various operating conditions, the values of  $R\tau$  in the main reactor cover the whole range from  $R\tau = 0$  to  $R\tau = \infty$ . Even allowing for the fact that the experimental error was estimated at 1.5 per cent, and bearing in mind that the maximum difference between the complete segregation and maximum mixedness conversions is of the order of 7 per cent, from Ng's results, we would still expect significant segregation under suitable conditions.

However, the runs were performed over only a limited range of operating conditions, and the geometry of the reactor did not make it possible to make direct comparisons with the results of other workers. The recommendations listed below were made to extend the usefulness of the work and help verify it.

### 6.2.2 Recommendations

The following recommendations for the verification of the Rippin-Ng model were made (18):

1. Test of the constancy of  $R$  at different  $k\tau_{ao}$  should be made by changing the initial concentration  $a_o$ , and if possible of  $k$ , holding  $\tau$  constant. If the model is perfect, the same value of  $R$  should be obtained for different values of  $ka_o\tau$  under identical hydrodynamic conditions.
2. The difference between the complete segregation and maximum mixedness conversions may be increased by the use of separate feed nozzles for the two reactants. The use of adiabatic reactions should also be considered to this end.
3. The simultaneous measurement of conversion and RTD should be considered. A possible system could use  $Cl_4$  in one of the reactants as a tracer.
4. The reactor system should be redesigned such that mixing conditions down to and at 0 rpm can be investigated.

5. More severe tests of the mixing model would be the use of dynamic response experiments e.g. frequency response method for comparison of the experimental and predicted behaviour of the reactor system.

### 6.3 Further Development

#### 6.3.1 Attempts at Verification

It was decided to develop the model by first rerunning some of the runs made by Ng, and then the extension of the work by changing  $k_{Ia0} \tau$  by a change in  $a_0$ . In the meanwhile, an examination of other suitable reactions, and a development of the unpremixed feeds equations would help decide which of the other recommendations (Section 6.2.2) would be of practical interest.

Experimental work was commenced with a view to obtaining familiarity with the equipment and the computer programs associated with the analysis of results. It was found that even after the elimination of all faulty techniques, both theoretical and experimental it was still not possible to reproduce the earlier results, and a comprehensive investigation of the flow system, analysis procedure and programs P3/Ng, P9E/Ng and PI2G/Ng was carried out.

#### 6.3.2 Investigation of the Experimental System

The reactor system used has been described earlier

(in Section 6.1.2) and a schematic diagram is given in Figure 6.3. Since the main interest centres on a mixing model for a single CSTR, the effects due to the premixer and outlet tube are to be eliminated, and an allowance made for them in the calculation of the experimental conversion and the RTD data. For purposes of these calculations, the premixer unit was approximated to a small well stirred region followed by a plug flow section.

FIGURE 6.3

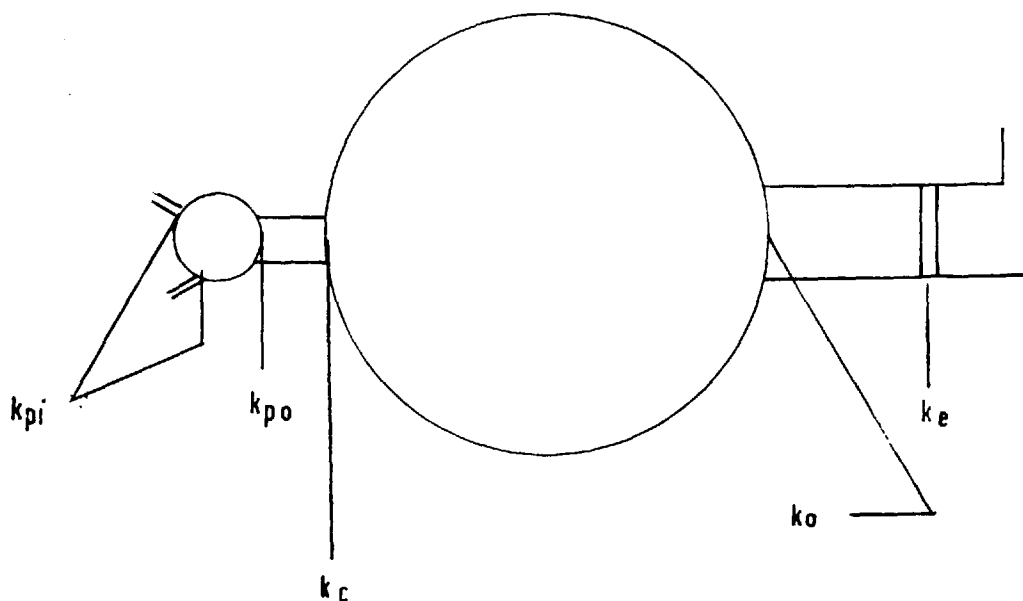


FIGURE 6.3  
SCHEMATIC REPRESENTATION OF  
REACTOR SYSTEM

## II O

The inlet conductivity was to be calculated, while the outlet conductivity  $\lambda(kc)$  was measured using a flow cell. The program P3/Ng requires the value of  $(kc)$ , the inlet conductivity at the entrance to the main reactor as a part of the data input, and this is calculated from a knowledge of the flow rates and normalities of the two reactant streams, the volumes of the perfectly mixed and plug flow sections of the premixer, and the rate constants of the reaction. Ng (I8) obtained the value of  $kc$  from:

$$kc = b(lOH' + lNa^+) \quad -(6.2)$$

where  $b$  was defined as the concentration of  $Na^+$  ions, and  $l$  as the ionic mobility.

He then goes on to state (I8)

'The initial conductivity cannot be easily measured experimentally as the reaction is fast. It was taken to be the initial conductivity of the sodium hydroxide at a concentration equivalent to the concentration of the sodium hydroxide in the starting mixtures'.

This statement does not quite clarify which concentration of sodium hydroxide was used, and seems to indicate that the value at the inlet to the premixer should be used for evaluating equation (6.2). It was later established (I9) that the value of  $b$  used in equation (6.2) was in fact the concentration of sodium hydroxide at the

inlet to the main reactor.

However, the conductivity ( $k_x$ ) at any point  $x$  in the system may be calculated from:-

$$\begin{aligned} k_x &= b \text{ } 1\text{Na}^+ + (b - Xx)1\text{OH}^{\prime} + Xx \text{ } 1\text{CH}_3\text{COO}^{\prime} \\ &= (b - Xx)(1\text{Na}^+ + 1\text{OH}^{\prime}) + Xx (1\text{Na}^+ + 1\text{CH}_3\text{COO}^{\prime}) \end{aligned}$$

where  $k_x$  = specific conductivity at  $X$

$Xx$  = concentration of acetate ions at  $X$

(6.3)

The equation (6.3) assumes that the conductivity of molecular ethyl acetate is negligible. At the start of the reaction i.e. at  $Xx = 0$ , this reduces to the form of equation (6.2), but at all other points  $Xx \neq 0$ .

In our case, this would apply to the conductivity at the inlet to the premixer and

$$k_{pi} = b_o (1\text{Na}^+ + 1\text{OH}^{\prime}) \quad \text{---(6.4)}$$

In all other cases the specific conductivity will be given by the concentration of sodium hydroxide at that point plus the contribution due to sodium acetate ions. In the results given in Tables IV.I and IV.3, the contribution of the sodium acetate ions has been neglected, and the actual conversion is higher than given by the values in Tables IV.I and IV.3. The extent of error will be discussed in Section 6.3.4.

### 6.3.3 Rate Constant

The results evaluated in Tables IV.I and IV.3

were obtained assuming the rate constant at 25°C for the reaction between sodium hydroxide and ethyl acetate as being 6.6 litre per mole per min. This value of the rate constant was measured by Denbigh, Stead and Page (6) in a continuous system, and is slightly higher than the value of 6.48 measured by Walker (29) and others (7,37,38) in a conductivity cell. The mixing equation is

$$\frac{da_L}{dx} = S(a_L) + \frac{R(\text{III } a_L - \text{IV } a_0)}{\text{II}} \quad (2.16)$$

where  $S(a_L)$  is the rate of disappearance of the reactant per unit volume in batch reaction.

Hence, although the reaction is performed in a continuous flow system, even in theory, the batch rate constant is the correct one for equation (2.16). Also it would appear that the value of 6.48 is more widely quoted in the literature. Therefor, in all future analysis, the value of the reaction rate constant will be assumed to be 6.48.

#### 6.3.4 Recalculation of Results

In the first instance, the initial concentrations at the premixer inlet which had not been published were obtained, and the original procedure for analysing the results verified (19). It was observed that the results were obtained using the specific conductivity from a graph plotted using published data. These results are given in

column A of Table 6.I, and are the same as those given in Table (IV.3). The conductivities  $k_c$  used for runs RI to RI7 are not available, and hence only runs RI8 to R36 were modified in accordance with equation (6.3), which in practice entailed the addition of the correction term  $X (1\text{Na}^+ + 1\text{CH}_3\text{COO}^-)$  to the value of  $k_c$  used for the results in column A. These results have been placed in column B of Table 6.I. Some inconsistency in runs RI9, 24 and 26 account for the absence of new values for these runs. On comparing the results in column B of Table 6.I with those in column E, wherein are placed the corresponding complete segregation conversions obtained using the experimentally measured RTDs, it will be observed that a large number of the results in column B fall outside the range of possible conversions, being higher than the corresponding conversions with complete segregation. The correction term causes an increase in conversion of the order of 3 to 4 per cent for a nominal total flow rate of 22.5 ml/min, and of 6 to 7 per cent when the nominal flow rate is 16 ml/min. The sodium acetate ions which necessitate the correction term are present in a greater concentration at the lower flow rate i.e. higher mean residence time in the premixer.

However, some dissatisfaction was felt with both the plot of specific conductivity vs concentration of Na OH, and the actual values read off at various concentrations

TABLE 6.1

Recalculated values for runs RI to R36

| Run<br>No. | A    | B    | C     | D     | E    |
|------------|------|------|-------|-------|------|
| R 3        | 80.6 | --   | 77.4  | 80.9  | 87.2 |
| R 4        | 73.4 | --   | 65.8  | 69.6  | 82.3 |
| R 5        | 72.6 | --   | 69.6  | 75.7  | 87.4 |
| R II       | 80.0 | --   | 78.5  | 84.1  | 90.8 |
| R I3       | 91.4 | --   | 87.9  | 93.1  | 91.6 |
| R I4       | 91.3 | --   | 87.0  | 92.1  | 91.8 |
| R I5       | 96.6 | --   | 100.1 | 105.5 | 92.5 |
| R I6       | 84.0 | --   | 79.0  | 84.5  | 90.3 |
| R I7       | 80.7 | --   | 76.7  | 82.1  | 90.6 |
| R I8       | 85.0 | 90.9 | 82.7  | 88.7  | 90.5 |
| R 20       | 85.0 | 91.1 | 82.0  | 88.2  | 91.0 |
| R 21       | 83.1 | 87.4 | 76.0  | 84.1  | 89.5 |
| R 23       | 85.0 | 91.1 | 82.0  | 88.2  | 91.0 |
| R 25       | 87.1 | 92.2 | 84.5  | 90.6  | 90.4 |
| R 27       | 87.9 | 90.9 | 87.4  | 93.1  | 91.1 |
| R 28       | 83.8 | 85.9 | 78.8  | 82.4  | 88.8 |
| R 29       | 85.9 | 89.5 | 82.5  | 86.1  | 89.0 |
| R 30       | 86.2 | 89.6 | 82.6  | 86.1  | 88.4 |
| R 31       | 86.4 | 89.8 | 82.8  | 86.3  | 87.7 |
| R 32       | 86.9 | 90.4 | 83.4  | 86.9  | 88.8 |
| R 33       | 84.6 | 88.1 | 81.0  | 84.5  | 88.3 |
| R 34       | 85.1 | 88.7 | 81.3  | 85.0  | 89.8 |
| R 35       | 82.3 | 85.9 | 78.0  | 81.7  | 88.1 |
| R 36       | 87.5 | 91.0 | 83.3  | 86.9  | 89.3 |

For some runs it was felt that the value of  $k_c$  was 3 per cent too high (8,10,11,21,22). It was decided that a more accurate method would be to determine the value of  $k_c$  obtaining  $\Lambda$  the equivalent conductance for sodium hydroxide from (8)

$$\Lambda = 248.85 + 116.38 \sqrt{c} + 103 c (1 - 0.2275 \sqrt{c}) \quad (6.5)$$

Columns C and D of Table (6.I) give the conversions using the original equation (6.I) and the new modified method of equation (6.3) respectively to determine the value of  $k_c$ , but obtaining the specific conductivity of sodium hydroxide using equation (6.5). The rate constant for these calculations was modified in accordance with Section 6.3.3.

An examination of Table (6.I) reveals that for some runs at a nominal flow rate of 22.5 ml/min, the decrease in the value of the specific conductivity of sodium hydroxide is approximately equal to the increase due to the correction factor of equation (3.6). However, many conversions for runs at 16 ml/min fall outside the range of possible conversions.

This reanalysis casts doubts about the validity of the previous experimental work, because far too many of the reaction runs result in conversions outside feasible limits. In many other cases, fairly low values of  $R\tau$  would be obtained indicating the presence of a high degree

of segregation. The reanalysis also shows that the sodium acetate ions in the premixer contribute significantly to the value of  $k_c$ , and their presence cannot be ignored. It was decided that further experimental work should be carried out, and methods to increase the difference between the complete segregation and maximum mixedness conversions be investigated.

#### 6.4 Further Experimental Work

Further experimental work was performed on the flow and reactor system described in Section 6.1 using the reaction between ethyl acetate and NaOH, and the data analysed using the computer programs mentioned in Section 6.2. However, the conductivities were calculated as for column D of Table 6.1, as described in Section 6.2.4. These experiments have been divided into two sets

- (1) Set S consisting of runs SI to S32
- (2) Set T consisting of runs TI to T2I

The runs for Set S were performed under similar operating conditions to those for the previous work discussed in Section 6.2, and were at reagent concentrations of approximately 0.075 N for both ethyl acetate and NaOH streams, at the start of the reaction. So as to be compatible with the RTD runs of Set D given in Table IV.2, they were performed at the two total nominal flow rates of 16 ml/min and 22.5 ml/min, the actual flow rate

for an individual run being in the vicinity of one of these values, but differing slightly in many cases. These operating conditions have been summarized in Table IV.4 of Appendix IV. The procedure for the analysis of the data has been described earlier in this section. The last column of Table (6.2) gives the difference between the experimental conversion and that for the maximum mixedness conversion using the experimental RTD. It may be pointed out that the difference between the complete segregation conversion and the corresponding maximum mixedness conversions is approximately 7 per cent for all runs of Set S. Some additional runs in which the steady state was not reached, generally due to a blockage in the flow system have been excluded. Runs SI3, SI4 have been excluded from Table 6.I due to an undetected error in the experimental data.

Set T consists of runs TI to T2I, which also consist of runs at 16 or 22.5 ml/min total flow rate. Other operating conditions are as for Set S, except the nominal inlet normalities were reduced to 0.04 N. This was in keeping with the first recommendation of Section 6.2.2. A decrease in concentration was favoured because

1. At higher concentrations the NaOH solution attacks the polythene tubing in the flow system.
2. The calculation of conductivities is less accurate at higher concentrations, common ion effects becoming very important (2I).

TABLE 6.2

Results for runs S I to S 32

| Run No. | RPM | Nominal Flow Rate | MMWs<br>RTD<br>Conv. | M.M<br>Conv. | Com Seq.<br>Conv. | Exptl.<br>Conv. | $\Delta$<br>Conv |
|---------|-----|-------------------|----------------------|--------------|-------------------|-----------------|------------------|
| S I     | 100 | 22.5              | 78.2                 | 81.9         | 84.3              | 80.8            | -1.1             |
| S 2     | 75  | 22.5              | 76.3                 | 79.9         | 83.0              | 72.8            | -7.1             |
| S 3     | 50  | 22.5              | 73.6                 | 77.7         | 80.5              | 73.2            | -4.5             |
| S 4     | 25  | 22.5              | ---                  | ---          | ---               | ---             | ---              |
| S 5     | 200 | 22.5              | 74.9                 | 78.4         | 81.7              | 77.4            | -1.0             |
| S 6     | 400 | 22.5              | 73.5                 | 76.4         | 80.4              | 74.3            | -2.1             |
| S 7     | 400 | 22.5              | 68.8                 | 71.6         | 75.0              | 70.4            | -1.2             |
| S 8     | 200 | 22.5              | 70.8                 | 74.3         | 77.4              | 70.0            | -4.3             |
| S 9     | 150 | 22.5              | 69.6                 | 73.1         | 76.0              | 71.8            | -1.3             |
| S 10    | 200 | 22.5              | 65.0                 | 68.6         | 70.3              | 67.7            | -0.9             |
| S 11    | 430 | 16.0              | 76.6                 | 78.3         | 83.7              | 75.8            | -2.5             |
| S 12    | 430 | 16                | 78.0                 | 79.7         | 85.0              | 76.9            | -2.8             |
| S 15    | 200 | 16                | 79.5                 | 81.2         | 86.3              | 75.4            | -4.1             |
| S 16    | 150 | 16                | 78.3                 | 80.2         | 85.2              | 77.3            | -2.9             |
| S 18    | 100 | 16                | 72.5                 | 74.2         | 78.9              | 75.4            | +1.2             |
| S 19    | 100 | 16                | 73.4                 | 75.3         | 80.0              | 78.8            | +3.5             |
| S 20    | 50  | 16                | 71.9                 | 74.6         | 78.1              | 73.3            | -1.3             |
| S 21    | 75  | 16                | 71.2                 | 73.0         | 77.4              | 72.8            | -0.2             |
| S 22    | 25  | 16                | 74.8                 | 77.6         | 81.7              | 77.8            | +0.2             |
| S 23    | 75  | 16                | 74.6                 | 76.6         | 81.5              | 73.4            | -3.2             |
| S 24    | 150 | 16                | 66.8                 | 69.8         | 71.4              | 65.5            | -4.3             |
| S 25    | 75  | 16.0              | 78.0                 | 80.8         | 85.0              | 82.7            | +1.9             |
| S 26    | 400 | 22.5              | 74.6                 | 76.2         | 81.4              | 75.4            | -0.8             |
| S 27    | 200 | 16                | 77.6                 | 79.3         | 84.6              | 77.2            | -2.1             |
| S 28    | 200 | 16                | 75.9                 | 77.5         | 82.9              | 78.2            | +0.5             |
| S 29    | 400 | 16                | 75.0                 | 76.7         | 81.9              | 75.2            | -1.5             |
| S 30    | 200 | 16                | 77.4                 | 79.1         | 84.4              | 81.5            | +2.4             |
| S 31    | 150 | 16                | 74.2                 | 76.2         | 81.0              | 71.1            | -5.1             |
| S 32    | 100 | 16                | 74.6                 | 76.3         | 81.6              | 75.4            | -0.9             |

Runs T1 to T3 were invalidated, probably due to the wrong reagent being put into one or both of the reagent bottles in the oil bath.

TABLE 6.3  
Derived Results for runs T1 to T21  
 Nominal Normality = 0.04N

| Run No. | RPM | Nominal Flow rate | MMWC RTD Conv. | M.M. Conv. | Com.Seg. WSRTD conv. | Exptl. Conv. | $\Delta$ Conv. |
|---------|-----|-------------------|----------------|------------|----------------------|--------------|----------------|
| T 4     | 150 | 22.5              | 66.7           | 69.9       | 72.8                 | 69.0         | -0.9           |
| T 5     | 100 | 22.5              | 68.2           | 71.9       | 74.3                 | 75.3         | -3.4           |
| T 6     | 75  | 22.5              | 64.2           | 67.5       | 70.1                 | 65.7         | -1.8           |
| T 7     | 50  | 22.5              | 64.7           | 68.4       | 70.7                 | 67.9         | -0.5           |
| T 8     | 50  | 22.5              | 68.8           | 72.5       | 74.8                 | 76.9         | +4.4           |
| T 9     | 200 | 22.5              | 71.1           | 74.1       | 76.7                 | 74.0         | -0.1           |
| T 10    | 400 | 22.5              | 66.3           | 68.8       | 72.3                 | 63.4         | -5.4           |
| T 11    | 400 | 22.5              | 68.5           | 71.0       | 74.5                 | 65.0         | -5.0           |
| T 12    | 100 | 16                | 64.7           | 65.9       | 70.7                 | 66.8         | +0.9           |
| T 13    | 150 | 16                | 67.6           | 68.9       | 74.0                 | 72.6         | +3.7           |
| T 14    | 75  | 16                | 64.8           | 67.0       | 70.8                 | 65.8         | -1.2           |
| T 15    | 50  | 16                | 67.0           | 68.8       | 73.3                 | 72.4         | +3.6           |
| T 16    | 25  | 16                | 67.7           | 69.2       | 74.1                 | 73.1         | +3.9           |
| T 17    | 150 | 16                | 67.4           | 68.7       | 73.8                 | 69.1         | +0.4           |
| T 18    | 400 | 16                | 65.2           | 66.7       | 71.3                 | 66.1         | -0.6           |
| T 19    | 200 | 16                | 67.1           | 68.4       | 73.5                 | 70.5         | +2.1           |
| T 20    | 400 | 16                | 65.9           | 67.4       | 72.1                 | 67.2         | -0.2           |
| T 21    | 150 | 16                | 65.8           | 67.1       | 72.0                 | 67.6         | +0.5           |

The actual operating conditions have been listed in Table IV.5, while the derived results are tabulated in Table 6.3. The actual values of  $R_T$  were not evaluated for reasons discussed in Section (6.5).

## 6.5 Discussion

Ng (I8) estimated the experimental error in the conversion to be 1.5 per cent, and attributed this chiefly to an error in the conductivity of 1.0 per cent, and in the flow rate of 0.5%. Though this is in itself quite a significant error, since there is only a 7 per cent difference between the (premixed) complete segregation and the corresponding maximum mixedness conversion, it was felt that this was an underestimate.

It was found that it was not possible to hold the flow rate constant to better than  $\pm 1$  per cent. The calculation of the conversion uses a model for mixing in the premixer and the value of the rate constant. It was felt that the errors in these would contribute 1.2% to the error in the conversion. Any evaluation of  $R_L$  must utilise the RTD, and the error associated with this has not been taken into account in the previous estimate. The non-linearity effect due to the tracer concentration not being zero has been estimated using a modified version of program PI2G/Ng to be about 0.5 per cent, and other errors must occur due to the deviation of the pulse from a delta function, changes in the flow rate, small differences in the operating conditions for the RTD and reaction runs etc, resulting in a cumulative error of 2 per cent. This is well borne out by the fact that for run R3I at 22.4ml/min flow rate and rpm of 25, the difference between the experimental RTD and WSRTD maximum mixedness conversions

is 2.8 per cent, while the corresponding figure for the run at 50 rpm is 4.1 per cent. It is unlikely that this difference is intrinsically larger at 50 rpm than at 25 rpm, and is more probably caused by experimental error.

However, the total error in the system is not additive, and assuming it to be random, may be estimated as the square root of the sum of the square of the individual errors, and is hence estimated at 2.7 per cent. Considering that the change in conversion attributable only to different values of  $R\tau$  is of the order of seven per cent at a maximum, this is likely to cause grave doubts about the reliability of any values of  $R\tau$  obtained.

#### 6.5.1 Results

Examining the final columns in Tables (6.2) and (6.3), in which are placed the differences between the experimental and maximum mixedness conversions using the experimental RTD, it will be observed, that unlike for the earlier results, very few have a high positive value indicating a large degree of segregation. A large number of these values fall within the range  $\pm 2.7$  per cent, indicating that within the range of experimental error, the system is near the maximum mixedness state. However, the random nature of the values would also indicate that the premixed system is not suitable to obtain reliable

values for  $R\tau$  . Hence, the actual values for  $R\tau$  have not been calculated.

For Set S, a large number of the differences lie between 0 and -1, but if the differences were evaluated using the WSRTD to obtain the maximum mixedness conversions, would give a small positive value. This leads one to believe that the RTDs are a little suspect, but have not been re-run because the premixed system is unlikely to provide suitable results.

It was decided to attempt to increase the difference between the conversion at  $R\tau = 0$  and  $R\tau = \infty$ , so as to be large in comparison with the experimental error. This would help us decide as to whether the high degree of segregation indicated previously (18) occurs in any case whatsoever.

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## CHAPTER 7.

### UNPREMIXED FEEDS

#### 7.I      Advantages of Unpremixed Feeds

As discussed in Chapter 6.5, the premixed feeds reactor system was found incapable of providing reliable estimates for the values of  $R_C$ , because the magnitude of the experimental error is of the same order as the change in conversion due to segregation. It was decided to investigate methods of increasing the difference between the complete segregation and maximum mixedness conversions and the choice appeared to be between:

1. Second order reactions using unpremixed feeds.
2. Autocatalytic reactions.
3. Non-isothermal reactions.

The third choice was eliminated as it would have required major changes in the flow system. Both second order unpremixed and Autocatalytic reactions share the characteristic that better micro mixing always increases the conversion, but the difference between the maximum mixedness and complete segregation conversions may be made much larger for the former, by suitable choice of parameters.

The effects of incomplete mixing with unpremixed feeds have not been quantified before, even though the qualitative effects have long been known intuitively. Also, since the theoretical development for the case of

unpremixed feeds has a special place in this study, it was decided to use the second order unpremixed reaction between NaOH and ethyl acetate to study the effects of incomplete mixing and to obtain values of  $R\tau$  .

## 7.2      Reactor System

### 7.2.1      Standard Reactor

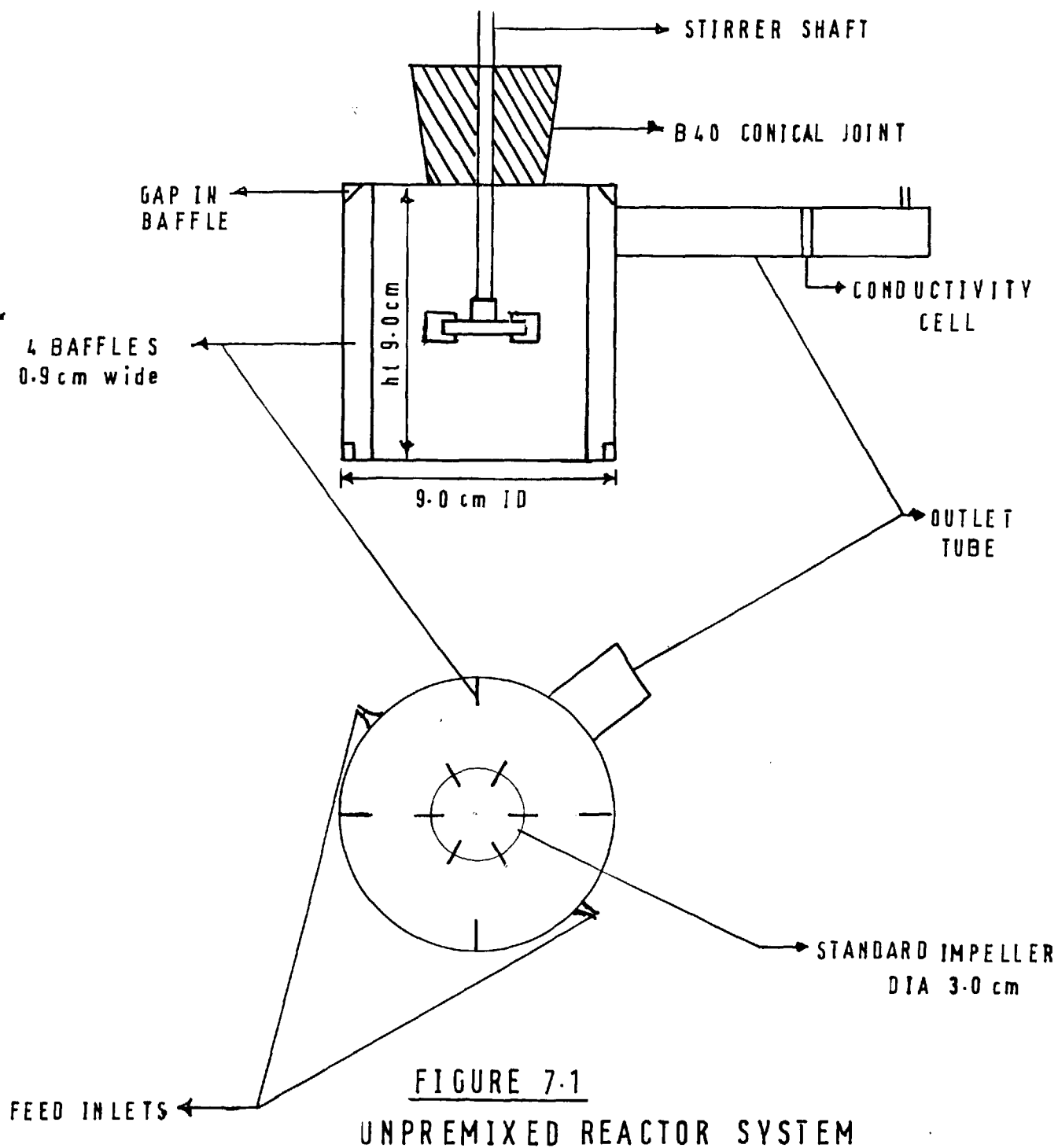
Since the reactor system used for the experimental work with premixed feeds was not directly suited for unpremixed feeds, it was necessary to modify it. The premixed feeds reactor described in Chapter 6.2 essentially consists of a sphere with four creases cut in the sides to act as baffles. It was felt that a vessel of this geometry was too individualistic to allow comparison of the data obtained with the data of other workers. Hence, the opportunity was taken to design the new reactor to fall in line with the 'Standard Reactor' put forward by Voncken et al. (25), and defined in Chapter 2.9.I.

### 7.2.2      Reactor System

In the choice of the new reactor system, some of the advantages of working on a larger scale than for premixed feeds were appreciated. However, the system was not scaled up because no reliable data had been obtained for the original size, and any major scale-up would require drastic changes in the remainder of the flow system.

From a point of view of materials of construction, the choice lay between a metallic or a glass vessel. A metallic vessel would have possessed the advantage of a more accurately defined geometry. However, a glass vessel was chosen because of the advantages that transparency provides in the removal of air from the system, and the absence of undetermined wall effects and corrosion which could arise with a metallic system. The actual construction of the vessel required great glass blowing skill, due to the necessity of sealing in the baffles.

The reactor system is illustrated schematically in Figure 7.1, and in general corresponds to the characteristics of a 'Standard Reactor'. The reactor proper consists of a glass cylinder of 9.0cm I.D. and is 9cm in depth, fitted with four baffles 90° apart. Except at the ends, the baffles run over the whole length of the wall, and are 0.9cm wide and  $\frac{1}{8}$ in thick. It was found necessary to cut off a piece at each end, so as to enable the baffles to be sealed into the reactor floor and ceiling. They were made from specially cut pyrex strips which were accurate to within 1 per cent of the width at all points. The geometry of the reactor is accurate to within 0.1cm of the stated dimensions at all points, except at the junction between the wall and the floor/ceiling, where there is a small curvature. The feed inlets were positioned half way between two baffles,



The volume of the reactor was measured with the stirrer in position, and was found to be 55ml. The volume of the outlet tube upto the middle of the conductivity cell was found to be 14.7ml. A B40 conical joint was formed at the mouth of the reactor with the help of a special mandrel. This was necessary as a standard B40 conical joint could not be attached to the reactor without leaving a neck, because heating would destroy the ground section. The remainder of the flow and stirring system is the same as described for premixed feeds in Chapter 6.

### 7.3        Experimental

#### 7.3.1     Reaction Runs

The unpremixed feeds reaction runs were performed using the flow system described in Chapter 6.1.1 and the reactor system of Section 7.2.2. The reaction between NaOH and ethyl acetate in aqueous solution was used for all runs, which have been numbered U1 to U40. The actual operating conditions are given in Table V.1 of Appendix V. Runs U1 to U7 were made using the impeller of diameter 3.3cm, while all the remaining runs used the Standard Reactor impeller of diameter 3.0cm (Section 7.2.2).

In general, the runs may be divided into those at the two nominal inlet normalities of 0.075N and 0.04N respectively. For each of these two normalities, runs were made at the two nominal total flow rates 23ml/min and

TABLE 7.I

Results for Runs U I to U 40

| Run No. | RPM | Nominal Total Flow Rate | Nominal Normality | M.M. Conv. | MMWS RTD Conv. | Exptl. Conv. Acetate | RT            |
|---------|-----|-------------------------|-------------------|------------|----------------|----------------------|---------------|
| U2      | 50  | I6                      | 0.075             | 80.9       | 80.8           | 81.4                 | <del>8</del>  |
| U3      | I50 | I6                      | 0.075             | 82.5       | 81.3           | 81.5                 | 70            |
| U5      | 50  | I6                      | 0.075             | 80.1       | 80.0           | 76.7                 | I7            |
| U6      | 75  | I6                      | 0.075             | 81.2       | 80.0           | 77.1                 | I4            |
| U7      | I50 | I6                      | 0.075             | 81.1       | 79.9           | 77.7                 | 30            |
| U8      | I00 | I6                      | 0.075             | 78.2       | 76.4           | 73.3                 | 40            |
| U9      | 20  | I6                      | 0.075             | 78.7       | 76.2           | 30.5                 | I.6           |
| UII     | 25  | I6                      | 0.075             | 79.3       | 76.8           | 45.6                 | 2.3           |
| UI2     | 50  | I6                      | 0.075             | 74.3       | 74.2           | 71.8                 | 23            |
| UI3     | 75  | I6                      | 0.075             | 76.4       | 75.2           | 78.0                 | <del>22</del> |
| UI4     | I00 | I6                      | 0.075             | 75.50      | 73.7           | 71.7                 | 40            |
| UI5     | I50 | I6                      | 0.075             | 78         | 76.8           | 75.3                 | 22            |
| UI6     | 75  | I6                      | 0.075             | 77.8       | 76.6           | 76.2                 | 42            |
| UI8     | 25  | I6                      | 0.075             | 78.4       | 75.9           | 49.1                 | 2.6           |
| UI9     | 30  | I6                      | 0.04              | 75.4       | 72.9           | 73.1                 | 24            |
| U20     | 50  | I6                      | 0.04              | 72.7       | 72.6           | 72.8                 | <del>8</del>  |
| U2I     | 75  | I6                      | 0.04              | 73.5       | 72.5           | 73.8                 | <del>8</del>  |
| U22     | I00 | I6                      | 0.04              | 74.0       | 72.2           | 73.1                 | 75            |
| U23     | 25  | I6                      | 0.04              | 75.9       | 73.4           | 73.2                 | 22            |
| U24     | 50  | I6                      | 0.04              | 71.2       | 71.1           | 70.0                 | 60            |
| U25     | 75  | I6                      | 0.04              | 72.5       | 71.5           | 73.0                 | <del>8</del>  |
| U26     | I00 | I6                      | 0.04              | 74.9       | 73.2           | 76.6                 | <del>8</del>  |

I28 (cont)

| Run No. | RPM | Nominal Total Flow Rate | Nominal Normality | M.M. Conv. | MMWS RTD Conv. | Exptl. Conv. Acetate. | RT            |
|---------|-----|-------------------------|-------------------|------------|----------------|-----------------------|---------------|
| U27     | 150 | 16                      | 0.04              | 74.3       | 73.3           | 76.7                  | <del>80</del> |
| U28     | 25  | 16                      | 0.04              | 72.7       | 70.2           | 59.9                  | 4.9           |
| U29     | 50  | 16                      | 0.04              | 71.3       | 71.2           | 71.4                  | <del>80</del> |
| U30     | 150 | 23                      | 0.075             | 70.8       | 70.1           | 67.5                  | 18            |
| U31     | 150 | 23                      | 0.075             | 72.8       | 72.1           | 68.7                  | 15            |
| U32     | 75  | 23                      | 0.075             | 74.1       | 72.1           | 73.3                  | 80            |
| U33     | 50  | 23                      | 0.075             | 72.7       | 71.4           | 70.5                  | 32            |
| U34     | 30  | 23                      | 0.075             | 74.0       | 71.8           | 69.2                  | 13            |
| U35     | 150 | 23                      | 0.04              | 66.0       | 65.4           | 65.0                  | 70            |
| U36     | 100 | 23                      | 0.04              | 65.9       | 64.5           | 66.8                  | <del>80</del> |
| U37     | 75  | 23                      | 0.04              | 68.9       | 67.1           | 69.0                  | <del>80</del> |
| U38     | 50  | 23                      | 0.04              | 67.6       | 66.5           | 68.9                  | <del>80</del> |
| U39     | 35  | 23                      | 0.04              | 70.2       | 68.0           | 67.9                  | 30            |
| U40     | 200 | 23                      | 0.04              | 67.0       | 66.2           | 67.3                  | <del>80</del> |

TABLE 7.2

Operating Conditions for RTD Runs

| <u>Run No.</u> | <u>RPM</u> | <u>EI to E9</u>         | <u><math>\tau</math></u> |
|----------------|------------|-------------------------|--------------------------|
|                |            | <u>Flow rate ml/min</u> |                          |
| E 1            | 100        | 24.05                   | 22.91                    |
| E 2            | 75         | 24.29                   | 22.68                    |
| E 3            | 50         | 23.98                   | 22.97                    |
| E 4            | 25         | 23.34                   | 23.6                     |
| E 5            | 150        | 24.34                   | 22.63                    |
| E 6            | 100        | 17.46                   | 31.557                   |
| E 7            | 75         | 17.22                   | 31.99                    |
| E 8            | 50         | 16.61                   | 33.19                    |
| E 9            | 25         | 16.35                   | 33.70                    |

16ml/min. The data were analysed using a modified version of program P3/Ng, which allows for the fact that there is no premixer in the system. These results are given in Table 7.I.

A graph of  $R\tau$  vs  $\Delta$  conversion, where  $\Delta$  conversion is the difference between the maximum mixedness conversion (using the experimental RTD) and the experimental conversion was drawn from the data given in Table V.2. When the  $\Delta$  conversion was less than 10 per cent, the value of  $R\tau$  was obtained using this data. When the value of  $\Delta$  conversion exceeds 10 per cent, the value of  $R\tau$  was obtained using program P9E/UP/UA, a modified version of program P9E/Ng. Program P9E/UP/UA calculates  $R\tau$  for a given experimental conversion with unpremixed feeds, in a similar fashion to program P9E/Ng (I8) which makes this calculation for premixed feeds. These results are placed in the last column of Table 7.I.

### 7.3.2 RTD Runs

In order to separate the effects of micromixing and RTD on the conversion, it was necessary to measure the RTD experimentally. RTD runs were made under approximately the same conditions as used for the reaction runs UI to U40 i.e. for the two nominal flow rates of 16ml/min and 23ml/min, and at the stirrer speeds of 25,50,75,100 and 150 rpm. The operating conditions for the RTD runs EI to E9 are

listed in Table 7.2, and the actual chart deflections are given in Tables V.3 to V.II.

All the data was obtained using an input pulse consisting of 2ml of a 4 per cent aqueous KCl solution, with methyl alcohol added to achieve a density correction. The output signal was measured by means of a conductivity cell in the outlet tube. This procedure has been described in detail by Ng (18).

The results thus obtained were analysed at intervals of 0.025 for  $t/\tau$  less than 0.3, and 0.05 for the remainder of the run. The minimum length for the results to be suitable data input for the associated computer programs is 4.30~~t~~, and most runs were continued for a longer period. The resulting data was then punched onto 5-hole tape.

Run E-8 at 16ml/min flow rate and 25rpm was made with a cell constant setting of 0.5 in place of the usual setting of 0.695. The two runs at 25 rpm i.e. E-4 and E9, showed a noticeable instability in the output signal, but the RTD could be obtained in a usable form. The run E9 at 16ml/min nominal flow rate was more unstable. The largest difference between the M.M conversion and the MMWSRTD conversion is 2.5 per cent for run E-9, and the lowest 0.1 per cent for run E-6. Below 25 rpm, the RTD of the system is no longer a time invariant process, and the

simultaneous measurement of the reaction runs and RTD must be made to provide meaningful results.

#### 7.4      Discussion

An examination of Table 7.I will reveal that with one exception, for all runs with a stirrer speed of 30 rpm or more, the value of  $R\tau$  is greater than 15. The exception is the run U34 at 30 rpm, for which the value of  $R\tau$  is 13. A value of  $R\tau = 15$  corresponds to a  $\Delta$  conversion of 3 per cent, and the experimental error has been estimated at 2.7 per cent (Chapter 6). Therefore, it may be stated that when the stirrer speed is above 30 rpm, the system is near the maximum mixedness end of the  $R\tau$  range. No indications of the low values of  $R\tau$ , reported under similar conditions (18) but with premixed feeds, were noticed.

For the runs carried out between 20 and 30 rpm, much larger amounts of segregation are indicated by the values of  $R\tau$  obtained. The calculated value of  $R\tau$  varies between 24 for UI9 at 30 rpm down to 1.6 for U9 at 20 rpm. However, the values of  $R\tau$  were not found to be reproducible within the range of experimental error, except for the values of  $R\tau$  at 30 rpm. A possible explanation is that the RTD is not a stationary phenomenon in this range of stirring speeds (Section 7.3.2), and in some of the runs a great deal of bypassing occurs, creating a deadwater region which considerably reduces the effective volume of the reactor.

Only the simultaneous measurement of the RTD and reaction runs could confirm whether very low values of  $R\tau$  actually occur at low stirrer speeds.

Another important conclusion which may be drawn is that unpremixed feeds have a great advantage in the study of segregation and ~~in~~complete mixing, due to the much larger values of  $\Delta$  conversion which will result if any significant degree of segregation occurs.

---

### 8.1      Conclusions

- (1)      The Rippin-Ng random mixing model was extended to cover Consecutive Parallel, Consecutive and Autocatalytic isothermal homogeneous reactions. The computer programs developed can handle any general arbitrary RTD over the whole range of  $R\tau$ . The inaccuracies at low  $R\tau$  of the original programs were eliminated.
- (2)      The effects associated with the entry of the inlet streams through different feed nozzles were formalised and quantified for the Rippin-Ng model.
- (3)      The values of  $R\tau$  obtained using the premixed feeds system were found to be unreliable due to the fact that the experimental error in the system is of the same order of magnitude as the changes in conversion due to partial segregation. Previous results were recalculated using a more accurate method of determining the inlet conductivity, and new experimental runs made. These confirmed that the premixed feeds system in its present form is not capable of providing useful estimates of  $R\tau$ .
- (4)      A 'Standard Reactor' was designed and constructed for work with unpremixed feeds. This new reactor system is capable of detecting high degrees of segregation with relative ease. The experimental results indicate that above 30 rpm,

the value of  $R\tau$  never falls below 15, indicating good micro-mixing within the system. Below a stirrer speed of 30 rpm, it is probable that the RTD is no longer a stationary phenomenon, and that the simultaneous measurement of the RTD and conversion is necessary to help decide whether the low values of  $R\tau$  obtained are in fact due to high degrees of segregation. An alternative explanation is that by-passing on a considerable scale occurs, decreasing the effective volume of the reactor, and hence lowering the conversion, without there necessarily being an increase in the extent of segregation.

(5) It appears that the choice for a model of incomplete mixing in a single CSTR lies between the Rippin-Ng and Consecutive Reactor models. A preliminary comparison was made between the behaviour of  $y^*$  and  $I/R\tau$ , and it was decided that the real criterion of suitability is the fit of the experimental data, the order of complexity for a general RTD program being the same for both models.

## 8.2 Recommendations

(1) The computer programs for the Consecutive Reactor model should be extended to be able to handle any general arbitrary RTD. This will enable a comparison of the fit of experimental data to this and the Rippin-Ng model.

(2) The system should be redesigned for larger degrees of segregation to be prevalent. This could be achieved either by an increase in the viscosity or a decrease in the mean residence time. An increase in the viscosity should reduce  $R$ , while a decrease in the mean residence will reduce  $\tau$ , the result being a decrease in  $R\tau$ .

(3) A system should be designed in which it is possible to study conversion with both premixed and unpremixed feeds under the same (or nearly the same) RTD and hydrodynamic conditions.

(4) The mixing equations for the Rippin-Ng model should be extended to cover adiabatic and other non-isothermal conditions.

(5) The fluid dynamics and micro-mixing conditions may not be reproduced in separate RTD experiments. Simultaneous measurement of conversion and RTD should be considered. A possible system would be the use of  $\text{Cl}_4$  in one of the reactants as a tracer.

(6) The reactor system should be redesigned such that mixing conditions down to and at 0 rpm could be investigated.

(7) The size of the reactor system should be scaled up. Experiments performed on a pilot plant scale would have

much more practical significance.

(8)           The use of dynamic response experiments for the comparison of the experimental and predicted behaviour of a reactor system should be considered.

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## Notations

|               |                                                                      |
|---------------|----------------------------------------------------------------------|
| a, b, c       | concentrations of A, B, C                                            |
| A, B, C       | $a/a_0$ , $b/a_0$ , $c/a_0$                                          |
| a             | concentration of ethyl acetate<br>in Experimental Section            |
| b             | concentration of NaOH in Experimental<br>Section.                    |
| D             | tank diameter.                                                       |
| F             | cumulative residence time distribution.                              |
| f             | residence time frequency function.                                   |
| J             | degree of segregation.                                               |
| k             | specific conductivity, $\Omega^{-1} \text{cm}^{-1}$<br>in Chapter 6. |
| $k_1$ , $k_2$ | reaction rate constants.                                             |
| $K_1$ , $K_2$ | $k_1 a_0$ , $k_2 a_0$                                                |
| $\bar{K}$     | $K_2/K_1$                                                            |
| l             | ionic mobility.                                                      |
| m             | amount of material in entering<br>environment                        |
| q             | volumetric flow rate                                                 |
| R             | mixing parameter.                                                    |
| t             | residence time.                                                      |
| V             | volume.                                                              |
| X             | concentration of acetate ions in<br>Chapter 6.                       |
| y             | dimensionless age $\omega/\tau$                                      |
| $y^*$         | Weinstein parameter.                                                 |

|             |                                                                      |
|-------------|----------------------------------------------------------------------|
| $z$         | dimensionless life expectation $\lambda/\tau$                        |
| $t$         | age of molecule.                                                     |
| $x$         | dimensionless concentration of<br>desired product.                   |
| $\theta$    | time.                                                                |
| $\wedge$    | equivalent conductance $\text{cm}^2 \Omega^{-1} \text{equiv}^{-1}$ . |
| $\lambda$   | life expectation of molecule.                                        |
| $\tau$      | mean residence time.                                                 |
| $F$         | cumulative age distribution                                          |
| $\phi$      | age frequency function                                               |
| $\Psi$      | cumulative life expectation distributio                              |
| $\psi$      | life expectation frequency function.                                 |
| RTD         | residence time distribution                                          |
| WSRTD       | well stirred RTD.                                                    |
| M.M.        | maximum mixedness.                                                   |
| MMWSRTD     | maximum mixedness with well stirred<br>RTD                           |
| I,II,III,IV | as defined.                                                          |

### Subscripts

|      |                               |
|------|-------------------------------|
| EXIT | at outlet from reactor.       |
| L    | value in leaving environment. |
| P    | value of a "point".           |
| o    | initial values.               |

special subscripts were defined for the conductivity  $k$   
at various points in Chapter 6.

## APPENDIX I

### Equations for 1 and 2 CSTRs RTD

We shall proceed to derive the equations employed for the specific programs for 1 and 2 CSTRs RTD. These are special cases of the more general equations derived in Chapter III.

#### I.I Consecutive Parallel Reactions

##### I.I.I 1 CSTR Premixed Feeds

In the case of Consecutive Parallel premixed reactions with a 1 CSTR RTD, the mixing equations for the leaving environment take the form:

$$\frac{dA}{dz} = K_1 A L B L - (I + R \tau) I A + A L$$

$$\frac{dB}{dz} = K_1 A L B L + K_2 B L C L - (I + R \tau) I B + B L$$

$$\frac{dC}{dz} = -K_1 A L B L + K_2 B L C L - (I + R \tau) I C + C L$$

where  $I A = \int_0^{\infty} \exp(-y(R\tau+1)) A(y) dy$   
 $I B = \int_0^{\infty} \exp(-y(R\tau+1)) B(y) dy$   
 $I C = \int_0^{\infty} \exp[-y(R\tau+1)] C(y) dy$

-(I.I)

These equations are a special case of equations (3.2I), and the values of  $A(y)$ ,  $B(y)$ ,  $C(y)$  are obtained

by the integration of the batch kinetics equation (3.20) to find the value of  $A(y)$ , the other two concentrations being obtained by substitution in equations (3.16 and 3.19).  $L_A$ ,  $L_B$ ,  $L_C$  are in fact constant with respect to  $z$ , and the concentrations at all points in the leaving environment are constant. This has been shown by Zwietering (30) to be true for simple kinetics and a I CSTR RTD.

The concentration of B at all points in the leaving environment ( $B_L$ ) is obtained from the following cubic

$$\begin{aligned} & B_L^3 [-K_1 K_2] \\ & + B_L^2 [-K_1 - K_2 + (K_B - K_C) K_1 K_2 - 2 K_A K_1 K_2] \\ & + B_L [-1 + K_B K_1 + (K_B - K_C) K_2 - K_A K_1] \\ & + K_B = 0 \end{aligned}$$

$$\begin{aligned} \text{where } K_A &= (1 + RT) L_A \\ K_B &= (1 + RT) L_B \\ K_C &= (1 + RT) L_C \end{aligned}$$

(I.2)

$B_L$  is obtained by Newton's iterative method, and the other concentrations at the exit from the leaving environment are obtained from

$$\begin{aligned} A_L &= K_A / (1 + K_1 B_L) \\ C_L &= (K_C + K_B - B_L) / (1 + 2 K_2 B_L) \end{aligned}$$

(I.3)

The concentrations in the stream leaving the CSTR are obtained in the usual manner by mixing the stream going directly from the entering environment to the exit, with the

### A3

stream from the leaving environment, in proportions compatible with the RTD, and are given by

$$\begin{aligned} A \text{ EXIT} &= \frac{KA + RTAL}{1 + RT} \\ B \text{ EXIT} &= \frac{KB + RTBL}{1 + RT} \\ C \text{ EXIT} &= \frac{KC + RTCL}{1 + RT} \end{aligned} \quad (I.4)$$

The mixing equations (I.I) have been integrated in program GP/PM/ I.CSTR. The batch kinetics for A were tabulated, and Routine 'B' was used for the interpolation, to obtain the desired values of A(y).

#### I.I.2 I CSTR Unpremixed Feeds

For Consecutive Parallel unmixed reactions with a I CSTR RTD, the mixing equations for the leaving environment take the form:

$$\begin{aligned} \frac{dA_L}{dz} &= K_1 A_L B_L - I + A_L \\ \frac{dB_L}{dz} &= K_1 A_L B_L + K_2 B_L C_L - B_L + B_L \\ \frac{dC_L}{dz} &= -K_1 A_L B_L + K_2 B_L C_L + C_L \end{aligned}$$

(I.5)

The value of BL at all points in the leaving environment may be obtained from the following cubic (see Appendix I.I.I)

$$\begin{aligned}
& B_L^3 [-K_1 K_2] \\
& + B_L^2 [K_1 K_2 B_0 - K_2 - K_1 - 2K_1 K_2] \\
& + B_L [K_2 B_0 + K_1 B_0 - 1 - K_1] \\
& + B_0 = 0
\end{aligned}$$

(I.6)

$B_L$  is obtained by Newton's iterative method, and the other concentrations at the exit from the leaving environment are:

$$\begin{aligned}
A_L &= \frac{1}{1 + K_1 B_L} \\
C_L &= \frac{B_0 - B_L}{1 + 2K_2 B_L}
\end{aligned}$$

(I.7)

The concentrations leaving the CSTR are given by

$$\begin{aligned}
A_{\text{EXIT}} &= \frac{1 + R\tau A_L}{1 + R\tau} \\
B_{\text{EXIT}} &= \frac{B_0 + R\tau B_L}{1 + R\tau} \\
C_{\text{EXIT}} &= \frac{R\tau C_L}{1 + R\tau}
\end{aligned}$$

(I.8)

The mixing equations (I.5) have been solved in program CP/UP/I CSTR.

### I.1.3    2 CSTRs RTD with Premixed Feeds

The mixing equations for the case of 2 CSTRs RTD with Consecutive Parallel premixed reaction are given by

$$\begin{aligned} \frac{dA_L}{dz} &= K_1 A_L B_L - \frac{RT(RT+z)^2}{\bar{I}_2} L_A + \frac{\bar{I}_1 A_L}{\bar{I}_2} \\ \frac{dB_L}{dz} &= K_1 A_L B_L + K_2 B_L C_L - \frac{RT(RT+z)^2}{\bar{I}_2} L_B + \frac{\bar{I}_1 B_L}{\bar{I}_2} \\ \frac{dC_L}{dz} &= -K_1 A_L B_L + K_2 B_L C_L - \frac{RT(RT+z)^2}{\bar{I}_2} L_C + \frac{\bar{I}_1 C_L}{\bar{I}_2} \end{aligned}$$

where

$$\begin{aligned} \bar{I}_1 &= RT(1 + RTz + z^2) \\ \bar{I}_2 &= RT + RTz + (RT/z)^2 + R^2 z^2 / z \\ L_A &= \int_0^\infty \exp(-y(RT+z)) A(y)(y+z) dy \\ L_B &= \int_0^\infty \exp(-y(RT+z)) B(y)(y+z) dy \\ L_C &= \int_0^\infty \exp(-y(RT+z)) C(y)(y+z) dy \end{aligned} \quad (I.9)$$

Applying Zwietering's boundary conditions, the initial value of BL for the integration of equations (I.9) is obtained from the following cubic in BL:

$$\begin{aligned} &B_L^3 [-K' K_1 K_2] \\ &+ B_L^2 [-(K')^2 K_1 - (K')^2 K_2 + (K_B - K_C) K_1 K_2 - z K_1 K_2 K_A] \\ &+ B_L [- (K')^3 + (K_B + K_C) K_1 (K') + K_B K_2 (K') - (K') K_C K_2 \\ &+ K_B (K')^2 = 0 \end{aligned}$$

where

$$\begin{aligned} (K_1) &= \bar{I}_1 / \bar{I}_2 \\ K_A &= L_A RT(RT+z)^2 / \bar{I}_2 \\ K_B &= L_B RT(RT+z)^2 / \bar{I}_2 \\ K_C &= L_C RT(RT+z)^2 / \bar{I}_2 \end{aligned} \quad (I.10)$$

BL is obtained by Newton's iterative method, and the other initial values obtained from

$$\begin{aligned}
 AL &= \frac{\overset{\Delta 6}{K_A}}{(K') + K_1 B_L} \\
 CL &= \frac{K_B + K_C - (K') B_L}{(K') + 2 K_2 B_L}
 \end{aligned}
 \tag{I.II}$$

The mixing equations (I.9) may now be integrated simultaneously, using the boundary conditions (I.I0 and I.II), and the concentrations at the exit from the reactor are obtained from

$$\begin{aligned}
 A \text{ EXIT} &= \left[ \frac{(RT+2)^2 L_A + \bar{I}_2 A_L}{1 + \bar{I}_2} \right]_{\bar{z}=0} \\
 B \text{ EXIT} &= \left[ \frac{(RT+2)^2 L_B + \bar{I}_2 B_L}{1 + \bar{I}_2} \right]_{\bar{z}=0} \\
 C \text{ EXIT} &= \left[ \frac{(RT+2)^2 L_C + \bar{I}_2 C_L}{1 + \bar{I}_2} \right]_{\bar{z}=0}
 \end{aligned}
 \tag{I.I2}$$

The mixing equations (I.9) have been integrated in program CP/PM/2CSTRs.

#### I.I.4 2 CSTRs Unpremixed Feeds

The mixing equations for Consecutive Parallel unmixed feeds and 2 CSTRs RTD take the form:

$$\begin{aligned}
 \frac{dA_L}{d\bar{z}} &= K_1 A_L B_L - \bar{I}' + \bar{I}' A_L \\
 \frac{dB_L}{d\bar{z}} &= K_1 A_L B_L + K_2 B_L C_L - \bar{I}' B_0 + \bar{I}' B_L \\
 \frac{dC_L}{d\bar{z}} &= -K_1 A_L B_L + K_2 B_L C_L + \bar{I}' C_L
 \end{aligned}$$

where  $\bar{I}' = \frac{RT(1 + 2\bar{z} + RT\bar{z})}{RT + RT\bar{z} + (RT/2)^2 + R^2 \tau^2 \bar{z}/2}$  (I.I3)

Applying Balancing's boundary conditions, the initial value of BL for the integration of equation (I.I3) may be obtained from:

$$\begin{aligned}
 & BL^2 [-K_1 K_2] \\
 & + BL^2 [-I' K_1 - I' K_2 + B_0 K_1 K_2 - 2K_1 K_2] \\
 & + BL [- (I')^2 + B_0 K_1 I' + B_0 K_2 I' - I' K_1] \\
 & + B_0 (I')^2 = 0
 \end{aligned}$$

where all terms are evaluated at  $z = 4$  (I.I4)

The other initial concentrations are obtained from

$$\begin{aligned}
 \frac{AL}{z=4} &= \left[ \frac{I'}{I' + K_1 BL} \right]_{z=4} \\
 \frac{CL}{z=4} &= \left[ \frac{I' B_0 - BL}{I' + 2 K_2 BL} \right]_{z=4}
 \end{aligned}$$

(I.I5)

The concentrations at the exit from the reactor are given by

$$\begin{aligned}
 A \text{ EXIT} &= \left[ \frac{1 + I_2 AL}{1 + I_2} \right]_{z=0} \\
 B \text{ EXIT} &= \left[ \frac{B_0 + I_2 AL}{1 + I_2} \right]_{z=0} \\
 C \text{ EXIT} &= \left[ \frac{I_2 CL}{1 + I_2} \right]_{z=0}
 \end{aligned}$$

where  $I_2 = \tau C + \tau C z + (\tau C / 2)^2 + \tau^2 C^2 z / 2$  (I.I6)

The equations have been integrated in program CP/UP/2CSTRs.

## I.2 Consecutive Premixed Reactions

### I.2.1 I CSTR RTD Consecutive Premixed Reactions

In this case, the mixing equations take the form:

$$\begin{aligned}\frac{dA_L}{dz} &= K_1 A_L^2 - L_A + A_L \\ \frac{dB_L}{dz} &= -K_1 A_L^2 + K_2 B_L^2 - L_B + B_L\end{aligned}\quad (I.I7)$$

where

$$L_A = \int_0^\infty \frac{\exp(-y)}{1 + K_1 y / (1 + R\tau)} dy$$

$$L_B = \int_0^\infty \exp(-y) B(y) dy$$

where  $B(y)$  is evaluated from

$$\frac{dB}{dy} = \frac{K_1 / (R\tau + 1)}{\left[1 + \frac{K_1 y}{1 + R\tau}\right]^2} - \frac{K_2}{1 + R\tau} B^2 \quad (I.I8)$$

b.c.  $B = 0$  at  $y = 0$ .

Equation (I.I8) is a modified version of the batch kinetics equation (3.10). Once again we have a well stirred RTD, and the R.H.S of equations (I.I7) are independent of  $z$ . The concentrations at all points in the leaving environment are given by

$$\begin{aligned}A_L &= \frac{1}{2K_1} \left[ -1 + \sqrt{1 + 4 L_A K_1} \right] \\ B_L &= \frac{1}{2K_2} \left[ -1 + \sqrt{1 + 4 (L_A + L_B - A_L) K_2} \right]\end{aligned}$$

The concentrations in the stream leaving the CSTR are given by

$$\begin{aligned} A_{EXIT} &= \frac{LA + RTAL}{1 + RT} \\ B_{EXIT} &= \frac{LB + RTBL}{1 + RT} \end{aligned} \quad (I.20)$$

The mixing equations (I.17) have been solved in program CON/I CSTR.

### I.2.2 Consecutive Premixed Reactions 2 CSTRs RTD

In this case the mixing equations take the form:

$$\begin{aligned} \frac{dA}{dz} &= K_1 A^2 - \frac{RT(RT+2)^2}{\bar{I}_2} LA + \frac{\bar{I}_1}{\bar{I}_2} AL \\ \frac{dB}{dz} &= -K_1 A^2 + K_2 B^2 - \frac{RT(RT+2)^2}{\bar{I}_2} LB + \frac{\bar{I}_1}{\bar{I}_2} BL \end{aligned}$$

where  $\bar{I}_1$ ,  $\bar{I}_2$  are as defined by equation (I.9)

$$\begin{aligned} LA &= \int_0^{\infty} \frac{\exp[-y(RT+2)] (y+z)}{1 + K_1 y} dy \\ LB &= \int_0^{\infty} B(y) \exp(-y(RT+2)) (y+z) dy \end{aligned} \quad (I.21)$$

$B(y)$  is evaluated using the batch kinetics equation for B i.e. equation (3.10). The initial values for the integration of equations (I.21) are

$$\begin{aligned} \frac{AL}{z=4} &= \frac{1}{2K_1} \left[ -[\bar{I}'] + \sqrt{(\bar{I}')^2 + 4(K_A + K_1)} \right]_{z=4} \\ \frac{BL}{z=4} &= \frac{1}{2K_2} \left[ -\bar{I}' + \sqrt{(\bar{I}')^2 + 4(K_B + K_A - \bar{I}'AL)K_2} \right]_{z=4} \end{aligned} \quad (I.22)$$

where  $\bar{I}$ ,  $K_A$ ,  $K_B$  are defined by equation (I.10)

### AIO

Equations (I.21) may now be integrated and the concentrations at the exit from the CSTR obtained from

$$\begin{aligned} A_{\text{EXIT}} &= \left[ \frac{(RT+Z)^2 LA + \bar{I} Z AL}{1 + \bar{I} Z} \right]_{Z=0} \\ B_{\text{EXIT}} &= \left[ \frac{(RT+Z)^2 LB + \bar{I} Z BL}{1 + \bar{I} Z} \right]_{Z=0} \end{aligned} \quad (I.23)$$

The equations (I.21) have been integrated in program CON/2CSTRs.

## I.3 Autocatalytic Reactions

### I.3.1 Autocatalytic Premixed Reactions I CSTR RTD

The mixing equation for Autocatalytic premixed reactions with I CSTR RTD is

$$\frac{dAL}{dz} = K_1 AL [1 + B_0 - AL] - (RT+1)(1+B_0)L_1 + AL$$

where  $L_I = \int_0^{\infty} \frac{\exp[-\gamma(1+RT)]}{1+B_0 \exp[K_1(1+B_0)\gamma]} d\gamma$  (I.24)

The concentration at all points in the leaving environment is given by

$$AL = \frac{1}{2K_1} \left[ K_1(1+B_0) + 1 \pm \sqrt{[K_1(1+B_0) + 1]^2 - 4K_1(RT+1)(1+B_0)L_1} \right] \quad (I.25)$$

The concentration at the exit from the CSTR is given by

$$A_{\text{EXIT}} = (1+B_0)L_1 + \frac{RT}{1+RT} AL \quad (I.26)$$

The mixing equation (I.24) has been solved in program AC/PM/I CSTR.

### I.3.2 Autocatalytic Unpremixed Reactions I CSTR RTD

The mixing equation for Autocatalytic unpremixed reactions with I CSTR RTD is given by

### III

$$\frac{dA_L}{dz} = K_1 [1 + B_0 - A_L] A_L - 1 + A_L$$

(I.27)

The concentration at all points in the leaving environment is given by

$$A_L = \frac{1}{2K_1} \left[ (1+B_0)K_1 + 1 \pm \sqrt{((1+B_0)K_1 + 1)^2 - 4K_1} \right]$$

(I.28)

The concentration at the exit from the reactor is given by

$$A_{EXIT} = \frac{1 + RT A_L}{1 + RT}$$

(I.29)

#### I.3.3 2 CSTRs RTD Autocatalytic Premixed Reactions

The mixing equation in this case is

$$\frac{dA_L}{dz} = K_1 A_L (1 + B_0 - A_L) + \frac{I_1}{I_2} A_L - \frac{(RT+2)^2}{I_2} L_A$$

where  $I_1$  and  $I_2$  are as defined by equation (I.9)

and 
$$L_A = \int_0^{\infty} \frac{\exp(-y(RT+2)(y+2)(1+B_0)) dy}{1 + B_0 \exp[K_1(1+B_0)y]}$$

(I.30)

The boundary condition at  $z=4$  for the integration of equation (I.20) is given by

$$\frac{A_L}{z=4} = \frac{1}{2K_1} \left[ \left( \frac{I_1}{I_2} \right) + 1 + B_0 \pm \sqrt{\left( \left( \frac{I_1}{I_2} + 1 + B_0 \right)^2 - 4K_1 \frac{(RT+2)^2}{I_2} L_A \right)} \right]$$

(I.31)

The concentration at the exit from the reactor  $z=4$  is given by

$$A_{EXIT} = \left[ \frac{\frac{AI_2}{(I_2\tau+2)^2} LA + \frac{I_2}{I_2} AL}{1 + \frac{I_2}{I_2}} \right]_{\tau=0} \quad (I.32)$$

These equations have been integrated in program AC/PM/2 CSTRs.

#### I.3.4 Autocatalytic Unpremixed Reactions 2 CSTRs RTD

The mixing equation in this case is

$$\frac{dAL}{d\tau} = K_1 AL \left[ 1 + B_0 - AL \right] - \frac{I_1}{I_2} \left[ 1 - AL \right]$$

where  $I_1$  and  $I_2$  are as defined by equations (I.9) (I.33)

The boundary condition at  $\tau=4$  for the integration of equation (I.33) is given by

$$AL_{\tau=4} = \frac{1}{2K_1} \left[ \frac{I_1}{I_2} + 1 + B_0 \pm \sqrt{\left( \frac{I_1}{I_2} + 1 + B_0 \right)^2 - 4K_1 \frac{I_1}{I_2}} \right]_{\tau=4} \quad (I.34)$$

The concentration at the exit from the reactor is given by

$$A_{EXIT} = \left[ \frac{\frac{I_2}{I_2} AL + 1}{1 + \frac{I_2}{I_2}} \right]_{\tau=0} \quad (I.35)$$

The mixing equation (I.33) has been integrated in program AC/UP/2 CSTRs.

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## APPENDIX II

### Codes for Computer Programs.

TABLE II.1

### Consecutive Parallel Reaction.

| No. | PROGRAM       | CONTENTS                                                                                                     |
|-----|---------------|--------------------------------------------------------------------------------------------------------------|
| 1   | CP/PM/I CSTR  | Calculates the conversion for Consecutive Parallel premixed reaction and I CSTR RTD.                         |
| 2   | CP/UP/ I CSTR | Same as 1 with unpremixed feeds.                                                                             |
| 3   | CP/PM/2 CSTR  | Calculates conversion with Consecutive Parallel premixed reaction and 2 CSTRs RTD.                           |
| 4   | CP/UP/2 CSTR  | Same as 3 with unpremixed feeds.                                                                             |
| 5   | CP/PM/GEN     | Calculates conversion with Consecutive Parallel premixed reaction for any arbitrary RTD when $\tau \neq 2$ . |
| 6   | CP/UP/GEN     | Same as 5 with unpremixed feeds.                                                                             |
| 7   | CP/PM/GLRT    | Same as 5 but for $2 > \tau > 0$                                                                             |
| 8   | CP/UP/GLRT    | Same as 6 but with $2 > \tau > 0$                                                                            |

TABLE II.2Consecutive Premixed Reaction

| No | PROGRAM    | CONTENTS                                                                                   |
|----|------------|--------------------------------------------------------------------------------------------|
| 1  | CON/I CSTR | Conversion with Consecutive premixed reaction and I CSTR RTD.                              |
| 2  | CON/2 CSTR | Conversion with Consecutive premixed reaction and 2 CSTR RTD.                              |
| 3  | CON/GEN    | Conversion with Consecutive premixed reaction and arbitrary RTD when $\infty > R_L \geq 2$ |
| 4  | CON/GLRT   | Same as 3 except $2 > R_L > 0$                                                             |

TABLE III.3Autocatalytic Reaction

| No | PROGRAM      | CONTENTS                                                        |
|----|--------------|-----------------------------------------------------------------|
| 1  | AC/PM/I CSTR | Conversion with Autocatalytic premixed reaction and I CSTR RTD. |
| 2  | AC/PM/2 CSTR | Conversion with Autocatalytic premixed reaction and 2 CSTR RTD. |
| 3  | AC/UP/2 CSTR | Same as for 2 with unpremixed feeds.                            |

A I4 (cont.)

| No | PROGRAM    | CONTENTS                                                                                                  |
|----|------------|-----------------------------------------------------------------------------------------------------------|
| 4  | AC/PM/GEN  | Calculates conversion with Autocatalytic premixed reaction and arbitrary RTD when $\infty > R\tau \geq 2$ |
| 5  | AC/UP/GEN  | Same as 4 with unpremixed feeds.                                                                          |
| 6  | AC/PM/GLRT | Same as 4 except $2 > R\tau > 0$                                                                          |
| 7  | AC/UP/GLRT | Same as 6 except with unpremixed feeds.                                                                   |

# APPENDIX III

Tables for Conversion vs  $R\tau$   
as depicted in Figures 5.1 to 5.9

TABLE III.1

Consecutive Parallel Premixed Reaction

$$\bar{K} = 5.00 \quad K_I = 0.544 \quad B_0 = 1.0$$

| $R\tau$ | Percentage Conversion |        |        |
|---------|-----------------------|--------|--------|
|         | 1 CSTR                | 2 CSTR | 5 CSTR |
| 1000    | 9.357                 | 10.82  | 12.07  |
| 100     | 9.402                 | 10.85  | 12.09  |
| 10      | 9.693                 | 11.08  | 12.22  |
| 1.0     | 10.26                 | 11.59  | 12.59  |
| 0.1     | 10.60                 | 11.90  | 12.74  |
| 0.01    | 10.62                 | 11.90  | 12.79  |

$$\bar{K} = 3.00 \quad K_I = 0.856 \quad B_0 = 1.0$$

| $R\tau$ | Percentage Conversion |        |        |
|---------|-----------------------|--------|--------|
|         | 1 CSTR                | 2 CSTR | 5 CSTR |
| 1000    | 13.19                 | 15.25  | 17.07  |
| 100     | 13.28                 | 15.31  | 17.11  |
| 10      | 13.84                 | 15.77  | 17.36  |
| 1.0     | 14.90                 | 16.75  | 18.13  |
| 0.1     | 15.55                 | 17.32  | 18.45  |
| 0.01    | 15.63                 | 17.35  | 18.51  |

TABLE III.2

Consecutive Parallel Premixed Reaction

$\bar{K} = 3.00$

$KI = 0.198$

$Bo = 3.00$

| RT   | Percentage Conversion |        |
|------|-----------------------|--------|
|      | I CSTR                | 2 CSTR |
| 1000 | 13.33                 | 15.59  |
| 100  | 13.33                 | 15.60  |
| 10   | 13.49                 | 15.72  |
| 1.0  | 13.83                 | 16.02  |
| 0.1  | 14.02                 | 16.21  |
| 0.01 | 14.04                 | 16.22  |

$\bar{K} = 5.00$

$KI = 0.138$

$Bo = 3.00$

| RT   | Percentage Conversion |        |
|------|-----------------------|--------|
|      | I CSTR                | 2 CSTR |
| 1000 | 9.442                 | 10.99  |
| 100  | 9.455                 | 11.00  |
| 10   | 9.540                 | 11.06  |
| 1.0  | 9.721                 | 11.22  |
| 0.1  | 9.827                 | 11.32  |
| 0.01 | 9.843                 | 11.33  |

TABLE III.3

Consecutive Parallel Unpremixed Reaction

$\bar{K} = 5.00$

$KI = 0.544$

$Bo = 1.0$

| R $\tau$ | Percentage Conversion |        |        |
|----------|-----------------------|--------|--------|
|          | 1 CSTR                | 2 CSTR | 5 CSTR |
| 1000     | 9.341                 | 10.86  | 12.06  |
| 100      | 9.258                 | 10.81  | 12.04  |
| 10       | 8.501                 | 10.17  | 11.63  |
| 1.0      | 4.675                 | 5.429  | 5.87   |
| 0.1      | 0.850                 | 0.886  | 0.912  |
| 0.01     | 0.093                 | 0.094  | 0.096  |

$\bar{K} = 3.00$

$KI = 0.856$

$Bo = 1.0$

| R $\tau$ | Percentage Conversion |        |        |
|----------|-----------------------|--------|--------|
|          | 1 CSTR                | 2 CSTR | 5 CSTR |
| 1000     | 13.17                 | 15.23  | 17.06  |
| 100      | 13.05                 | 15.16  | 17.03  |
| 10       | 11.98                 | 14.29  | 16.46  |
| 1.0      | 6.591                 | 7.664  | 8.578  |
| 0.1      | 1.198                 | 1.255  | 1.298  |
| 0.01     | 0.131                 | 0.134  | 0.136  |

TABLE III.4

Consecutive Parallel Unpremixed Reaction

$\bar{K} = 3.00$

$KI = 0.198$

$Bo = 3.00$

| $R\tau$ | Percentage Conversion |        |
|---------|-----------------------|--------|
|         | 1 CSTR                | 2 CSTR |
| 1000    | 13.30                 | 15.66  |
| 100     | 13.18                 | 15.58  |
| 10      | 12.10                 | 14.65  |
| 1.0     | 6.657                 | 7.78   |
| 0.1     | 1.210                 | 1.270  |
| 0.01    | 0.132                 | 0.135  |

$\bar{K} = 5.00$

$KI = 0.138$

$Bo = 3.00$

| $R\tau$ | Percentage Conversion |        |
|---------|-----------------------|--------|
|         | 1 CSTR                | 2 CSTR |
| 1000    | 9.431                 | 11.02  |
| 100     | 9.347                 | 10.96  |
| 10      | 8.582                 | 10.30  |
| 1.0     | 4.720                 | 5.471  |
| 0.1     | 0.858                 | 0.892  |
| 0.01    | 0.093                 | 0.095  |

TABLE III.5Consecutive Premixed Reaction

$\bar{K} = 0.118$

$KI = 3.50$

$Bo = 0$

| $R\tau$ | Percentage Conversion |        |        |
|---------|-----------------------|--------|--------|
|         | 1 CSTR                | 2 CSTR | 5 CSTR |
| 1000    | 49.04                 | 56.03  | 61.38  |
| 100     | 49.17                 | 56.09  | 61.37  |
| 10      | 49.99                 | 56.55  | 61.48  |
| 1.0     | 51.12                 | 57.60  | 62.17  |
| 0.1     | 52.01                 | 58.29  | 62.34  |
| 0.01    | 52.18                 | 58.37  | 62.37  |

TABLE III.6Consecutive Premixed Reaction

$\bar{K} = 1.36$

$KI = 1.20$

$Bo = 0$

| $R\tau$ | Percentage Conversion |        |
|---------|-----------------------|--------|
|         | 1 CSTR                | 2 CSTR |
| 1000    | 28.27                 | 32.87  |
| 100     | 28.25                 | 32.84  |
| 10      | 28.21                 | 32.73  |
| 1.0     | 28.40                 | 32.80  |
| 0.1     | 28.62                 | 33.05  |
| 0.01    | 28.66                 | 33.08  |

TABLE III.7Consecutive Premixed Reaction

$\bar{K} = 3.00$

$KI = 0.862$

$Bo = 0$

| R $\tau$ | Percentage Conversion |        |
|----------|-----------------------|--------|
|          | 1 CSTR                | 2 CSTR |
| 1000     | 22.53                 | 26.22  |
| 100      | 22.50                 | 26.22  |
| 10       | 22.37                 | 26.03  |
| 1.0      | 22.38                 | 25.93  |
| 0.1      | 22.49                 | 26.07  |
| 0.01     | 22.51                 | 26.09  |

TABLE III.8Autocatalytic Premixed Reaction

$KI = 3.3$

$Bo = 0.1$

| R $\tau$ | Percentage Conversion |        |        |
|----------|-----------------------|--------|--------|
|          | 1 CSTR                | 2 CSTR | 5 CSTR |
| 500      | 73.21                 | 82.04  | 85.86  |
| 50       | 72.14                 | 81.21  | 85.54  |
| 5.0      | 64.97                 | 74.30  | 80.02  |
| 0.5      | 54.94                 | 63.19  | 68.87  |
| 0.05     | 52.46                 | 60.49  | 66.06  |

TABLE III.9Autocatalytic Unpremixed Reaction

$$K_I = 3.3$$

$$B_0 = 0.1$$

| R <sub>T</sub> | Percentage Conversion |        |        |
|----------------|-----------------------|--------|--------|
|                | 1 CSTR                | 2 CSTR | 5 CSTR |
| 500            | 73.19                 | 82.00  | 85.78  |
| 50             | 71.90                 | 80.97  | 84.95  |
| 5.0            | 61.12                 | 69.66  | 73.95  |
| 0.5            | 24.45                 | 24.92  | 23.36  |
| 0.05           | 3.50                  | 3.26   | 2.85   |

Comparison of Rippin-Ng  
and Consecutive Reactor Models

Tables for Percentage Conversion vs  $y^*$  or  $I/RT$

TABLE III.10

Consecutive Premixed Reaction

$\bar{K} = 0.118$        $\bar{K}I = 3.50$        $Bo = 0$

| $y^*$ or<br>$I/RT$ | Conversion | ICSTR RTD | Conversion | 5CSTR RTD |
|--------------------|------------|-----------|------------|-----------|
|                    | C-R model  | Rippin-Ng | C-R model  | Rippin-Ng |
| 0                  | 49.0       | 49.0      | 61.4       | 61.4      |
| 0.1                | 50.3       | 49.9      | 61.7       | 61.5      |
| 0.4                | 51.5       | 50.5      | 62.2       | 61.9      |
| 0.8                | 51.8       | 50.9      | 62.3       | 62.1      |
| 1.2                | 51.9       | 51.3      | 62.4       | 62.2      |
| 2.0                | 52.0       | 51.8      | 62.5       | 62.3      |

TABLE III.11

Consecutive Premixed Reaction

$\bar{K} = 1.36$        $KI = 1.20$        $Bo = 0$

| $y^*$ or<br>$I/RT$ | Conversion | I CSTR    |
|--------------------|------------|-----------|
|                    | C-R model  | Rippin-Ng |
| 0                  | 28.27      | 28.27     |
| 0.1                | 28.33      | 28.25     |
| 0.4                | 28.40      | 28.30     |
| 0.8                | 28.60      | 28.39     |
| 1.2                | 28.65      | 28.45     |
| 2.0                | 28.66      | 28.50     |

TABLE III.12

Consecutive Parallel Premixed Reaction

$\bar{K} = 3.0$

$KI = 0.856$

$Bo = 1.0$

| y* or<br>-1/RT | Conversion | I CSTR    |
|----------------|------------|-----------|
|                | C-R model  | Rippin-Ng |
| 0              | 13.19      | 13.19     |
| 0.1            | 14.2       | 13.84     |
| 0.4            | 15.30      | 14.25     |
| 0.8            | 15.60      | 14.75     |
| 1.2            | 15.60      | 15.0      |
| 2.0            | 15.60      | 15.55     |

APPENDIX IVTABLE IV.IOperating Conditions for runs R I to R 36

| Run No | RPM | $k\tau_{ao}$ | $\tau$ | Calculated conv. of ethyl acetate |
|--------|-----|--------------|--------|-----------------------------------|
| R I    | 530 | 3.10         | 20.8   | 81.8                              |
| R 2    | 0   | 9.90         | 21.6   | ----                              |
| R 3    | 160 | 8.85         | 20.7   | 80.6                              |
| R 4    | 280 | 10.7         | 20.1   | 73.4                              |
| R 5    | 150 | 15.7         | 36.4   | 72.6                              |
| R 6    | 90  | 15.2         | 38.2   | 85.4                              |
| R 7    | 150 | 15.2         | 38.2   | 85.4                              |
| R 8    | 400 | 15.2         | 38.2   | 87.3                              |
| R 9    | 50  | 15.2         | 38.2   | 98.4                              |
| R 10   | 0   | 15.2         | 35.6   | ----                              |
| R 11   | 200 | 12.3         | 35.0   | 80.0                              |
| R 13   | 67  | 21.1         | 34.0   | 91.4                              |
| R 14   | 67  | 11.6         | 33.1   | 91.3                              |
| R 15   | 30  | 11.8         | 33.1   | 96.6                              |
| R 16   | 90  | 12.6         | 34.8   | 84.0                              |
| R 17   | 250 | 11.9         | 33.5   | 80.7                              |
| R 18   | 200 | 15.0         | 28.8   | 85.0                              |
| R 19   | 200 | 14.4         | 29.2   | 85.1                              |
| R 20   | 430 | 15.3         | 29.6   | 85.0                              |
| R 21   | 150 | 15.1         | 29.2   | 83.1                              |
| R 23   | 200 | 15.3         | 29.6   | 85.0                              |
| R 24   | 100 | 16.1         | 30.1   | 85.2                              |
| R 25   | 50  | 16.1         | 30.3   | 87.1                              |
| R 26   | 25  | 14.4         | 29.2   | 91.5                              |
| R 27   | 50  | 14.7         | 28.5   | 87.9                              |
| R 28   | 200 | 8.66         | 20.7   | 83.8                              |
| R 29   | 100 | 8.95         | 21.4   | 85.9                              |
| R 30   | 75  | 8.85         | 20.8   | 86.2                              |
| R 31   | 25  | 8.85         | 20.8   | 86.4                              |

| Run No. | RPM | $k\tau_{ao}$ | $\tau$ | Calculated conv. of ethyl acetate. |
|---------|-----|--------------|--------|------------------------------------|
| R 32    | 30  | 8.85         | 20.8   | 86.4                               |
| R 33    | 150 | 8.85         | 20.8   | 84.6                               |
| R 34    | 200 | 8.54         | 21.0   | 85.1                               |
| R 35    | 400 | 8.80         | 21.0   | 82.3                               |
| R 36    | 50  | 8.43         | 21.0   | 87.5                               |

TABLE IV.2

Operating conditions for pulse RTD Experiments D 16 to D 40.

| Run No | RPM | Total Flow rate ml/min | $\tau$ min |
|--------|-----|------------------------|------------|
| D 16   | 30  | 16.8                   | 28.0       |
| D 17   | 0   | 16.8                   | 28.0       |
| D 18   | 200 | 15.6                   | 30.1       |
| D 19   | 100 | 15.6                   | 30.1       |
| D 20   | 100 | 15.4                   | 30.5       |
| D 21   | 200 | 15.4                   | 30.5       |
| D 22   | 200 | 15.6                   | 30.1       |
| D 23   | 150 | 15.8                   | 29.8       |
| D 24   | 100 | 15.9                   | 29.6       |
| D 25   | 75  | 16.0                   | 29.4       |
| D 26   | 75  | 16.4                   | 28.6       |
| D 27   | 0   | 16.4                   | 28.6       |
| D 28   | 200 | 16.4                   | 28.6       |
| D 29   | 150 | 16.4                   | 28.6       |
| D 30   | 100 | 16.2                   | 29.0       |
| D 31   | 50  | 16.4                   | 28.6       |
| D 32   | 25  | 16.1                   | 29.2       |
| D 33   | 400 | 22.5                   | 20.9       |
| D 34   | 200 | 22.5                   | 20.9       |
| D 35   | 150 | 22.5                   | 20.9       |

A 26

| Run<br>No | RPM | Total Flow<br>rate ml/min | $\tau$ min |
|-----------|-----|---------------------------|------------|
| D 36      | 100 | 22.5                      | 20.9       |
| D 37      | 75  | 22.5                      | 20.9       |
| D 38      | 50  | 22.5                      | 20.9       |
| D 39      | 25  | 22.5                      | 20.9       |
| D 40      | 30  | 11.8                      | 39.8       |

TABLE IV.3

Results derived by Ng for runs R1 to R36

| Run No. | MMWSRTD Conv. | MM Conv | Comp Seg Conv WSRTD | Comp Seg Conv. | Exptl Conv | RT       |
|---------|---------------|---------|---------------------|----------------|------------|----------|
| R3      | 77.3          | 80.6    | 83.7                | 87.2           | 80.6       | 530      |
| R4      | 74.8          | 75.4    | 81.8                | 82.3           | 73.4       | ---      |
| R5      | 78.9          | 80.4    | 86.0                | 87.4           | 72.6       | ---      |
| RII     | 83.5          | 85.2    | 89.1                | 90.8           | 80.0       | ---      |
| RI3     | 83.4          | 86.2    | 89.0                | 91.6           | 91.4       | 0.65     |
| RI4     | 83.7          | 86.5    | 89.1                | 91.8           | 91.3       | 0.70     |
| RI5     | 86.6          | 88.3    | 90.0                | 92.5           | 96.6       | 0        |
| RI6     | 82.6          | 84.4    | 88.6                | 90.3           | 84.0       | ---      |
| RI7     | 83.3          | 85.0    | 88.9                | 90.6           | 80.7       | ---      |
| RI8     | 82.6          | 85.1    | 88.9                | 90.5           | 85.0       | $\infty$ |
| RI9     | 83.5          | 85.1    | 89.5                | 91.0           | 85.1       | $\infty$ |
| R20     | 83.2          | 84.9    | 89.4                | 91.0           | 85.0       | $\infty$ |
| R21     | 80.8          | 82.8    | 87.6                | 89.5           | 83.1       | 210      |
| R23     | 83.2          | 84.9    | 89.4                | 91.0           | 85.0       | $\infty$ |
| R24     | 81.3          | 83.0    | 88.1                | 89.8           | 85.2       | 78       |
| R25     | 81.9          | 83.9    | 88.6                | 90.4           | 87.1       | 10.5     |
| R26     | 83.5          | 86.3    | 89.5                | 92.0           | 91.5       | 7.7      |
| R27     | 83.1          | 85.1    | 89.3                | 91.1           | 87.9       | 10.6     |
| R28     | 79.4          | 83.0    | 85.4                | 88.8           | 83.8       | 27.5     |
| R29     | 79.4          | 83.1    | 85.5                | 89.0           | 85.9       | 9.1      |
| R30     | 78.7          | 82.3    | 84.9                | 88.4           | 86.2       | 1.28     |
| R31     | 78.7          | 81.5    | 84.9                | 87.7           | 86.4       | 0.45     |
| R32     | 78.7          | 82.8    | 84.9                | 88.8           | 86.9       | 1.25     |
| R33     | 78.7          | 82.2    | 84.9                | 88.3           | 84.6       | 11.3     |
| R34     | 80.9          | 84.4    | 86.4                | 89.8           | 85.1       | 28       |
| R35     | 79.4          | 82.2    | 85.4                | 88.1           | 82.3       | $\infty$ |
| R36     | 79.4          | 83.5    | 85.4                | 89.3           | 87.5       | 1.26     |

TABLE IV.4  
Operating Conditions for runs SI to S32

| Run No. | RPM | FLOW RATE |       |         | N at Premixer Entry |         | Final Conductivity | Conv % Ethyl Acetate |
|---------|-----|-----------|-------|---------|---------------------|---------|--------------------|----------------------|
|         |     | NaOH      | Total | Acetate | NaOH                | Acetate |                    |                      |
| SI      | 100 | 12.54     | 23.13 | 10.59   | 0.08023             | 0.06684 | 9.3                | 80.8                 |
| S2      | 75  | 11.96     | 22.81 | 10.85   | 0.07762             | 0.06947 | 9.15               | 72.8                 |
| S3      | 50  | 11.32     | 22.40 | 11.08   | 0.07413             | 0.07204 | 8.1                | 73.15                |
| S5      | 200 | 11.39     | 22.13 | 10.74   | 0.07565             | 0.07135 | 8.1                | 77.36                |
| S6      | 400 | 11.58     | 22.80 | 11.22   | 0.07466             | 0.07234 | 8.1                | 74.27                |
| S7      | 400 | 10.96     | 23.10 | 12.14   | 0.0680              | 0.07364 | 6.95               | 70.4                 |
| S8      | 200 | 10.84     | 22.6  | 11.76   | 0.06971             | 0.07204 | 7.50               | 69.9                 |
| S9      | 150 | 10.50     | 22.00 | 11.50   | 0.06835             | 0.07336 | 6.9                | 71.8                 |
| SI0     | 200 | 10.69     | 23.56 | 12.87   | 0.06520             | 0.07647 | 6.35               | 67.7                 |
| SI1     | 430 | 7.82      | 15.66 | 7.84    | 0.07171             | 0.07009 | 7.51               | 75.4                 |
| SI2     | 430 | 7.94      | 15.72 | 7.78    | 0.07471             | 0.07077 | 7.95               | 76.9                 |
| SI5     | 200 | 7.71      | 15.06 | 7.34    | 0.07575             | 0.06975 | 8.39               | 75.4                 |
| SI6     | 150 | 7.92      | 15.64 | 7.72    | 0.07489             | 0.07058 | 8.00               | 77.3                 |
| SI8     | 100 | 7.79      | 16.24 | 8.45    | 0.07165             | 0.07701 | 6.75               | 75.4                 |
| SI9     | 100 | 7.99      | 16.46 | 8.47    | 0.0724              | 0.0761  | 6.70               | 78.8                 |
| S20     | 50  | 7.79      | 16.34 | 8.55    | 0.07117             | 0.07747 | 6.80               | 73.3                 |
| S21     | 75  | 8.06      | 16.96 | 8.91    | 0.07095             | 0.07771 | 6.78               | 72.8                 |
| S22     | 25  | 7.68      | 15.64 | 7.96    | 0.07331             | 0.07531 | 7.05               | 77.8                 |
| S23     | 75  | 7.92      | 16.11 | 8.19    | 0.07339             | 0.07524 | 7.49               | 73.39                |
| S24     | 150 | 7.09      | 15.78 | 8.69    | 0.06704             | 0.08150 | 6.30               | 65.5                 |
| S25     | 75  | 8.11      | 15.88 | 7.76    | 0.07634             | 0.0723  | 7.60               | 82.7                 |
| S26     | 400 | 7.45      | 15.61 | 8.16    | 0.07373             | 0.07632 | 7.25               | 75.4                 |
| S27     | 200 | 7.57      | 15.34 | 7.76    | 0.07631             | 0.07318 | 7.88               | 77.2                 |
| S28     | 200 | 7.66      | 15.78 | 8.12    | 0.07499             | 0.07512 | 7.40               | 78.1                 |
| S29     | 400 | 7.54      | 15.71 | 8.17    | 0.07415             | 0.07592 | 7.40               | 75.2                 |
| S30     | 200 | 7.72      | 15.64 | 7.92    | 0.07626             | 0.07392 | 7.48               | 81.5                 |
| S31     | 150 | 7.59      | 15.95 | 8.35    | 0.07358             | 0.07647 | 7.60               | 71.1                 |
| S32     | 100 | 7.90      | 16.46 | 8.55    | 0.07421             | 0.07587 | 7.45               | 75.4                 |

TABLE IV.5  
Operating Conditions for runs TI to T2I

| Run No. | RPM | FLOW RATE |       |         | N at Premixer Entry |         | Final Conductivity | Exptl. Conversion |
|---------|-----|-----------|-------|---------|---------------------|---------|--------------------|-------------------|
|         |     | N.O.H     | TOTAL | ACETATE | N.O.H               | ACETATE |                    |                   |
| T4      | I50 | II.58     | 22.54 | IO.96   | 0.039I9             | 0.03637 | 5.0                | 69.0              |
| T5      | I00 | II.78     | 22.40 | IO.62   | 0.040I2             | 0.03554 | 4.92               | 75.3              |
| T6      | 75  | II.09     | 22.46 | II.37   | 0.03767             | 0.03795 | 4.70               | 65.7              |
| T7      | 50  | II.35     | 22.7I | II.36   | 0.03805             | 0.03752 | 4.65               | 67.9              |
| T8      | 50  | II.9I     | 22.35 | IO.44   | 0.04065             | 0.0350I | 5.03               | 76.9              |
| T9      | 200 | II.40     | 22.63 | II.23   | 0.04I3I             | 0.03250 | 5.60               | 74.0              |
| TI0     | 400 | IO.3I     | 22.25 | II.94   | 0.03799             | 0.035I5 | 5.I                | 63.4              |
| TII     | 400 | IO.86     | 22.57 | II.7I   | 0.03946             | 0.03399 | 5.45               | 65.0              |
| TI2     | I00 | 7.86      | I6.20 | 8.34    | 0.03459             | 0.03745 | 3.93               | 66.8              |
| TI3     | I50 | 7.96      | I5.84 | 7.88    | 0.03583             | 0.036I9 | 4.03               | 72.6              |
| TI4     | 75  | 7.77      | I6.02 | 8.25    | 0.03458             | 0.03746 | 3.97               | 65.8              |
| TI5     | 50  | 8.05      | I6.II | 8.06    | 0.03562             | 0.03639 | 3.98               | 72.4              |
| TI6     | 25  | 8.I3      | I6.I0 | 7.97    | 0.03600             | 0.0360I | 4.07               | 73.I              |
| TI7     | I50 | 7.97      | I5.89 | 7.92    | 0.03575             | 0.03626 | 4.I8               | 69.I              |
| TI8     | 400 | 7.95      | I6.27 | 8.32    | 0.03484             | 0.03720 | 4.04               | 66.I              |
| TI9     | 200 | 8.I0      | I6.I6 | 8.06    | 0.03573             | 0.03629 | 4.04               | 70.5              |
| T20     | 400 | 8.03      | I6.27 | 8.24    | 0.035I9             | 0.03684 | 4.I0               | 67.2              |
| T2I     | I50 | 8.00      | I6.23 | 8.23    | 0.035I4             | 0.03689 | 4.06               | 67.6              |

N.B. Runs SI to SI6 and TI to TII used Ng premixer  
Runs SI7 to S32 and TI2 to T2I used new  
premixer.

Dimensions of new premixer:

Total volume = 3.363 ml.

Plug flow section = 0.997 ml.

## APPENDIX V

## UNPREMIXED FEEDS EXPERIMENTAL DATA

Table V.I

Operating Conditions for Runs UI to U40

| Run<br>NO | RPM | FLOW RATE |       |        | NORALITY |         | Final<br>Conduct. | CONV.<br>ACET<br>ATE |
|-----------|-----|-----------|-------|--------|----------|---------|-------------------|----------------------|
|           |     | NaOH      | TOTAL | Acetic | NaOH     | ACETATE |                   |                      |
| UI        | 100 |           |       |        |          |         |                   | 73.1                 |
| U2        | 50  | 7.91      | 16.31 | 8.39   | 0.07669  | 0.07103 | 7.92              | 81.4                 |
| U3        | 150 | 7.97      | 16.33 | 8.35   | 0.07717  | 0.07059 | 8.05              | 81.5                 |
| U5        | 50  | 7.97      | 16.59 | 8.61   | 0.07597  | 0.07164 | 8.13              | 76.7                 |
| U6        | 75  | 7.97      | 16.59 | 8.61   | 0.07597  | 0.07164 | 8.10              | 77.1                 |
| U7        | 150 | 7.95      | 16.56 | 8.61   | 0.07583  | 0.07172 | 8.00              | 77.7                 |
| U8        | 100 | 7.82      | 16.31 | 8.49   | 0.07539  | 0.07940 | 7.48              | 73.3                 |
| U9        | 25  | 7.74      | 16.07 | 8.33   | 0.07463  | 0.07907 | 11.0              | 30.5                 |
| UII       | 25  | 8.09      | 16.35 | 8.25   | 0.07452  | 0.07724 | 9.9               | 45.6                 |
| UI2       | 50  | 7.91      | 16.49 | 8.57   | 0.07226  | 0.07953 | 7.0               | 71.8                 |
| UI3       | 75  | 8.05      | 16.56 | 8.51   | 0.07317  | 0.07861 | 7.16              | 78.0                 |
| UI4       | 100 | 7.89      | 16.52 | 8.63   | 0.07190  | 0.07990 | 6.9               | 71.7                 |
| UI5       | 150 | 8.31      | 16.74 | 8.43   | 0.07471  | 0.07714 | 7.4               | 75.3                 |
| UI6       | 75  | 8.31      | 16.78 | 8.47   | 0.07453  | 0.07722 | 7.26              | 76.2                 |
| UI7       | 50  | 8.31      | 16.84 | 8.53   | 0.07427  | 0.07749 | 7.62              | 71.8                 |
| UI8       | 25  | 8.35      | 16.98 | 8.63   | 0.07402  | 0.07775 | 9.6               | 49.1                 |
| UI9       | 25  | 8.53      | 17.23 | 8.69   | 0.04126  | 0.03885 | 4.9               | 73.1                 |
| U20       | 50  | 8.26      | 16.81 | 8.56   | 0.04090  | 0.03918 | 4.8               | 72.8                 |
| U21       | 75  | 8.34      | 16.97 | 8.63   | 0.04091  | 0.03918 | 4.75              | 73.8                 |
| U22       | 100 | 8.22      | 16.84 | 8.62   | 0.04066  | 0.03941 | 4.70              | 73.1                 |
| U23       | 25  | 8.49      | 17.01 | 8.51   | 0.04159  | 0.03854 | 5.0               | 73.2                 |
| U24       | 50  | 8.51      | 17.37 | 8.85   | 0.03897  | 0.03792 | 4.68              | 70.0                 |
| U25       | 75  | 8.73      | 17.71 | 8.97   | 0.03921  | 0.03749 | 4.62              | 73.0                 |
| U26       | 100 | 8.61      | 17.11 | 8.49   | 0.04002  | 0.03674 | 4.69              | 76.6                 |
| U27       | 150 | 8.61      | 17.09 | 8.47   | 0.04007  | 0.03669 | 4.70              | 76.7                 |
| U28       | 25  | 8.04      | 16.77 | 8.73   | 0.03809  | 0.03853 | 4.95              | 59.9                 |
| U29       | 50  | 8.50      | 17.22 | 8.73   | 0.03921  | 0.03752 | 4.70              | 71.4                 |
| U30       | 150 | 11.01     | 23.09 | 12.08  | 0.07009  | 0.07952 | 7.1               | 67.5                 |

| Run No | RPM | FLOW RATE |       |         | NORMALITY |         | Final Conduct | Conv Aceto % |
|--------|-----|-----------|-------|---------|-----------|---------|---------------|--------------|
|        |     | NaOH      | TOTAL | Acetone | NaOH      | Acetate |               |              |
| U31    | 150 | 11.21     | 23.07 | 11.86   | 0.07141   | 0.07815 | 7.33          | 68.7         |
| U32    | 75  | 11.41     | 23.17 | 11.76   | 0.07236   | 0.07711 | 7.20          | 73.3         |
| U33    | 50  | 11.26     | 23.07 | 11.80   | 0.07179   | 0.07776 | 7.30          | 70.5         |
| U34    | 30  | 11.42     | 23.29 | 11.86   | 0.07212   | 0.07736 | 7.55          | 69.2         |
| U35    | 150 | 10.98     | 23.32 | 12.34   | 0.03814   | 0.03981 | 4.61          | 65.0         |
| U36    | 100 | 10.88     | 23.32 | 12.44   | 0.03774   | 0.04014 | 4.4           | 66.8         |
| U37    | 75  | 11.60     | 23.81 | 12.12   | 0.03946   | 0.03858 | 4.80          | 69.0         |
| U38    | 50  | 11.62     | 24.02 | 12.39   | 0.03919   | 0.03884 | 4.72          | 68.9         |
| U39    | 35  | 11.72     | 23.72 | 12.00   | 0.04002   | 0.03806 | 5.03          | 67.9         |
| U40    | 200 | 11.70     | 24.24 | 12.53   | 0.03910   | 0.03892 | 4.78          | 67.3         |

TABLE V.2

R<sub>T</sub> vs  $\Delta$  Conversion

Data obtained assuming K = 10.157 and the  
RTD data of run D 33

| R <sub>T</sub> | $\Delta$ Conversion per cent. |
|----------------|-------------------------------|
| 100            | 0.51                          |
| 20             | 3.51                          |
| 9.0            | 6.97                          |
| 7.5            | 8.31                          |
| 5.0            | 12.23                         |

TABLE V.3

Original data of Run E-I

| Chart      | 100 RPM    | $\tau = 22.91$ min | Chart         |
|------------|------------|--------------------|---------------|
| Deflection | Chart      | Chart              | Chart         |
| Deflection | Deflection | Deflection         | Deflection    |
| 0          | 35         | 5.8                | I.7           |
| I08        | 34         | 5.5                | I.6           |
| II7        | 33         | 5.3                | I.6           |
| I22        | 31         | 5.1                | I.5           |
| I25        | 30         | 4.8                | I.5           |
| I26        | 28         | 4.5                | I.4           |
| I26        | 26         | 4.3                | I.4           |
| I20        | 25.5       | 4.1                | I.4           |
| II7        | 24         | 3.9                | I.3           |
| II5        | 23         | 3.8                | I.3           |
| III        | 21.5       | 3.4                | I.2           |
| I08        | 20.5       | 3.3                | I.2           |
| I06        | I9.5       | 3.2                | I.1           |
| I02        | I7.7       | 3.0                | I.0           |
| 99         | I6.7       | 2.9                | 0.9           |
| 96         | I5.7       | 2.8                | 0.9           |
| 93         | I5.1       | 2.8                | 0.9           |
| 87         | I5.4       | 2.7                | 0.8           |
| 82         | I3.4       | 2.6                | 0.8           |
| 77         | I2.8       | 2.5                | 0.7           |
| 74         | I2.1       | 2.5                | 0.7           |
| 71         | II.5       | 2.4                | 0.7           |
| 67         | I0.8       | 2.3                | 0.7           |
| 63         | I0.3       | 2.3                | 0.6           |
| 61         | 9.6        | 2.3                | 0.6           |
| 57         | 9.1        | 2.2                | 0.6           |
| 54         | 8.9        | 2.2                | 0.6           |
| 51         | 8.5        | 2.2                | 0.5           |
| 49         | 8.1        | 2.2                | 0.5           |
| 45         | 8.6        | 2.1                | 0.4           |
| 43         | 7.1        | 2.1                | 0.4           |
| 41         | 6.7        | 2.0                | 0.4           |
| 38         | 6.4        | I.9                |               |
| 36         | 6.1        | I.8                | at $y = 6.35$ |

TABLE V.4  
Original Data of Run E-2

75 RPM       $\tau = 23.77$  min

| Chart Deflection | Chart Deflection | Chart Deflection | Chart Deflection |
|------------------|------------------|------------------|------------------|
| 0                | 41               | 9.1              | 2.25             |
| 94               | 40               | 8.7              | 2.20             |
| 118              | 37               | 8.1              | 2.10             |
| 125              | 35               | 7.5              | 2.00             |
| 126              | 33               | 6.8              | 1.90             |
| 127              | 32               | 6.7              | 1.85             |
| 127              | 30               | 6.3              | 1.75             |
| 121              | 28               | 6.0              | 1.68             |
| 118              | 27               | 5.9              | 1.60             |
| 117              | 27               | 5.8              | 1.52             |
| 115              | 25               | 5.5              | 1.45             |
| 112              | 24               | 5.35             | 1.40             |
| 105              | 23               | 5.10             | 1.32             |
| 100              | 21.8             | 4.80             | 1.25             |
| 97               | 20.8             | 4.60             | 1.20             |
| 93               | 19.7             | 4.40             | 1.14             |
| 87               | 18.7             | 4.18             | 1.09             |
| 85               | 17.8             | 4.00             | 1.02             |
| 80               | 16.7             | 3.90             | 0.97             |
| 76               | 15.9             | 3.70             | 0.92             |
| 71               | 15.2             | 3.55             | 0.87             |
| 68               | 14.5             | 3.45             | 0.82             |
| 64               | 13.7             | 3.30             | 0.76             |
| 58               | 13.0             | 3.20             | 0.72             |
| 55               | 12.4             | 3.05             | 0.68             |
| 52               | 11.8             | 2.95             | 0.63             |
| 50               | 11.1             | 2.80             | 0.58             |
| 47               | 10.8             | 2.70             | 0.50             |
| 45               | 10.0             | 2.55             | at $y = 5.65$    |
| 43               | 9.5              | 2.35             | .                |

TABLE V.5

Original data of Run E-3

50 RPM

 $\tau = 23.88$  min

| Chart<br>Deflection | Chart<br>Deflection | Chart<br>Deflection | Chart<br>Deflection |
|---------------------|---------------------|---------------------|---------------------|
| 0                   | 31                  | 4.3                 | 0.71                |
| 77                  | 29.5                | 4.1                 | 0.68                |
| II6                 | 29                  | 3.8                 | 0.64                |
| II6                 | 26                  | 3.7                 | 0.61                |
| II6                 | 25                  | 3.5                 | 0.57                |
| II6                 | 24                  | 3.3                 | 0.53                |
| II5                 | 22                  | 3.2                 | 0.51                |
| II5                 | 21                  | 3.0                 | 0.48                |
| II4                 | 20                  | 2.9                 | 0.46                |
| I09                 | 19                  | 2.8                 | 0.44                |
| I08                 | 18                  | 2.6                 | 0.42                |
| I05                 | 17                  | 2.5                 | 0.39                |
| I03                 | 16                  | 2.4                 | 0.37                |
| 98                  | 15                  | 2.3                 | 0.35                |
| 90                  | 14                  | 2.2                 | 0.32                |
| 87                  | 13                  | 2.0                 | 0.30                |
| 84                  | 12.5                | 1.81                | 0.28                |
| 79                  | 12                  | 1.81                | 0.28                |
| 74                  | 11.5                | 1.79                | 0.26                |
| 70                  | 11                  | 1.67                | 0.24                |
| 69                  | 10.5                | 1.57                | 0.22                |
| 65                  | 10                  | 1.49                | 0.21                |
| 62                  | 9.5                 | 1.41                | 0.21                |
| 59                  | 8.5                 | 1.34                | 0.20                |
| 55                  | 8.0                 | 1.26                | 0.17                |
| 53                  | 8.0                 | 1.21                | 0.16                |
| 50                  | 7.3                 | 1.16                | 0.16                |
| 48                  | 6.8                 | 1.10                | 0.16                |
| 45                  | 6.4                 | 1.08                | 0.14                |
| 44                  | 6.0                 | 1.03                | 0.14                |
| 41                  | 5.6                 | 0.98                | 0.14                |
| 39                  | 5.2                 | 0.90                | 0.12                |
| 36                  | 5.0                 | 0.85                | 0.12                |
| 34                  | 4.78                | 0.81                |                     |
| 32                  | 4.52                | 0.77                | at $y = 6.6$        |

A 35  
TABLE V.6

Original data of Run E-4

25 RPM       $\tau = 23.65 \text{ min}$

| <u>Chart</u><br><u>Deflection</u> | <u>Chart</u><br><u>Deflection</u> | <u>Chart</u><br><u>Deflection</u> | <u>Chart</u><br><u>Deflection</u> |
|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| 0                                 | 36                                | 7.6                               | 1.46                              |
| 82                                | 35                                | 7.3                               | 1.40                              |
| I03                               | 33                                | 6.8                               | 1.31                              |
| I08                               | 32                                | 6.5                               | 1.25                              |
| II2                               | 29                                | 6.2                               | 1.19                              |
| II4                               | 28                                | 5.9                               | 1.12                              |
| II4                               | 27                                | 5.5                               | 1.10                              |
| II4                               | 26.5                              | 5.3                               | 1.06                              |
| III                               | 25.1                              | 5.0                               | 0.96                              |
| I08                               | 24.2                              | 4.7                               | 0.90                              |
| I07                               | 22.6                              | 4.5                               | 0.85                              |
| I03                               | 21.4                              | 4.3                               | 0.80                              |
| I00                               | 21.0                              | 4.1                               | 0.76                              |
| 96                                | 20.0                              | 3.8                               | 0.73                              |
| 90                                | 18.8                              | 3.6                               | 0.69                              |
| 86                                | 18.0                              | 3.5                               | 0.66                              |
| 83                                | 17.2                              | 3.3                               | 0.62                              |
| 79                                | 16.2                              | 3.2                               | 0.57                              |
| 74                                | 15.6                              | 3.0                               | 0.55                              |
| 72                                | 14.8                              | 2.8                               | 0.53                              |
| 69                                | 14.0                              | 2.7                               | 0.47                              |
| 65                                | 13.4                              | 2.5                               | 0.46                              |
| 62                                | 12.6                              | 2.4                               | 0.41                              |
| 59                                | 12.0                              | 2.3                               | 0.41                              |
| 55                                | 11.2                              | 2.1                               | 0.39                              |
| 51                                | 10.8                              | 2.0                               | 0.36                              |
| 49                                | 10.2                              | 1.91                              | 0.36                              |
| 46                                | 9.8                               | 1.78                              | 0.35                              |
| 44                                | 9.0                               | 1.71                              | 0.32                              |
| 42                                | 8.8                               | 1.70                              | at y = 5.75                       |
| 39                                | 8.3                               | 1.64                              |                                   |
| 38                                | 7.9                               | 1.55                              |                                   |

TABLE V.7

Original data of Run E-5150 RPM  $\tau_c = 22.63$  min

| Chart<br>Deflection | Chart<br>Deflection | Chart<br>Deflection | Chart<br>Deflection |
|---------------------|---------------------|---------------------|---------------------|
| 0                   | 44                  | 9.9                 | 2.0                 |
| 67                  | 41                  | 9.5                 | 1.80                |
| 112                 | 39                  | 9.0                 | 1.65                |
| 116                 | 37                  | 8.5                 | 1.50                |
| 118                 | 35                  | 7.9                 | 1.40                |
| 117                 | 33                  | 7.7                 | 1.30                |
| 116                 | 32                  | 7.2                 | 1.25                |
| 113                 | 30                  | 7.0                 | 1.15                |
| 111                 | 29                  | 6.5                 | 1.05                |
| 108                 | 27                  | 6.0                 | 0.85                |
| 106                 | 26                  | 5.8                 | 0.80                |
| 104                 | 25                  | 5.5                 | 0.70                |
| 99                  | 23.5                | 5.2                 | 0.55                |
| 94                  | 22.5                | 5.0                 | 0.35                |
| 89                  | 21.5                | 4.6                 | 0.32                |
| 85                  | 20                  | 4.2                 | 0.30                |
| 82                  | 19                  | 4.0                 | 0.23                |
| 77                  | 18                  | 3.8                 | 0.15                |
| 74                  | 17                  | 3.6                 | 0.1                 |
| 70                  | 16                  | 3.4                 | 0.1                 |
| 67                  | 15.5                | 3.2                 | 0.05                |
| 64                  | 14.5                | 3.0                 | 0.05                |
| 60                  | 14                  | 2.8                 | at $y=4.8$          |
| 56                  | 13                  | 2.4                 |                     |
| 53                  | 12                  | 2.4                 |                     |
| 49                  | 11.5                | 2.2                 |                     |
| 47                  | 10.5                | 2.1                 |                     |

$\Lambda$  37  
 TABLE V.8  
Original Data of Run E-6

100 RPM       $\tau = 31.557$  min

| Chart<br>Deflection | Chart<br>Deflection | Chart<br>Deflection | Chart<br>Deflection |
|---------------------|---------------------|---------------------|---------------------|
| 0                   | 54                  | I3                  | 2.8                 |
| I04                 | 51                  | I2.5                | 2.6                 |
| I24                 | 48                  | II                  | 2.4                 |
| I25                 | 47                  | II.5                | 2.3                 |
| I25                 | 44                  | IO.5                | 2.1                 |
| I24                 | 42                  | IO                  | 2.0                 |
| II8                 | 40                  | 9.3                 | 1.9                 |
| II4                 | 37                  | 8.9                 | 1.8                 |
| III                 | 35                  | 8.5                 | 1.7                 |
| I08                 | 33                  | 8.0                 | 1.6                 |
| I07                 | 31                  | 7.6                 | 1.4                 |
| I04                 | 30                  | 7.1                 | 1.3                 |
| I03                 | 28                  | 6.9                 | 1.2                 |
| 98                  | 27                  | 6.4                 | 1.2                 |
| 93                  | 26                  | 6.0                 | 1.0                 |
| 90                  | 25                  | 5.6                 | 0.9                 |
| 85                  | 23                  | 5.5                 | 0.84                |
| 87                  | 22                  | 5.3                 | 0.76                |
| 82                  | 21                  | 5.1                 | 0.67                |
| 78                  | 20                  | 4.9                 | 0.59                |
| 75                  | 19                  | 4.3                 | 0.30                |
| 71                  | 18                  | 4.0                 | 0.28                |
| 68                  | 17                  | 3.8                 | 0.20                |
| 64                  | 16                  | 3.6                 | 0.16                |
| 61                  | 15.5                | 3.4                 | 0.16                |
| 58                  | 15                  | 3.2                 | at y= 5.0           |
| 56                  | 14                  | 3.0                 |                     |

TABLE V.9

Original Data of Run E-775 RPM  $\tau = 31.99$  min

| Chart<br>Deflection | Chart<br>Deflection | Chart<br>Deflection | Chart<br>Deflection |
|---------------------|---------------------|---------------------|---------------------|
| 0                   | 30                  | 5.2                 | 0.79                |
| I03                 | 29.5                | 5.0                 | 0.74                |
| I2I                 | 27.5                | 4.8                 | 0.70                |
| I23.5               | 26                  | 4.6                 | 0.65                |
| I23.5               | 25                  | 4.3                 | 0.61                |
| I2I                 | 24.5                | 4.1                 | 0.61                |
| II6.5               | 23.5                | 3.9                 | 0.56                |
| II2.5               | 22.5                | 3.7                 | 0.52                |
| II0                 | 21.5                | 3.5                 | 0.48                |
| I08.5               | 20                  | 3.4                 | 0.43                |
| I06                 | 18.5                | 3.2                 | 0.43                |
| I01.5               | 17.5                | 3.1                 | 0.43                |
| 98                  | 16                  | 2.9                 | 0.38                |
| 92                  | 15.5                | 2.8                 | 0.38                |
| 9I                  | 15                  | 2.6                 | 0.24                |
| 86                  | 14                  | 2.5                 | 0.24                |
| 82                  | 13.5                | 2.3                 | 0.24                |
| 78.5                | 13                  | 2.2                 | 0.24                |
| 74                  | 12                  | 2.1                 | 0.24                |
| 7I                  | 11.5                | 2.0                 | 0.24                |
| 67.5                | 11                  | 1.9                 | 0.20                |
| 64                  | 10.5                | 1.8                 | 0.20                |
| 6I                  | 10                  | 1.7                 | 0.20                |
| 57.5                | 9.5                 | 1.6                 | 0.15                |
| 54                  | 9.0                 | 1.5                 | 0.10                |
| 52                  | 8.4                 | 1.48                | 0.10                |
| 49.5                | 8.1                 | 1.34                | 0.10                |
| 47                  | 7.6                 | 1.29                | 0.10                |
| 45                  | 7.2                 | 1.24                | 0.05                |
| 43                  | 6.7                 | 1.19                | 0.05                |

TABLE V.9 (cont)

| <u>Chart</u><br><u>Deflection</u> | <u>Chart</u><br><u>Deflection</u> | <u>Chart</u><br><u>Deflection</u> | <u>Chart</u><br><u>Deflection</u> |
|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| 40.5                              | 6.4                               | 1.10                              | 0.05                              |
| 38                                | 5.5                               | 1.02                              | 0.05                              |
| 36                                | 5.5                               | 0.97                              | at y= 6.5                         |
| 34.5                              | 5.4                               | 0.93                              |                                   |
| 31                                | 5.3                               | 0.84                              |                                   |

TABLE V.IIOriginal Data of Run E-9

25 RPM

 $\tau = 33.70 \text{ min}$ 

| <u>Chart</u><br><u>Deflection</u> | <u>Chart</u><br><u>Deflection</u> | <u>Chart</u><br><u>Deflection</u> | <u>Chart</u><br><u>Deflection</u> |
|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| 0                                 | 45                                | 11.8                              | 2.8                               |
| 83                                | 44                                | 11.2                              | 2.7                               |
| 104                               | 41                                | 10.8                              | 2.5                               |
| 110                               | 39                                | 10.0                              | 2.4                               |
| 113                               | 38                                | 9.8                               | 2.3                               |
| 115                               | 36                                | 9.3                               | 2.1                               |
| 115                               | 35                                | 8.9                               | 2.0                               |
| 115                               | 34                                | 8.7                               | 1.91                              |
| 114                               | 32                                | 8.3                               | 1.78                              |
| 112                               | 30                                | 7.8                               | 1.69                              |
| 109                               | 29                                | 7.5                               | 1.64                              |
| 107                               | 28                                | 7.2                               | 1.55                              |
| 104                               | 27                                | 6.9                               | 1.46                              |
| 100                               | 26.5                              | 6.5                               | 1.30                              |
| 97                                | 25.1                              | 6.3                               | 1.25                              |
| 90                                | 24.2                              | 6.0                               | 1.15                              |
| 87                                | 23.6                              | 5.7                               | 1.05                              |
| 84                                | 22.4                              | 5.5                               | 0.85                              |
| 79                                | 22.0                              | 5.1                               | 0.80                              |
| 74                                | 21.0                              | 4.8                               | 0.70                              |
| 72                                | 19.8                              | 4.7                               | 0.55                              |
| 69                                | 19.0                              | 4.5                               | 0.35                              |
| 66                                | 17.2                              | 4.3                               | 0.32                              |
| 62                                | 16.6                              | 4.2                               | 0.23                              |
| 60                                | 15.6                              | 3.9                               | 0.15                              |
| 56                                | 14.8                              | 3.7                               | at $y = 5.35$                     |
| 53                                | 14.0                              | 3.4                               |                                   |
| 50                                | 13.4                              | 3.3                               |                                   |
| 48                                | 12.6                              | 3.1                               |                                   |
|                                   | 12.2                              | 3.0                               |                                   |

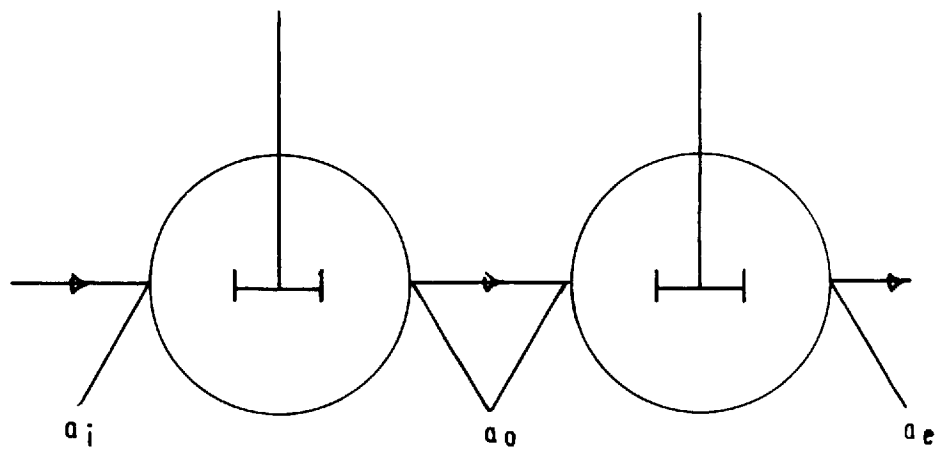


FIGURE VI-1  
TWO REAL VESSELS

$$a_0 = \frac{R\tau}{1+R\tau} \frac{I}{2k_I\tau} \left[ \frac{-I + \frac{\Lambda}{42}}{k_I\tau} (1 - 4 k_I\tau a_2 \eta \xi_i (-\eta) \exp(\eta)) - \frac{\exp(\eta) \xi_i(-\eta)}{k_I\tau} \right]$$

$$\text{where } \eta = \frac{I + R\tau}{k_I\tau a_2} \quad - \text{ (VI.I)}$$

The value of  $R\tau$  for the system B which gives the same conversion as for system A was obtained from program P9A/Ng (I8). The program P9A/Ng employs an estimate of  $R\tau$ , and calculates the concentration at the exit from a system with 2 CSTRs RTD. By comparison with the desired exit concentration, an iterative procedure is set up to find the desired value of  $R\tau$ .

Table (VI.I) gives the exit concentration ( $a_e$ ) for system A and the two values  $R(A1)$  and  $R(A2)$  for the first and second CSTR comprising the system. The corresponding value for system B is contained in Column  $R(B)$ .

| No. | $R(A1)$      | $R(A2)$      | $a_{\text{exit}}$ | $R(B)$ |
|-----|--------------|--------------|-------------------|--------|
| 1   | 0            | 0            | 0.01266           | 0.0675 |
| 2   | <del>0</del> | 0            | 0.01445           | 0.501  |
| 3   | 0            | <del>0</del> | 0.01355           | 0.21   |
| 4   | <del>0</del> | <del>0</del> | 0.01573           | 2.228  |
| 5   | 0.1          | 0.1          | 0.01342           | 0.185  |
| 6   | 1.0          | 1.0          | 0.01476           | 0.7    |

It is interesting to note that the conversions at extremes of micro-mixing for system B lie outside those for system A. This is to be expected because the

specification of a 2 CSTRs RTD is less restricting than of two successive vessels of the same total RTD.