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EXAMINATION OF TURBULENT MIXING WITH MULTIPLE SECOND ORDER CHEMICAL REACTIONS BY THE STATISTICAL ANALYSIS TECHNIQUE

The Ohio State University

Ph.D. 1986

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EXAMINATION OF TURBULENT MIXING WITH MULTIPLE SECOND ORDER CHEMICAL REACTIONS BY THE STATISTICAL ANALYSIS TECHNIQUE

DISSertation

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of the Ohio State University

By

Thomas Gregory Heeb, B.Ch.E., M.S.

* * * * *

The Ohio State University
1986

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To Sherry and Nick
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\( a' \) Root-Mean-Square Concentration Fluctuation, \( a'^2 = \overline{a^2} \)

\( \langle A \rangle \) Ensemble Average of \( A \)

\( A_j \) Value of \( A \) for the \( j \)th Simulation

\( A_t \) Value of \( A \) at Time \( t \)

\( A_v \) Volume Average of \( A \)

\( A_x \) Value of \( A \) in a Cell

\( C_i \) Instantaneous Concentration of Component \( i \)

\( \overline{C_i} \) Average Concentration of Component \( i \)

\( C_p \) Heat Capacity

\( d_{\text{jet}} \) Diameter of the Jets

\( D_i \) Molecular Diffusivity of Component \( i \)

\( F_i \) Fractional Conversion of Component \( i \)

\( g_s(r) \) Scalar Correlation Function

\( H \) Enthalpy

\( i \) The \( i \)th Component's Concentration Fluctuation

\( \overline{I_{ij}} \) The \( ij \) Average Covariance

\( I_i \) The \( i \)th Component's Instantaneous Concentration

\( \overline{I_i} \) The \( i \)th Component's Average Concentration


$I_{\alpha}$

Intensity of Segregation in Time

$I_{s}$

Intensity of Segregation at a Point

$J$

Total Number of Simulations

$k_i$

The $i^{th}$ Reaction's Rate Constant

$L$

Characteristic Dimension

$L_s$

Scalar Macroscale

$N$

Total Number of Cells

$r_i$

Instantaneous Rate Equation for Component $i$

$R_i$

The Average Rate Equation for Component $i$

$t$

Time

$T$

Total Time or Temperature

$U$

Instantaneous Velocity Vector

$U_i$

Instantaneous Velocity in $i$-direction

$\overline{U}_i$

Average Velocity in $i$-direction

$V$

Voltage

$x$

Distance

$Y$

Non-dimensional Distance

**Greek Letters**

$\alpha$

Thermal Diffusivity

$\beta$

Stoichiometric Ratio, $\beta = \overline{A}_o/\overline{B}_o$

$\nabla$

Vector Operator

$\epsilon$

Turbulent Kinetic Energy Dissipation

$\epsilon_{hx}$

Eddy Diffusivity for Heat in the $x$ Direction
\( \varepsilon_x \)  
Eddy Diffusivity for Mass in the x Direction

\( \lambda_s \)  
Scalar Microscale

\( \mu \)  
Viscosity

\( \nu \)  
Kinematic Viscosity = \( \mu/\rho \)

\( \pi \)  
\( \pi \), 3.14159

\( \rho \)  
Density

\( \tau \)  
Time Constant of Mixing

**Dimensionless Numbers**

\( N_{Dm1,i} \)  
First Damköhler Number for the \( i^{th} \) Reaction = \( L k_i C_j C_k / U C_m \)

\( N_{Dm2,i} \)  
Second Damköhler Number for the \( i^{th} \) Reaction = \( L^2 k_i C_j C_k / D C_m \)

\( N_1 \)  
First Damköhler Number Ratioed with Average Rapid Reaction

\( N_2 \)  
Second Damköhler Number Ratioed with Average Rapid Reaction

\( N_{Re} \)  
Reynolds Number, \( N_{Re} = \frac{U d}{\mu} \)

\( N_{Sc} \)  
Schmidt Number = \( \nu/D \)

**Subscripts**

\( \alpha \)  
In Time

\( f \)  
Final Value

\( i \)  
Component Symbol

\( \circ \)  
Initial Value

\( s \)  
Scalar or Segregation

\( x \)  
\( x \) Direction

**Overmarks and Other Symbols**

\( \infty \)  
Infinity
' Root-Mean-Square Value of
'' Second Derivative
'' Averaged Quantity
< > Ensemble Average
CHAPTER I
INTRODUCTION

Introduction

Modern industries often manufacture products in processes which involve turbulent flow chemical reactions as important steps. Industry strives to minimize production costs which include evolution of by-products via competing or consecutive reactions. The minimization of by-product yields requires proper design of the turbulent flow reactor system. Design of turbulent flow reactors requires an understanding of the mechanisms of the flow, mass, and heat transport in a turbulent flow system, knowledge of reactor geometry, and a description of the chemical kinetics. The current work was attempted to help gain a better understanding into basics of the multi-reaction turbulent mixing section of the design problem.

Turbulence complicates reactor design because the reaction rates, velocities, concentrations, temperatures, and physical properties are instantaneous or point values. Another complication that turbulence adds is the coupling or interaction between the chemical reaction, energy transfer, physical mixing, and flow related turbulent phenomena. The interaction is shown by the velocity field effects upon the concentration field while reaction and mixing affect the turbulence
or velocity field. Throughout the remainder of this work, the scalar field (either concentration or temperature) is assumed passive with respect to the velocity field. Thus, the scalar concentration field is assumed to have no effect on the velocity field.

Theoretically predicted conversions for specific chemical reactions which are the objective of much modelling and design work, depend on achievement of the desired stoichiometric balance of reactants in volumes which are disappearingly small. Any deviation from correct stoichiometry results in diminished conversion. The rate of reaction is another important parameter in the turbulent mixing and reaction problem. Reaction rate determines the extent to which a reaction system will show effects of turbulent mixing. Three ranges of rates were defined by Vassilatos and Toor [62] and Mao and Toor [42] as slow, rapid, and very fast: very fast reactions had a rate constant greater than about $10^6$ l/mole/sec, slow was less than about $10^3$ l/mole/sec, and rapid was in between. The slow reaction is kinetically controlled and occurs when mixing is essentially complete before reaction occurs. The system is therefore essentially premixed. For this case, conversions depend only on the homogeneous reaction rate and the residence time distribution. The very fast reaction is controlled by the mixing rate since the reaction occurs almost instantaneously at the interface between segregated regions of components. This case requires additional information concerning the mixing, such as the intensity of segregation: a measure of the degree to which the
multiple reactants are isolated in space. The rapid reaction condition is controlled jointly by chemical kinetics and mixing rates. This case requires all the information provided for the other two cases: both mixing and kinetics data.

The design of turbulent flow chemical reactors by the methodology suggested requires the solution of the turbulent mass, momentum, and heat conservation equations. The heat balance equation is neglected in this work because the problem is quite complicated enough. The investigation concentrates on interactions between turbulent mixing and chemical reaction rates. The interactions occur when reactive components react and diffuse within a turbulent flow field. The solution to the problem predicts concentrations over time and space for reactant and product species.

Overview of Areas of Analysis

The approach to the turbulent mixing and reaction problem depends upon solution of the Reynolds averaged, turbulent mass balance equations. A problem arises in that the number of unknowns exceeds the number of equations. Otherwise stated, closure is lacking between the algebraic elements. Closure can be effected by an additional supply of equations, called "closures" which provide the necessary additional relationships. With an adequate closure provision the Reynolds averaged turbulent mass balance equations can, in theory at least, be solved. This work examines critically a closure proposed recently by Brodkey and LeWalle [16], and evaluates alternative closures as well. In particular, the work analyzes five aspects of the turbulent mixing
and reaction problem. The first aspect was a theoretical examination of the Brodkey and LeWalle [16] closure and the development of additional closures. The second developed a statistical simulation program to determine the sign and possible size range of the second reaction's covariance term, $\overline{bp}$, which is involved in the closures. The third aspect compares various closures and their predicted results with available data. The fourth examined the mixing characteristics of a multi-jet reactor system, and the fifth evaluated some polymerization systems for application of the closure. The five areas are individually linked to the turbulent mixing and reaction problem and to each other by the idea that the first reaction's covariance term, $\overline{ab}$, which is essentially the intensity of segregation ($I_s$), is related to all subsequent reactions' covariance terms (i.e., second reactions covariance term is $\overline{bp}$). Relationships among the covariances must be made since unmeasurable covariances appear in the averaged second order kinetic rate equations.

Theoretical examination of the Brodkey and LeWalle closure and development of additional closures occur in Chapter II. The closures postulate relationships between the covariance terms important to the first and second reaction. The closure equations make formally possible a solution to the averaged component mass balance equations. Development of the closure equations of Chapter II depended upon assignment of the actual sign and size of the covariance terms. A statistical simulation program described in Chapter III was developed to determine the sign of the covariances, to determine the extent to
which the Brodkey and LeWalle closure predicted the second reaction's covariance value, and to evaluate prediction potential of ideas for multiple reaction covariances.

After the simulation program was applied to the examination of the sign of the covariances, Chapter IV compared the conversions predicted by the various closures to the experimental conversion data of Li. The analysis applied numerical integration techniques to the simultaneous mass balance and kinetic rate equations. The numerical solution was possible since the closures related unmeasurable covariances to measurable variables. The relationship between covariances tied the work together. One measurable variable was the intensity of segregation or the covariance, $ab$, of the first reaction. This covariance served as the measurable variable in most of the closures examined. As such the covariance of the first reaction assumed major importance and was therefore measured in a multi-jet reactor system as described in Chapter V. In summary of the work plan to this point, the development of multiple reaction covariance relationships or closures was performed in Chapter III to make possible the solution of the averaged turbulent component mass balance equations for a polymerization system. The multiple reaction system was examined in Chapter IV. In Chapter VI, actual measurements were made of another variable critical to the work the rate constant for the rate limiting step of one polymerization system. Rate constants were essential to the solution of the turbulent mixing and reaction problem. The extension of the work to a polymerization system was a logical progression of the treatment for the simpler simultaneous-consecutive reaction systems.
Chapter VI also required specification of the physical conditions of the reaction system. Finally, Chapter VII summarizes the conclusions from all the prior chapters. Thus the link throughout the various phases of this work is the idea that the closures needed to solve the balance equations are supplied by relationships between the measurable covariance, $\bar{ab}$, for the first reaction and other covariance terms from subsequent reactions.

**Review of Turbulent Flow Reaction Processes and Methods of Solution**

Past work pursued the turbulent flow reaction problem so that reactor designs could be performed more precisely. Reactors are commonly either tubular flow reactors or stirred tank reactors. Procedures for the stirred tank reactor, which was not examined in this work, can be found, for example, in Rao and Brodkey [54]; Klein, David, and Villermaux [34]; Paul and Treybal [53]; Nabholz, Ott, and Rys [47]; David and Villermaux [24]; Ghodsizadeh and Alder [26]; and Baldyga and Bourne [4]. Designs for the tubular flow reactor are often based upon the initial scale of mixing. Mixing may be single jet or multi-jet. Single jet tubular reactors have been examined by Lee and Brodkey [35]; Amerja [1]; Singh [56]; and Singh and Toor [57], for example.

Tubular multi-jet reactors were the object of this study. Multi-jet reactors have two different jet patterns. In an early design by Vassilatos and Toor [62], the jets were arranged in an open square array packing. In the latter design, the tubes followed a close packed array. The close-packed, multi-jet reactor was exclusively
used in this study so that subsequent references to a multi-jet reactor are to this configuration unless otherwise stated.

The earlier, open-array, jet reactor was redesigned by Toor and co-workers [1, 2, 40, 41, 42, 56, 57] into the close packed form so as to produce a flatter velocity profile across the reactor and to minimize the mixing between jets in the initial small recirculation region. Work on the close packed multi-jet tubular reactor has been presented by McKelvey et al. [44], Singh and Toor [57], Zakanycz [64], and Li [37]. The open-array multi-jet reactor was used by Vassilatos and Toor [62], Yieh [63], McKelvey [43], Mao [40], Mao and Toor [41, 42], and Singh [56]. Other literature is available which compares models to data available for the multi-jet reactor.

Models such as coalescence-redispersion, mass transfer between two slabs, lamellar stretching, and interchange with the mean have been proposed to describe the turbulent mixing and reaction problem. All of these models have adjustable parameters which must be fit to experimental data. These models do not necessarily describe correctly the underlying physical reality of the mixing-reaction process. An alternate approach, followed in this work, was to use the Reynolds averaged turbulent balance equations and as logical as possible simplifying assumptions so as to solve the problem in a general form. The resulting equations are then used to solve the turbulent mixing and reaction problem. This approach is that often used in fluid mechanics for solution of the turbulence problem.

Several imperfections are associated with the statistical analysis technique. Of prime importance is the need for assumptions which
require that experimental data be obtained for each specific reactor. The Reynolds averaging or statistical analysis technique is also limited by the need for closure of the set of equations so that a solution can be obtained.

**Turbulent Mixing Information**

The investigation pursued a specific multi-jet reactor system for which previous work by McKelvey [43], Yieh [63], and Zakanycz [64] had defined the flow measurements. Another needed assumption, previously established, was the observation that the covariance between the velocity fluctuations and the concentration fluctuations was small enough to be neglected. This assumption provided considerable simplification in the analysis and in the equations. Singh and Toor [57] and Mao and Toor [41, 42] provided data for this reactor on an almost infinitely fast second order irreversible reaction. The data provided a basis for comparison of data obtained in this study on a similar almost infinitely fast irreversible second order reaction. Previous work also provides for this reaction the most complete turbulent mixing information available for any reactor. Turbulent mixing information includes the average velocity at the center, velocity fluctuations at the center, radial variations of both the average and fluctuating velocity, pure mixing data, infinitely fast reaction data at the center, and velocity autocorrelation and frequency spectrum data for liquid and gas systems. Much of this information was gathered by previous workers and used to show that most of the previously made assumptions were reasonable. One such assumption is Toor's invariance
hypothesis which states that infinitely fast reaction data and pure mixing experiments both yield the same scalar mixing information and that this result can be used when more modest reactions take place (slower than infinitely fast). This hypothesis has been shown by McKelvey et al. [44] to be valid for stoichiometric ratios up to about 3.88.

Review of the Problem

One part of the current work involved a search for and tests of a reaction which involved multiple simultaneous-consecutive second order chemical reactions (i.e. a fast polymerization). If possible, the rate constant of the rate limiting step of the reaction was to be defined. A second, theoretical effort, involved examining the most recently proposed covariance closure equation of Brodkey and LeWalle [16] and comparing this closure to available experimental data. The third phase involved setting up a statistical modelling program. Finally, the last effort involved determining the mixing characteristics (intensity of segregation) of the reactor, examining other possible closure equations, and comparing the new closure results to available data.

The above areas of study define the information described in the subsequent chapters. Chapter II provides an examination of the theories on statistical mixing including the newly proposed ideas. Chapter III contains a discussion of the statistical simulation routine and results obtained from a number of case studies. Chapter IV shows the numerical integration of the descriptive equations with results
compared to the available simultaneous-consecutive reaction data of Li [37]. Chapter V discusses the equipment and procedures used to obtain an estimated "rate limiting step rate constant" for one possible polymerization system. Chapter V also includes the design information and results of the multi-jet tubular reactor system using an almost infinitely fast second order irreversible reaction. Chapter VI provides a description of the possible reaction mechanism and possible assumptions that lead to a second order rate equation.

This work is a preliminary view on the use of the statistical turbulent mixing analysis for analysis of the initial steps of polymerization reaction systems. The effort applies to the polymerization reactions that are fast enough to show effects of mixing on the product distribution. The speed of the reaction is of vital importance in determining if a reaction system shows turbulent mixing effects. Three ranges defined by Vassilatos and Toor [62] and Mao and Toor [42] are slow, rapid, and very fast. For the system considered by Mao and Toor [42], the ranges (of the rate constants) for the three classifications are greater than about $10^6$ l/mole/sec for the very fast, less than about $10^3$ l/mole/sec for slow, and inbetween for rapid. Thus a reaction polymerization system must be extremely fast (have large rate constants) before possible turbulence effects will be noticed upon the product distribution. In solution polymerization reactions, the viscosity is initially low and increases as higher molecular weight products are produced. The initially low viscosity allows turbulence to have an influence on the remainder of the process even if the flow
becomes laminar and the reaction becomes diffusion controlled due to the viscosity changes. Thus, the reaction system is affected by turbulence through the low viscosity and through the initial conditions by decreasing the clump size of components to the smallest eddy size. Any further size reduction must occur by molecular diffusion and the turbulence does not affect this stage of the process even though mixing does.
CHAPTER II
STATISTICAL THEORY OF TURBULENT MIXING

Pure Mixing Review

Statistical analysis of turbulent mixing is based upon Reynolds averaging of the turbulent mass transport equations. The averaging techniques are given by Reynolds [55] and reviewed by Brodkey [15]. Turbulent mixing terms must be defined. "Mixing means the blending into one mass and mixture means a complex of two or more ingredients which do not bear a fixed proportion to one another and which, however thoroughly commingled are conceived as retaining a separate existence. [13, 14]" Mixing depends upon the scale or size of the final solution or mixture. The scale needed for chemical reaction to occur is the submicroscopic scale (by submicroscopic is meant that the scale is larger than molecular but still not visible even with the best microscope) [13, 14]. The submicroscopic scale can only be obtained by molecular diffusion since even the smallest turbulent eddies are much larger in size than the submicroscopic scale.

Danckwerts [22, 23] has provided two criteria for the mixing process, the scale of segregation and the intensity of segregation. The scale of segregation is related to the size of the unmixed pure component clumps (also to be called points or cells). Intensity of segregation describes the effect of the molecular diffusion on the
mixing process. The intensity of segregation measures the component concentration differences between clumps. The intensity of segregation used throughout this work is the spatial or local intensity of segregation and not the intensity of segregation in time used in self-mixing or back-mixing and reactor design. The intensity of segregation in time ($I_a$) is defined in terms of the "age of a fluid at a point rather than the concentration at a point" [15]. The spatial intensity of segregation ($I_s$) and the scale of segregation are defined based on initially pure component clumps or points as Danckwerts [22, 23] calls them and as pointed out by Rao and Brodkey [54]. Thus utilization of these two criteria might require modification of the method of evaluating the averages and fluctuations of each component. Danckwerts defined the mixing criteria so that they describe the mixing process and still could be estimated from measurable statistical quantities.

An important restriction placed upon the two criteria is they cannot apply to cases which involve gross segregation such as two equal liquid parts. This implies that the parameters are approximately uniform over the mixing field which eliminates the first part or gross mixing of the mixing process. The scale of segregation must be relatively small before this restriction is satisfied.

The intensity of segregation is defined so that its value ranges from unity at complete segregation to zero for a completely uniform mixture. When no molecular diffusion is present, the scale is the size of the smallest turbulent eddies and the intensity of segregation
is unity because the mixture is not uniform on a submicroscopic scale. The intensity of segregation is a function of time-averaged variables at a point. It must be specified over the entire volume for a given system or some space-averaged value used to solve the turbulent mixing problem.

The evaluation of the turbulent mixing problem is based on the turbulent component mass balance equations which are coupled with the turbulent momentum balance equation. Assumptions are made which allow the two to be separated and solved. The main assumptions are an isotropic turbulent field, the covariance term of the velocity fluctuations and concentration fluctuations are zero, and a one-dimensional system is to be used. The turbulent momentum balance equation is transformed into the von Karman-Howarth equation by assuming that the turbulence is isotropic, that there are no external forces, and that the mean velocity is constant in the region under consideration and independent of time. All the terms in this equation can be obtained experimentally in terms of the correlation functions. The spectrum and the autocorrelation function allow relationships and calculations to be made for the velocity energy dissipation per unit mass, for the microscale of turbulence, for the low wave number cut-off, and for the macroscale of turbulence which are the main parameters used in the mixing problem. The mass balance equations can similarly be transformed into a von Karman-Howarth type equation. The equation at a point is
This equation eventually leads to

$$I_s = I_{s_0} e^{-t/\tau}$$

(2)

where \(\lambda_s\) and \(D\) are assumed constant. \(\lambda_s\) is expressed in terms of the second derivative of the scalar correlation function, \(g(r)\), as \(r \to 0\), i.e., \(\lambda_s = -2/g''(0)\) and where

$$\tau = \frac{\lambda_s^2}{12D} = \frac{5}{4} \left(\frac{2}{3} - \frac{N_{Sc}^2}{3} \right) \left(\frac{L_s^2}{\varepsilon}\right)^{1/3}$$

(3)

for low Schmidt numbers and

$$\tau = \frac{\lambda_s^2}{12D} = \frac{1}{2} \left[3 \left(\frac{5}{\pi}\right)^{2/3} \left(\frac{L_s^2}{\varepsilon}\right)^{1/3} + \left(\frac{\nu}{\varepsilon}\right)^{1/2} \ln(N_{Sc})\right]$$

(4)

for high Schmidt numbers. \(I_{s_0}\) is unity in most cases. These equations were derived by Corrsin [19] by assuming no chemical reaction and by assuming that the scalar microscale does not vary drastically in the region considered. Equation (2) describes the decrease in the
intensity of segregation for a pure mixing experiment as exponential and will be referred to as the exponential decay law. A discussion of the effects of adding chemical reaction will be given later in this Chapter. A more in depth look at the derivation of these equations is given in Brodkey [15] along with a discussion of phenomenological approaches to the problem.

The available literature on turbulent mixing and chemical reaction falls into two main categories, premixed and unpremixed. The premixed condition requires that the reactants be introduced in the same feed streams. This requires that the reaction be initiated by some external means such as by light. This case always has a positive covariance for a two component system compared to the unmixed which always has a negative covariance. The unpremixed case has the reactants introduced in separate streams. The unpremixed case has no restriction on the reaction's being initiated by external means. The unpremixed case should produce less of a single reactions product than an ideally mixed (homogeneous) system. Likewise, more will be produced by a premixed system.

Some work on the premixed system has been done by Corrsin [19, 20, 21], Pao [51, 52], and Bourne and Toor [12]. The more industrially significant unpremixed case is considered in more detail in this work. This case is broken down by speed of reaction. The speed of the reaction is either very fast (almost infinitely fast when diffusion controls), rapid (where diffusion and reaction are about of equal magnitude), or slow (where reaction controls). Work on very fast reactions has been done by Toor and coworkers [2, 41, 42, 57, 59, 60,
O'Brien and coworkers [48, 49], Bourne and coworkers [3, 4, 5, 6, 7, 8, 9, 10, 11, 12], Keeler et al. [33], Ottino and coworkers [17, 18, 50], and by Libby [38]. The rapid reactions have been worked on by Brodkey and LeWalle [16], Bourne and coworkers [3, 4, 5, 6, 7, 8, 9, 10, 11, 12], Toor and coworkers [2, 41, 42, 57, 59, 60, 61, 63], Ottino and coworkers [17, 18, 50], Kattan and Adler [32], and by Harris and Srivastava [29]. Slow reaction systems are considered fairly unimportant in the turbulent mixing problem since mixing is completed before any reaction occurs. For information concerning this case, one can cite reaction kinetics texts such as that by Smith [58]. These works include discussions of models used to examine the reaction-mixing system, different number and order of reactions, and experimental data on different types of reactors used.

**Single Second Order Chemical Reaction with Mixing**

The development of the equations used for the statistical analysis of the turbulent mixing and reaction problem starts by considering a nonreactive system as described above. This development leads to the exponential decay of the intensity of segregation. The intensity of segregation is defined for a pure mixing experiment to be

\[
I_s = \frac{a_1^2}{a_0^2} = \frac{a_1^2}{A \cdot B} \tag{5}
\]
The normalization of $I_s$ differs depending upon the system due to the different factors influencing the mixing. Brodkey and LeWalle [16] used

$$I_s = - \frac{ab}{A_0B_0} \quad (6)$$

while Lee and Brodkey [35] used

$$I_s = - \frac{ab}{A B} \quad (7)$$

For pure mixing experiments there is no difference between the two but once reaction is allowed to produce or deplete the concentration of the components then the two are different. The form used by Lee and Brodkey was for a single jet while that of Brodkey and LeWalle [16] was for a multi-jet system. Lee and Brodkey [35] used equation (7) since their concentration at the center line would decay without mixing because of the dispersion in the radial direction of the single centrally located contaminant jet. Equation (7) was used to describe the dispersion or dilution contribution of the decrease in the concentrations of component $A$ and $B$ on the mixing. This dispersion or dilution is not present in the multi-jet configuration and therefore the form used by Brodkey and LeWalle [16], which applies when mixing and reaction occur, is used in this work.
Equations (2) and (6) allow the time constant for mixing to be evaluated from measurements of the covariance term and conversely they also allow the covariance term of the pure mixing experiment to be evaluated for a system once the time constant of mixing is known. This equation is used in conjunction with the component mass continuity equations when a reaction is included to form a solvable set of equations. The main objection to the exponential decay law is that it was derived for an isotropic turbulent system. There are no known truly isotropic turbulent flow systems. However, if the mixing has been accomplished on the gross scale then the average of a scalar in a given region should be the same as the average of a scalar in other given regions. Thus, the scalar field would be isotropic-like and independent of the boundaries for its initial conditions. However, local conditions could vary due to the nonisotropic velocity field and thus local mixing could be different. Thus it is common to use the exponential decay law as an approximation for the decay of the intensity of segregation for a realistic turbulent flow system. If such conditions do not prevail, the data obtained for the covariance term can be used in a power law decay, such as the -3/2 law as observed by McKelvey et al. [44], by Gibson and Schwartz [27], and by Keeler et al. [33]. The value of -3/2 for the power was theoretically determined by Hinze [31].

Toor [59] has shown that a single very fast (almost infinitely fast) second-order reaction can also be used to obtain $I_s$ from the relationship
\[ I_S = (1-F)^2 \] (8)

where \( F \) is the fractional conversion.

The component mass balance equations are

\[
\frac{dC_i}{dt} + (U \cdot \nabla)C_i = \nabla \cdot (D \nabla C_i) + r_i \tag{9}
\]

where \( i \) is the component number or designating symbol, \( C_i \) is the instantaneous concentration of \( i \), \( U \) is the instantaneous velocity, and \( r_i \) is the instantaneous reaction rate of \( i \). The one-dimensional form of these equations is

\[
\frac{dC_i}{dt} + U \frac{dC_i}{dx} = \frac{d}{dx} \left( D \frac{dC_i}{dx} \right) + r_i \tag{10}
\]

The Reynolds averaged one-dimensional component mass balance equations are

\[
\frac{d\bar{C}_i}{dt} + \bar{U} \frac{d\bar{C}_i}{dx} + u \frac{d\bar{C}_i}{dx} = \frac{d}{dx} \left( D \frac{d\bar{C}_i}{dx} \right) + R_i \tag{11}
\]

where \( R_i \) is the time-averaged reaction rate at a point in the system. The terms \( \frac{d\bar{C}_i}{dx} / dx \) and any other covariance of velocity and concentration is assumed zero since they have been shown by McKelvey et al.
to be small or negligible compared to the other terms in the equations for the multi-jet tubular reactor. Other assumptions are: the process is operating under steady-state conditions and the diffusivity of all components is the same and equal to a constant value. The assumption of equal diffusivities has been shown by Angst et al. [3] to be a good approximation of the more realistic case of unequal diffusivities. The time-averaged equation is thus reduced to

\[
\frac{\bar{U}}{x} \frac{d\bar{C}_i}{dx} = D \frac{d^2\bar{C}_i}{dx^2} + R_i
\]  

(12)

McKelvey et al. [44] have shown that the diffusion term is small in comparison to the other terms and can be assumed zero. The diffusion effects are considered part of the \( I_\Sigma \) term from the pure mixing or fast reaction experiments. One assumption made is that the diffusivity from the determination of \( I_\Sigma \) is approximately the same as the diffusivity of the reaction system under investigation. Thus the averaged equation reduces to

\[
\frac{\bar{U}}{x} \frac{d\bar{C}_i}{dx} = R_i
\]

(13)

and likewise the instantaneous equation becomes
\[ U \frac{dC_i}{dx} = r_i \]  

(14)

These equations are used to determine the invariance hypothesis that Toor [59] proposed and a balance equation for the covariance term \( \overline{ab} \) which is also related to \( I_s \). The method is: 1) multiply the equation (13) for term A by \( B \), 2) multiply the equation (13) for term B by \( A \), 3) add the resulting equations together, 4) multiply the equation (14) for term A by \( B \), 5) multiply the equation (14) for term B by \( A \), 6) add the resulting equations together, 7) subtract the result of step (6) from the result of step (3), 8) collect appropriate terms, and 9) average the resulting equation. This procedure yields an equation of the form

\[ \overline{U} \frac{d\overline{ab}}{dx} = A \overline{r}_B - \overline{A} \overline{R}_B + \overline{B} \overline{r}_A - \overline{B} \overline{R}_A \]  

(15)

For the second order reaction

\[ A + B \xrightleftharpoons{\text{eq}} P + Z \]  

(16)

the reaction terms are

\[ r_i = -k(AB) \]  

(17)
Toor's hypothesis results from considering the limits on the reaction term from the $ab$ equation. From the two extreme cases of $k \to 0$ and $k \to \infty$, Toor showed that the bracketed term must be zero. When the value of $k \to 0$, there is no reaction and $b^2 = a^2$, $ab = -a^2$, and $ab^2 = -ba^2$. Using these equations, the bracketed term is zero and the decrease of $\bar{ab}$ is by diffusion alone. When $k \to \infty$, the bracketed term must be zero to balance the kinetic term with all the other terms in the equation. Thus Toor conjectured that

$$\left(\bar{ab}^2 + a^2b + \bar{A} \bar{b}^2 + \bar{A} a^2 + \bar{ab} (\bar{A}+\bar{B})\right) = 0$$

approximately for all values of $k$. This result means that $\bar{ab}$ and likewise $I_s$ can be determined from pure mixing experiments or by very fast reaction experiments and will apply to the mixing and reaction problem for a single second order reaction. This result determined by Toor suggests that $I_s$ is a direct function of the mechanisms of diffusion and turbulence but not of the reaction. The result does not suggest that $I_s$ is not related to the kinetics since $I_s$ is a function of the average component values, which are functions of the kinetics, and therefore $I_s$ is an indirect function of the kinetics or reaction
mechanism. Toor's result shows that any interaction terms between the reaction mechanism effects on \( I_s \) and the mixing (diffusion and turbulence) effects on \( I_s \) are small or zero for all values of \( k \) and that the mixing effects are greater than the reaction effects on \( I_s \). This hypothesis was tested by Yieh [63] and by McKelvey et al. [44] and the agreement with their experimental data was very good for the range of available data (i.e., \( \beta \) up to 3.88). Hill [30] also tested the hypothesis using a two-dimensional simulation and found encouraging results supporting the hypothesis. The results obtained from the various experiments compared favorably to the theories that assumed one-dimensional isotropic turbulence. Once again the scalar field should be isotropic-like with a nonisotropic velocity field (varying velocity). The results suggest that the flow system is not too critical to the mixing in this type reactor since the isotropic scalar condition is approximated in shear flow experiments. An important note is that use of the isotropic assumption was made because the problem of determining the three-dimensional flow field is much too complicated and time consuming. Thus the assumption of an isotropic flow field is not a physical reality but is used to simplify the set of equations so that an approximate solution can be found.

The next step in analysis of reaction and mixing would be the simultaneous-consecutive reaction sequence which involves determination of the selectivity of an intermediate. This reaction is theoretically more interesting because establishing the second covariance term and the selectivity of the reactions exists. Many models and
assumptions have lead to reasonable results for the single second-order reactive mixing system. The statistical analysis technique was investigated by Brodkey and LeWalle [16] for the simultaneous-consecutive reaction. They proposed a closure relationship which allowed the mass continuity equations to be solved. They based their closure equation on results that they obtained from a simple simulation of a single two-cell mixing reaction system. They suggested the closure

\[ \bar{bp} = \bar{ab} \frac{\bar{P}}{\bar{A}} \]  

(21)

This equation was used with the \( I_s \) (or \( \bar{ab} \)) obtained from experiments on the desired equipment and the mass continuity equations for the components to attain a solvable set of equations that describe the mixing problem.

**New Ideas Concerning Closures**

The closure proposed by Brodkey and LeWalle [16] was the result of a simple two-cell model and was suggested without any fundamental theoretical basis. In fact, the closure can be shown to be a result of extending Toor's hypothesis to both reactions. This will now be demonstrated. The mass continuity equations are (one-dimensional system assumed) given by equations (14) and the averaged mass continuity balance equations are given by equations (13). The difference between the one reaction case and the simultaneous-consecutive case is
in the reaction terms. The simultaneous-consecutive reaction system is

\[ a + b \rightarrow p + z \]  
\[ b + p \rightarrow s + z \]

where Z is a by-product of the reaction system. This leads to the following reaction terms

\[ \text{reaction 1 term} = k_1(a \bar{b} + ab + bA + ab) \]  
\[ \text{reaction 2 term} = k_2(b \bar{p} + bp + pB + bp) \]

From these, one obtains

\[ r_A = -k_1(a \bar{b} + ab + bA + ab) \]  
\[ r_B = -k_1(a \bar{b} + ab + bA + ab) - k_2(b \bar{p} + bp + pB + bp) \]  
\[ r_P = k_1(a \bar{b} + ab + bA + ab) - k_2(b \bar{p} + bp + pB + bp) \]  
\[ r_S = k_2(b \bar{p} + bp + pB + bp) \]

and the averaged terms are

\[ \text{averaged reaction 1 term} = k_1(a \bar{b} + ab) \]  
\[ \text{averaged reaction 2 term} = k_2(b \bar{p} + bp) \]
with

\[ R_A = -k_1(\overline{A} \overline{B} + \overline{ab}) \]  \hspace{1cm} (32)

\[ R_B = -k_1(\overline{A} \overline{B} + \overline{ab}) - k_2(\overline{B} \overline{P} + \overline{bp}) \]  \hspace{1cm} (33)

\[ R_P = k_1(\overline{A} \overline{B} + \overline{ab}) - k_2(\overline{B} \overline{P} + \overline{bp}) \]  \hspace{1cm} (34)

\[ R_S = k_2(\overline{B} \overline{P} + \overline{bp}) \]  \hspace{1cm} (35)

The closure that Brodkey and LeWalle [16] deduced was utilized in their paper and the results were shown to be qualitatively correct. The procedure to generate this closure is basically the same as given for the \( \overline{ab} \) continuity equation. In particular the continuity equations for the \( \overline{b^2}, \overline{ab}, \) and \( \overline{bp} \) covariance terms are used to derive the closure needed. The kinetic terms are assumed zero for all \( k_1 \) and \( k_2 \) following the reasoning of Toor [59]. Thus

\[ \overline{ap} \overline{B} + \overline{bp} \overline{A} + \overline{apb} - \overline{ab} \overline{B} - \overline{b^2} \overline{A} - \overline{ab}^2 = 0 \]  \hspace{1cm} (36)

\[ b^2 \overline{P} + \overline{bp} \overline{B} + pb^2 + \overline{bp} \overline{P} + p^2 \overline{B} + bp^2 = 0 \]  \hspace{1cm} (37)

\[ \overline{ap} \overline{B} + b^2 \overline{A} + ab^2 = 0 \]  \hspace{1cm} (38)

\[ b^2 \overline{P} + \overline{bp} \overline{B} + pb^2 = 0 \]  \hspace{1cm} (39)

\[ a^2 \overline{B} + ba^2 + ab^2 + b^2 \overline{A} + \overline{ab} (\overline{A} + \overline{B}) = 0 \]  \hspace{1cm} (40)

\[ \overline{ab} \overline{P} + \overline{ap} \overline{B} + \overline{apb} = 0 \]  \hspace{1cm} (41)
Adding equations (36) and (38) and subtracting equation (41) from the result yields the following equation

\[ \bar{bp} \bar{A} - a\overline{bP} = 0 \]  

(42)

This equation is the closure that Brodkey and LeWalle [16] have deduced from a two-cell system. Thus their closure is an extension of Toor's invariance hypothesis to include the second reaction. If the closure is inadequate, then Toor's hypothesis is not valid for the second reaction in the two reaction case. The closure will be shown in a following Chapter to be insufficient for predicting the experimental results of a simultaneous-consecutive reaction system for a jet Reynolds numbers from 500 to 5000.

One major problem with this closure is that it does not satisfy the overall balance equation for the fluctuating components. The overall mole balance for the reaction system given is

\[ A + B + 2P + 3S = A_0 + B_0 + 2P_0 + 3S_0 = A_0 + B_0 \]  

(43)

(assume no P or S initially so that \( P_0 = S_0 = 0 \)). The overall averaged mole balance is

\[ \overline{\bar{A}} + \overline{\bar{B}} + 2\overline{\bar{P}} + 3\overline{\bar{S}} = \overline{\bar{A}_0} + \overline{\bar{B}_0} \]  

(44)

and the overall fluctuating mole balance is
\[ a + b + 2p + 3s = a_o + b_o = 0 \quad (45) \]

The equations that the closure does not satisfy is equations of the form

\[ \text{equation (45) } \star \vec{1} = 0 \quad (46) \]

such as

\[ a^2 + ab + 2ap + 3as = 0 \quad (47) \]

These equations are directly from the mole balance equation and thus must be satisfied by any closure presuming to be strictly correct.

The crux of the simultaneous-consecutive reactive mixing problem is the evaluation of the covariance term \( \overline{bp} \). This term is not set by previous methods of solution. The limits on this term can be evaluated by assuming limiting forms of \( \overline{bp} \). These are zero, \( \overline{B}_0 \overline{P} \), and \( \overline{B} \overline{P} \). These forms will also be simulated to check whether experimental results fall within the bounds of the term \( \overline{bp} \). The limit \( \overline{bp} \) equal zero was chosen since the \( p \) fluctuations are initially small while the \( b \) fluctuations are large thus resulting in a small \( \overline{bp} \). As reaction proceeds, the \( p \) fluctuations become large while the \( b \) fluctuations become small again resulting in a small \( \overline{bp} \). Thus a value of zero was tried for the \( \overline{bp} \) covariance. The limit \( \overline{bp} \) equal to \( \overline{B}_0 \overline{P} \) is the maximum
realistic average upper limit for the $\overline{bp}$ covariance term since $B_0$ is constant and $\overline{P}$ initially increases as the first reaction proceeds and then decreases as the second reaction occurs. The limit $\overline{bp}$ equal to $\overline{B}$ $\overline{P}$ is a more reasonable upper limit on the $\overline{bp}$ covariance which allows the $\overline{bp}$ covariance to change from increasing to decreasing as both $\overline{B}$ and $\overline{P}$ change. Other closures can be used which are a change of sign different from those listed. This would correspond to assuming premixed conditions for the $\overline{bp}$ term in terms of the definitions of premixing of a two component system.

Another technique is using the Damköhler number to relate the $\overline{bp}$ term to the $\overline{ab}$ or $I_s$ term. The major problems with this technique are the definitions of the concentration and length scale that is used. These present problems because the length scale is not truly known and could possibly vary from the size of the submicroscopic range up to the reactor radius. Scales that will be tried are the scalar microscale, the scalar macroscale and the Kolmogoroff scale. The averaged Damköhler number, assumed to be the correct parameter, requires the use of the time-averaged values of the concentrations. Another problem is the rate expressions involved in the Damköhler numbers. The Damköhler numbers will be based on the first and/or second reactions so that the reaction terms are related only to these reaction rate equations. There are two methods of averaging using the ratio of Damköhler numbers. First, (using the first Damköhler number)
\[
N_{Dm_{1},i} = \frac{\text{Rate of Reaction } i}{\text{Convection Rate}} = \frac{Lk_{i}C_{i}C_{y}}{U_{C_{2}}}
\]  

(48)

so for

\[
\frac{bp}{ab} = \frac{N_{Dm_{1},2}}{N_{Dm_{1},1}} = \frac{k_{2}p}{k_{1}A}
\]

(49)

assuming equivalent \( C_{2} \) for both reactions and secondly

\[
\frac{bp}{ab} = \frac{N_{Dm_{1},2}}{N_{Dm_{1},1}} = \frac{k_{2}(\bar{B} - \bar{p}) + \bar{bp}}{k_{1}(\bar{A} \bar{B} + \bar{ab})}
\]

(50)

which is equivalent to

\[
\bar{bp} = abk_{2}B \bar{p}/(k_{1}A \bar{B} + k_{1}ab - k_{2}ab)
\]

(51)

Other possible relationships can be obtained if the convected component is assumed to be the average of the two reactant terms in the reaction expressions. These approximations were tried with both the first and second Damköhler numbers. Additional relationships can be generated which are combinations of previously derived forms; as an example, one was based on changing from the Brodkey-LeWalle closure to a negative Brodkey-LeWalle closure to zero depending upon the value of
the second Damköhler number ratio. A list of closures tested is given in Table 1. No second Damköhler number closures are given since the results were indistinguishable from the first Damköhler number results. The equations that have been deduced are compared to some available data in Chapter IV.
Table 1  
Closure Forms Tested

<table>
<thead>
<tr>
<th>Closure Number</th>
<th>Equation relating $\bar{b}p$ to $ab$ or $I_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\bar{b}p = \frac{ab}{A} \bar{p}$</td>
</tr>
<tr>
<td>2</td>
<td>$\bar{b}p = 0$</td>
</tr>
<tr>
<td>3</td>
<td>$\bar{b}p = B \bar{p}$</td>
</tr>
<tr>
<td>4</td>
<td>$\bar{b}p = \bar{B}_0 \bar{p}$</td>
</tr>
<tr>
<td>5</td>
<td>$\bar{b}p = - \frac{ab}{A} \bar{p}$</td>
</tr>
<tr>
<td>6</td>
<td>$\bar{b}p = - \frac{ab}{A} \bar{p}$</td>
</tr>
<tr>
<td></td>
<td>$\bar{b}p = \frac{ab}{A} \bar{p}$</td>
</tr>
<tr>
<td></td>
<td>$\bar{b}p = 0$</td>
</tr>
<tr>
<td>7</td>
<td>$\bar{b}p = \frac{ab}{A} \bar{p}$</td>
</tr>
<tr>
<td></td>
<td>$\bar{b}p = - \frac{ab}{A} \bar{p}$</td>
</tr>
<tr>
<td></td>
<td>$\bar{b}p = 0$</td>
</tr>
<tr>
<td>8</td>
<td>$\bar{b}p = \frac{ab}{B} \bar{p}$</td>
</tr>
<tr>
<td>Table 1 (continued)</td>
<td></td>
</tr>
<tr>
<td>---------------------</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>[ \overline{bp} = \overline{ab} \frac{\overline{P}}{\overline{A}} ] (64)</td>
</tr>
</tbody>
</table>
| 10 | \[ \overline{bp} = \overline{ab} N_{Dm_{1,2}} \text{ where } C_x = \overline{B}, C_y = \overline{P}, \] 
|     | \[ \text{and } C_z = \frac{(\overline{B} + \overline{P})}{2} \] (65) |
| 11 | \[ \overline{bp} = \overline{ab} \frac{N_{Dm_{1,2}}}{N_{Dm_{1,1}}} \text{ where } N_{Dm_{1,2}} \text{ same as above} \] 
|     | \[ \text{and } N_{Dm_{1,1}} \text{ has } C_x = \overline{A}, \] 
|     | \[ C_y = \overline{B} \text{ and } C_z = \frac{(\overline{A} + \overline{B})}{2} \] (66) |
| 12 | \[ \overline{bp} = \overline{ab} \left( \frac{N_{Dm_{1,2}}}{N_{Dm_{1,1}}} \right) = \frac{k_2 \overline{P}}{k_1 \overline{A}} \overline{ab} \] (67) |
| 13 | \[ \overline{bp} = \overline{abk_2B \overline{P}}/(k_1 \overline{A} \overline{B} + k_1 \overline{ab} - k_2 \overline{ab}) \] (68) |
| 14 | \[ \overline{bp} = \overline{ab} \frac{\overline{P}}{\overline{A}} \text{ K = constant at each N Re} \] (69) |
CHAPTER III
STATISTICAL SIMULATION ANALYSIS

Assumptions of the Analysis Technique

The statistical simulation analysis of the turbulent mixing problem was tested by setting up a model to determine if the statistics of real mixing problems could be generated by a limited model. The model used was a static one with no flow involved. The model allowed random events such as mass transfer and reaction to occur. The model represented the fluid as cells or clumps of molecules as in Figure 1. The number of components initially in a cell was set for each trial. Many assumptions were needed to evaluate the model. The assumptions were 1) binary equimolar mass transfer between cells when diffusion occurred, 2) one event, such as one reaction or one equimolar counterdiffusion between cells, occurred per cell per time step where the time units for the simulations is seconds, 3) reactions always involved at least one of the two main reactants, 4) probabilities were equated to the fraction represented by the specific events occurrence divided by all events occurrence value, 5) reactions were considered to be bimolecular second order elementary reactions, 6) all rate constants were normalized with respect to the diffusivity of the first main reactant as in the second Damköhler number and the ratio
Figure 1  Visualization of a Two-Cell Model
has units of 1/mole/cm², 7) the diffusivity of the first and second reactant were considered equal, 8) all other diffusivities were calculated using Le Bas volume method of estimating diffusivities or were set equal to the diffusivity of the first component, 9) mass transferred between cells which had common borders, and 10) cells remained in the same configuration throughout the test period.

The cell model was suggested by Danckwerts' [22, 23] definition of points which are in essence cells. The model allowed cells to be rectangular (including square) and circular. The shapes could be either two and three dimensional so that the rectangular shape became a box and the circular shape a cylinder. The shape most used in analysis was the rectangular for ease of picturing the cells at a point in space and time. The model allowed statistics, such as the average component values and the covariance values, to be determined for various input conditions.

The model could examine desired closures by insertion of the correct form of the closure into the simulation routines at the appropriate places. The statistics, such as the averaged values and covariance values, allowed qualitative results to be determined for various input conditions. Time averages at a point were approximated by two techniques: ensemble averaging and volume averaging. The two techniques differ in the assumptions used to approximate the true time average. Details are discussed later in this chapter. Several modified methods of calculating the component averages and fluctuations have been incorporated into the model simulation routines. These are
1) the Rao and Brodkey [54] method of closure which reduces the component averages by the average amount of each component in the opposite type of cell, 2) reduction of the number of cells to a mass equivalent two cell system (degeneration) followed by regular calculation methods, 3) subtraction of the minimum amount of each component from every cell or from the calculated average (omission) before regular calculations are made, 4) degeneration with omission then regular calculations, and 5) regular calculations without any changes to the system.

The time steps used in the model are considered to be the time required for one event, such as one reaction or one equimolar counter-diffusion, to occur in each cell. The events that are considered are 1) binary diffusion between two cells, 2) reaction in a cell, and 3) no change to a cell. The model assumes that each cell has one of these events occurring each time interval. Once a cell event occurs then that cell is no longer available until a new time interval is started. The assumption assures that each cell is considered only once during each time interval. If diffusion occurs then two cells are involved and both cells are no longer available until a new time interval starts. The size of the time interval is considered an approximation for the time required for a real mixing system to change, but the scale or proportionality constant relating the time interval of the simulation and the time of the real mixing system is unknown.
Methods of Averaging

The statistical simulation model is used to generate statistics, such as the covariance terms, and to check closures for mixing situations. The techniques used to calculate the averages and fluctuation components of the instantaneous concentrations need to be examined, because different definitions could apply to the intensity of segregation and closures. Danckwerts defines the intensity of segregation \( I_s \) in terms of initially pure component points. This definition requires that all the cells in a simulation have the component amounts adjusted to amounts in cells containing only one of the two initial reactants. The adjustment is done by subtracting the lesser amount of each of the two initial reactants from all cells. Different definitions for some closures have been demonstrated by Rao and Brodkey [54]. They have redefined the averages in the \( I_s \) expression to account for the initially impure cells (cells which contain both types of components). They obtained this result from examination of a recycle system. Thus a number of techniques for calculating the averages of the components have been considered as were previously mentioned in this chapter.

Two views of averaging can be used with this model: the ensemble average of many simulations at equal time steps and the volume average of many cells or points for one simulation. The ensemble averaging technique uses the ergodic assumption that the ensemble average, a property value of many runs, is equivalent to the time
average at the same location. Ensemble means a group producing together a single effect. This averaging technique is shown by the equations

\[
\langle A \rangle = \bar{A} \quad \text{ergodic assumption} \quad (70)
\]

\[
\langle A \rangle = \frac{\sum A_j}{J} \quad \text{ensemble average} \quad (71)
\]

\[
\bar{A} = \frac{\sum A_t}{T} \quad \text{time average} \quad (72)
\]

where \( A_j \) is a value of \( A \) for the \( j^{th} \) simulation, \( J \) is the total number of simulations, \( A_t \) is the value of \( A \) at time \( t \), and \( T \) is the total time. The ergodic assumption allows each simulation to represent the instantaneous concentration of the components and the average value is then calculated from all the simulations.

The volume averaging technique requires just one simulation with many cells. This technique assumes that each cell is equivalent to a time measurement and therefore the volume average at a specific time step in the simulation is equivalent to the time average at the same position. The underlying assumption that each time measurement is represented by one cell requires that the cells are assumed independent as the time measurements. This technique is shown by the equations

\[
A_v = \bar{A} \quad \text{volume assumption} \quad (73)
\]

\[
A_v = \frac{\sum A_x}{N} \quad \text{volume average} \quad (74)
\]
where $A_v$ is the volume average at a time step and $N$ is the total number of cells in the volume. Thus this technique utilizes each cell as a time measurement and calculates the corresponding averages and fluctuations from the cells' component values. Another assumption made by the volume averaging technique is that each cell has the same volume or size as the measuring probe and that the probe volume measures only one cell at any one time interval. The ensemble averaging technique utilizes a random selection of each simulation's cells. This technique uses only one cell per run to approximate the instantaneous component values since fluctuations from the averages can not be determined if all the cells are used. Thus both cases presume that the concentration of a component as a function of time can be approximated by cell values at the same position.

Discussion of the Simulation Computer Program

The simulation program and all programs developed in this work are on file at The Ohio State University with Dr. R. S. Brodkey. The simulation routines are divided into 1) input routine, 2) base cell routine, 3) configuration routine, 4) event determining routine, 5) concentration setting routine, 6) statistics routine, and 7) closure equations routine. The simulation proceeds by entering the desired input conditions via routine 1) (see flow diagram Figure 2). The necessary data are passed to the base cell routine 2) which chooses the base cell randomly by using a random number generator. Routine 2) checks to ensure that the chosen cell is available for use
Figure 2  Simulation Computer Program Flow Diagram
prior to completion of this routine. Then the cells are set into the
desired configuration by routine 3) as specified from the input condi-
tions. Routine 3) sets up a three dimensional array to store the
position of each of the cells based on the row, column and depth of
the cell. The routine then numbers the cells from one to the number
specified in the input data. Routine 3) must be called for every time
step to determine which cells share a common border. The determi-
nation of a common border is based on the three dimensional array which
locates the cells with respect to one another. After the configura-
tion routine 3), the event determining routine 4) is called. Routine
4) calculates the binary mass transfer rates between the base cell and
all available common border cells. The reaction rates are calculated
for the base cell. The rates are summed and fractions calculated
which represent the occurrence probabilities of the events such as
reaction or mass transfer. The event to occur for the current time
step and for the current base cell is chosen by random selection using
a random number generator. If reaction occurs then the routine can
include a diluent effect which allows reactants to be in the same cell
and not react because the reactants are too distant due to the large
volume of the solvent or diluent. The diluent effect is also randomly
selected based on the amount of each component present in the base
cell. If a reaction or the diluent effect were selected then routine
4) is completed. However, if diffusion occurs then the second diffus-
ing component must be selected. The selection is done by re-evaluat-
ing the mass transfer rates of the remaining components of the two
cells between which the diffusion is occurring, calculating fractions
representing the probabilities for the diffusion of the remaining components, and randomly selecting the second component. Control is passed next to the concentration setting routine 5) which adjusts the amount of the specific components for the desired event that was chosen to occur. Routine 5) as well as the input routine 1) uses whole integer numbers as the amount (moles) of each component while most of the other routines use the amount (mole) fractions of each component for the cell of interest. The program then calls the routine which sets the current base cell unavailable and if mixing occurred then the complimentary mixing cell also becomes unavailable for further use until a new time interval is started. The program returns to the base routine 2) to chose another base cell and the iteration continues until every cell becomes unavailable.

Next, the program follows one of two paths depending on the type of approximation used to express the time average at a point. The first path is the ensemble path which prints output (when desired) and then increments the time step. The procedure repeats the previously discussed loop on determining the events for all the cells. After all the time steps occur then this path requires resimulating the same system with different random number generator seeds. This method runs the simulation a number of times and calculates at a single time step the output data of the simulations. The assumptions for this averaging technique were discussed previously.

The second path is the volume averaging path which assumes that a single simulation produces cells which are equivalent to individual measurements at a point and thus can be averaged to produce
the time average at a point. This path does calculations at the current time step and then increments the time step before looping back to the event determining loop. Note that both paths have assumed that the time step for each measurement or group of cell values at the desired point are the same.

The program allows output of information such as 1) a description of the events chosen, 2) a picture of the cells at each time step, 3) summation of the averaged terms from continuity, and 4) closure information with regard to the values of the second order covariance terms.

**Simulation Input Conditions and Results**

The program was used to test the various input conditions which are listed in Tables 2 and 3. Table 4 lists the controlling mechanisms and the type of reaction for the various conditions of Tables 2 and 3. The range of kinetic ratios was from one to 2000. The value of 2000 approximately corresponds to the ratio of Li's experimental data [37] used in Chapter IV. The value of one was chosen to simulate the first few reactions of a polymerization with a single rate constant. The values between one and 2000 were used to determine the sensitivity of the results to the kinetic ratio. The results of these tests are shown in Figures 3 through 40.

The normalization of all the second order covariances, such as \( \overline{bp} \), used the same denominator as \( I_s \) normalization of Brodkey and LeWalle [16]; i.e., \( \overline{A_0B_0} \). Figures that have a second order covariance
such as $\bar{bp}$ as the ordinate variable are really using the normalized form such as $\bar{bp}/\bar{A}_0\bar{S}_o$. Various results from the two-cell volume-averaging technique for a simultaneous-consecutive reaction system are shown in Figures 3 through 15. Figures 3 and 4 show an expected result: the statistical program demonstrates that different diffusivities for the various components does not significantly change $I_s$ or $\bar{bp}$. The result means that the second order covariance terms for the two reactions case are insensitive to differences in the diffusivity used and therefore the diffusivities can all be assumed to be equal. The plots are for a high ratio of $k_1/D_i$ which was used to simulate a rapid reaction system. The expected result has previously been discussed by Angst et al. [3]. The $k_1/D_i$ value for Li's reaction system assuming a diffusivity of $1.24 \times 10^{-5}$ cm$^2$/sec was $5.9 \times 10^{11}$ l/mole/cm$^2$ which is within the range of values examined by the statistical simulations. The conversion to $S$ was 0.287 for the two-cell simulation and 0.169 for the multi-cell simulation utilizing approximately the same conditions as Li [37] (i.e., $k_1/D_i = 10^{12}$ and $k_1/k_2$ of 2000). The multi-cell value is accepted as the more accurate value due to an interaction effect (discussed later in this chapter). The value of 0.169 is approximately twenty percent greater than the largest of Li's experimental values (the low Reynolds number values). Figures 5 through 37 use different diffusivities for all the components. Results for equal diffusivity simulations are similar to the unequal diffusivity results.
## Table 2
Simulation Input Conditions

<table>
<thead>
<tr>
<th>$k_1/k_2$</th>
<th>Unequal Diffusivity</th>
<th>Equal Diffusivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$0.1, 1, 10, 100, 1000, 10^6, 10^9, 10^{12}$</td>
<td>$10^9$</td>
</tr>
<tr>
<td>10</td>
<td>$1, 1000, 10^6$</td>
<td>$10^9$</td>
</tr>
<tr>
<td>100</td>
<td>$1, 1000, 10^6, 10^9, 10^{12}$</td>
<td>$10^9$</td>
</tr>
<tr>
<td>1000</td>
<td>$1, 1000, 10^6, 10^9, 10^{12}$</td>
<td>$10^9$</td>
</tr>
<tr>
<td>2000</td>
<td>$0.1, 1, 10, 100, 1000, 10^6, 10^9, 10^{12}$</td>
<td>$10^9$</td>
</tr>
</tbody>
</table>
Table 3
Multi-cell and Multi-run Simulation Input Conditions

<table>
<thead>
<tr>
<th>Multi-cell and Multi-run Simulations</th>
<th>Unequal Diffusivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1/k_2$</td>
<td>$k_1/D_1$</td>
</tr>
<tr>
<td>1</td>
<td>$10^3, 10^6, 10^{12}$</td>
</tr>
<tr>
<td>2000</td>
<td>$10^3, 10^6, 10^{12}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Multi-cell and Multi-run Simulations</th>
<th>Unequal Diffusivity, Multiple Reactions with Equal $k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Reactions</td>
<td>$k/D_1$</td>
</tr>
<tr>
<td>3</td>
<td>$10^6, 10^{12}$</td>
</tr>
<tr>
<td>5</td>
<td>$10^6, 10^{12}$</td>
</tr>
<tr>
<td>7</td>
<td>$10^6, 10^{12}$</td>
</tr>
<tr>
<td>9</td>
<td>$10^6, 10^{12}$</td>
</tr>
</tbody>
</table>
Table 4  
Simulation Reaction Classifications

<table>
<thead>
<tr>
<th>$k_1/D_1$</th>
<th>$k_1/k_2$</th>
<th>Controlling Mechanism</th>
<th>Reaction Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1,2000</td>
<td>Kinetics</td>
<td>Slow</td>
</tr>
<tr>
<td>1</td>
<td>1,10,100,1000,2000</td>
<td>Kinetics</td>
<td>Slow</td>
</tr>
<tr>
<td>10</td>
<td>1,2000</td>
<td>Kinetics</td>
<td>Slow</td>
</tr>
<tr>
<td>100</td>
<td>1,2000</td>
<td>Both</td>
<td>Rapid</td>
</tr>
<tr>
<td>1000</td>
<td>1,10,100,1000,2000</td>
<td>Both</td>
<td>Rapid</td>
</tr>
<tr>
<td>$10^6$</td>
<td>1,10,100,1000,2000</td>
<td>Both</td>
<td>Rapid</td>
</tr>
<tr>
<td>$10^9$</td>
<td>1,10,100,1000,2000</td>
<td>Diffusion</td>
<td>Very Fast</td>
</tr>
<tr>
<td>$10^{12}$</td>
<td>1,10,100,1000,2000</td>
<td>Diffusion</td>
<td>Very Fast</td>
</tr>
</tbody>
</table>
Comparison Between Equal and Unequal Diffusivities on the Intensity of Segregation for Various Kinetic Ratios and for \( k_1/D_1 = 10^9 \).
Figure 4  Comparison Between Equal and Unequal Diffusivities on the $\overline{bp}$ Covariance for Various Kinetic Ratios and for $k_1/D_1 = 10^9$. 
Figures 5 through 8 show that limits are established for a reaction system due to the different mechanisms that cause the change in concentration of a species. The one limit is the kinetically controlled limit (region A in the figures) which occurs when kinetics are so much slower than the diffusion (or mixing) that the reactants are approximately premixed before any reaction occurs. This is shown by the curves with a low \( k_1/D_1 \) ratio in Figures 5 to 8. The lowest curves in Figures 5 and 6 are zero in Figures 7 and 8. The other limit is the diffusion or mixing controlled limit (region B in the figures). This limit is shown by high \( k_1/D_1 \) ratios in the Figures 5 and 6 (region B curves) and in the Figures 7 and 8 (region A curves). The limit corresponds to reaction at the interface between two component cells. The region in between involves both mechanisms. The figures show that the results are valid for \( k_1/k_2 \) ratios of 1 to 2000. The result of controlling limits and mechanisms is not new but the idea that a statistical simulation model using randomly selected events can generate these limits is encouraging.

The values of \( k_1/D_1 \) from the figures result in somewhat different ranges for the classifications as given by Mao and Toor for the slow, rapid, and very fast reactions. From the figures the approximate values for the ranges are: \( k_1/D_1 < 10^2 \) for slow reaction (kinetic control), \( k_1/D_1 > 10^9 \) for very fast reaction (diffusion control), and values in between for rapid reactions. The \( k_1/D_1 \) values of
Figure 5  Diffusivity Effects on the Intensity of Segregation with $k_1/k_2 = 1$. 

- $k_1/D_1 = 0.1$
- $k_1/D_1 = 1.0$
- $k_1/D_1 = 10$
- $k_1/D_1 = 10^2$
- $k_1/D_1 = 10^3$
- $k_1/D_1 = 10^6$
- $k_1/D_1 = 10^9$
- $k_1/D_1 = 10^{12}$
Figure 6  Diffusivity Effects on the Intensity of Segregation with $k_1/k_2 = 2000$. 
Figure 7  Diffusivity Effects on the $\bar{b}p$ Covariance with $k_1/k_2 = 1$. 

- $k_1/D_1 = 0.1$
- $k_1/D_1 = 1.0$
- $k_1/D_1 = 10$
- $k_1/D_1 = 10^2$
- $k_1/D_1 = 10^3$
- $k_1/D_1 = 10^6$
- $k_1/D_1 = 10^9$
- $k_1/D_1 = 10^{12}$
Figure 8  Diffusivity Effects on the \( \overline{bp} \) Covariance with \( k_1/k_2 = 2000 \).
Mao and Toor (assuming a diffusivity of $5.0 \times 10^{-6}$ cm$^2$/sec) are: less than $10^6$ for slow reaction, greater than $10^{12}$ for very fast reaction, and in between for rapid reactions. The main point is that controlling mechanisms have been predicted by the simulation.

Figures 9 through 15 are used to determine whether Toor's hypothesis, applied to the first reaction, was satisfied by the statistical program. Figures 9 through 12 show that $I_s$ is insensitive to the ratio $k_1/k_2$ at the two controlling limits and is relatively insensitive when both mechanisms occur, i.e., in the region between either diffusion or kinetics controlling. The worst case is when $k_1/D_1$ is $10^6$ with a maximum deviation of 0.07 or about twenty five percent. This shows that $I_s$ is virtually independent of the kinetic rate constants at the controlling limits but when both kinetics and diffusion contribute then the hypothesis could be in error by an amount as large as twenty-five percent at the maximum. This error was not present when only one reaction was involved since Toor's hypothesis has been shown by experimentation to be valid within about five percent and since the added effect of the second reaction were not present. Figures 13 through 15 show the effect of the kinetic rate constants on the $\overline{bp}$ covariance term. The figure for $k_1/D_1$ equal one is not shown because the $\overline{bp}$ covariance was always zero for this case. Figure 15 along with the result at $k_1/D_1$ equal to one shows that Toor's hypothesis applies well at the two controlling limits for the $\overline{bp}$ covariance
Figure 9  Kinetic Ratio Effects on the Intensity of Segregation for $k_1/D_1 = 1$. 

- $k_1/k_2 = 1$
- $k_1/k_2 = 10$
- $k_1/k_2 = 100$
- $k_1/k_2 = 1000$
- $k_1/k_2 = 2000$
Figure 10  Kinetic Ratio Effects on the Intensity of Segregation for $k_1/D_1 = 10^3$. 
Figure 11  Kinetic Ratio Effects on the Intensity of Segregation for $k_1/D_1 = 10^6$. 
Figure 12  Kinetic Ratio Effects on the Intensity of Segregation for $k_1/D_1 = 10^9$. 
Figure 13  Kinetic Ratio Effects on the $bp$ Covariance for $k_1/D_1 = 10^3$. 
Figure 14  Kinetic Ratio Effects on the bp Covariance for $k_1/D_1 = 10^6$. 
Figure 15 Kinetic Ratio Effects on the \( \bar{b}_p \) Covariance for \( k_1/D_1 = 10^9 \).
but Figures 13 through 15 show that errors occur when both mechanisms contribute. When $k_1/D_1$ was one the $bp$ covariance was always zero. This result corresponds to closure (2) of Table 1. The conversion to $S$ for this case was 0.001 which is similar to the experimental results obtained at high Reynolds numbers by Li [37] and examined in Chapter IV.

From Figure 11 the effect of increasing the kinetic ratio is to decrease the value of $I_{s}$ (both mechanisms contributing), while Figures 9, 10, and 12 show that at the kinetic and diffusion limits the effect of the kinetic ratio on $I_{s}$ is undetectable. From Figures 13 and 14 the effect of increasing the kinetic ratio is to increase the value of the $bp$ covariance from more negative values (region B in figures) towards zero (region A in figures) when the controlling mechanism is either kinetics or both kinetics and diffusion. Figure 15 shows no effect of $k_1/k_2$ on $bp$ at the diffusion limit. The result of increasing the $bp$ covariance term is expected since as $k_1/k_2$ increases, the first reaction becomes much more prevalent and therefore less of the product $P$ is used to produce product $S$. Therefore, as $P$ is produced in both types of cells the instantaneous difference of $P$ between cells should be very small or zero since there is little consumption of $P$ in forming $S$. Another expected result is that as the kinetic controlling limit is approached ($k_1/D_1$ small), the $bp$ covariance term should approach zero since mixing or diffusion occurs quickly in comparison to the reaction. Thus the amount of $P$ in both types
of cells is quickly equilibrated by the relatively fast diffusion. The result which showed no effect of \( k_1/k_2 \) on \( \bar{bp} \) at the diffusion limit is unexpected and is shown later to be a structural deficiency with the two-cell simulation technique. A short summary of the results obtained for the two-cell simulations is listed in Table 5.

These results were obtained using single two-cell volume averaging simulations. Statistically a larger number of cells should be used to determine if the two-cell volume average simulation technique yields valid information. The requirement leads to the ensemble averaging technique simulations. The ensemble technique involved many computer runs of two-cell simulations. The number of simulations was two hundred. Random selection determined which of the two cells per run (with the requirement that the sum of each type of cell be the same) were used in the calculations. Thus for two hundred simulations an average was obtained from two hundred cells. This type of analysis was performed to define the number of runs necessary to yield relevant results.

Figures 16 and 17 show that the covariance terms have settled to near the final value when the number of runs is between fifty and one hundred. Figures 18 and 19 show the covariances with respect to time. The \( \bar{bp} \) covariance curves are much smoother than the two-cell volume averaged curves. From these figures the results from the two-cell volume averaged simulations are confirmed. Thus if only general results are desired then computer time can be saved by using a two-cell volume averaging simulation over a multi-run simulation. Another
Table 5
Summary of Results from Two-Cell Statistical Simulations

<table>
<thead>
<tr>
<th>Result Number</th>
<th>Description of Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Unequal diffusivities do not effect $I_S$ or $\overline{bp}$ significantly</td>
</tr>
</tbody>
</table>
| 2             | Limits are: $k_1/D_1 \leq 10^2$ kinetic control  
                 $k_1/D_1 \geq 10^9$ diffusion control  
                 $10^9 > k_1/D_1 > 10^2$ both control |
| 3             | $I_S$ insensitive to $k_1/k_2$ ratio |
| 4             | $\overline{bp} \rightarrow 0$ as $k_1/k_2$ ratio increases except at diffusion limit (no effect) |
| 5             | $\overline{bp} \rightarrow 0$ as $k_1/D_1$ decreases |
Figure 16  Intensity of Segregation Variation with the Number of Runs in a Multi-run Simulation with $k_1/D_1 = 10^{12}$ and $k_1/k_2 = 2000$. 
Figure 17  $\overline{b^p}$ Covariance Variation with the Number of Runs in a Multi-run Simulation with $k_1/D_1 = 10^{12}$ and $k_1/k_2 = 2000$. 
Figure 18 Multi-run Intensity of Segregation Variation with the Kinetic and the $k_1/D_1$ Ratios.
Figure 19 Multi-run $\bar{b}p$ Covariance Variation with the Kinetic and the $k_1/D_1$ Ratios.
type of simulation involving multiple cells is the multi-cell simulation which uses the previously discussed volume averaging technique.

Figures 20 and 21 show the effect of the number of cells on the covariance terms. The plots show that the volume averaging technique is more variable at the 64 cell level compared to the multi-run case at the 64 run level. Figures 22 and 23 show the same information that the two-cell volume averaged technique showed. Some of the results from the two-cell simulations were unexpected. The reason that these two-cell results were not entirely expected is that too few mixing interactions occur in a two-cell simulation. The expected results are demonstrated by Figures 22 and 23 which are results of the multi-cell simulations. From these figures, increasing the $k_1/k_2$ ratio (from region A to B for $k_1/D_1 = 10^3$, from region C to D for $k_1/D_1 = 10^6$, and from region E to F for $k_1/D_1 = 10^{12}$) slightly decreases $I_S$ and makes $\bar{bp}$ approach zero for all possible controlling mechanisms. Thus, an increasing kinetic ratio causes $I_S$ and $\bar{bp}$ to approach zero. This result was expected for the $\bar{bp}$ covariance since as the kinetic ratio increases the amount of P consumed in the second reaction decreases causing the amount of P in each cell to be about equal since equimolar counterdiffusion was assumed and since the first reaction should occur at equivalent rates in both types of cells. The decrease of $I_S$ is equivalent to a decrease in $\bar{ab}$ which is expected since more reactions involving A and B will occur and therefore the
Figure 20  Intensity of Segregation Variation with the Number of Cells in a Multi-cell Simulation with $k_1/D_1 = 10^{12}$ and $k_1/k_2 = 2000$. 
Figure 21  \( \overline{bp} \) Covariance Variation with the Number of Cells in a Multi-cell Simulation with \( k_1/D_1 = 10^{12} \) and \( k_1/k_2 = 2000 \).
Figure 22 Multi-cell Intensity of Segregation Variation with the Kinetic and the $k_1/D_1$ Ratios.
Figure 23  Multi-cell bp Covariance Variation with the Kinetic and the $k_1/D_1$ Ratios.
amount of both should decrease faster than at equal kinetics. Thus $I_s$ should decrease with an increasing kinetic ratio. The maximum difference in the $I_s$ curves is about 0.05 or twenty-five percent error based on the lower kinetic ratio while the maximum difference in the $\bar{bp}$ curves is also 0.05. This value corresponds to about eighty-five percent error based on the lower kinetic ratio. Thus, the difference has approximately the same absolute size for both covariances. The effect is shown to be much greater on the $\bar{bp}$ covariance since the absolute size of the $\bar{bp}$ covariance is so much less that the absolute size of the $\bar{ab}$ covariance ($I_s$).

Figure 24 used 196 cells volume averaged to ensure that the covariance terms had settled to a stable value. A comparison of Figures 24 and 23 shows that there is no difference in the graphs and therefore 64 cells yields results equivalent to a larger number of cells. A short summary of the results obtained from Figures 16 through 24 is listed in Table 6.

A comparison of the results from the two-cell volume averaging, the multi-run ensemble averaging, and the multi-cell volume averaging simulations is shown in Figures 25 through 27. A comparison between the multi-cell, multi-run, and two-cell simulations' results for $I_s$ (not shown) are: the multi-cell curves are slightly lower than the two-cell volume averaging curves and the multi-run curves which are equivalent. This result is attributed to the interaction effects that the multi-cell simulations possess, which the two cell and multi-run simulations do not. The interactions are the ability of the cells
Table 6
Summary of Results from Figures 16 through 24

<table>
<thead>
<tr>
<th>Result Number</th>
<th>Description of Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Multi-run simulation requires only 50 to 100 runs for stable results</td>
</tr>
<tr>
<td>2</td>
<td>Multi-cell simulation requires about 64 cells for stable results</td>
</tr>
<tr>
<td>3</td>
<td>Multi-run results in equal but smoother curves compared to the two-cell simulations</td>
</tr>
<tr>
<td>4</td>
<td>Multi-cell mixing interactions allows $b_p \rightarrow 0$ as $k_1/k_2$ increases for diffusion control even though two-cell and multi-run techniques do not</td>
</tr>
<tr>
<td>5</td>
<td>$I_s$ decreases slightly as $k_1/k_2$ increases</td>
</tr>
</tbody>
</table>
Figure 24  Multi-cell $\overline{bp}$ Covariance Variation with the Kinetic and the $k_1/D_1$ Ratios Utilizing 196 Cells instead of 64 Cells.
to mix with one another. Figures 25 through 27 show the $\bar{bp}$ covariance of the three methods of simulation (two-cell, multi-run, and multi-cell). The effect of the additional mixing interactions of the multi-cell simulation over the multi-run and two-cell simulations is greatest at the controlling limits (kinetics and diffusion). At the kinetics controlled limit of $k_1/D_i = 10^3$, Figure 25, the maximum difference between the multi-cell simulation results and the multi-run or two-cell simulation results occurs for equal kinetics (region B). At the diffusion controlled limit of $k_1/D_i = 10^{12}$, Figure 27, the maximum difference between the multi-cell simulation results and the multi-run or two-cell simulation results occurs for a kinetics ratio of 2000. The smallest difference occurs when both kinetics and diffusion contribute as shown in Figure 26 by region B for equal kinetics and region A for unequal kinetics. The interactions that are part of the multi-cell simulation increase the $\bar{bp}$ covariance value (towards zero from negative values) over that from the other two methods. The two-cell and multi-run simulations yield approximately equivalent results. Figure 28 shows a four cell configuration and a two cell configuration with the respective paths of mixing or interactions. The $\bar{bp}$ covariance curves that are not always zero appear to have a shape similar to the curve of the P product as given in Levenspiel [36] (called R in reference).

The statistical simulation can also be used to determine if a particular closure produces the desired values for the $\bar{bp}$ covariance and therefore for the solution to the mixing problem. The following
Figure 25  Comparison between Multi-cell, Multi-run, and Two-cell
bp Covariance Results for $k_1/D_1 = 10^3$. 
Figure 26 Comparison between Multi-cell, Multi-run, and Two-cell bp Covariance Results for $k_1/D_1 = 10^6$. 
Figure 27  Comparison between Multi-cell, Multi-run, and Two-cell bp Covariance Results for $k_1/D_1 = 10^{12}$. 

- $k_1/k_2 = 2000$, Multi-run Average
- $k_1/k_2 = 2000$, Multi-cell Average
- $k_1/k_2 = 2000$, Two-cell Average
- $k_1/k_2 = 1$, Multi-run Average
- $k_1/k_2 = 1$, Multi-cell Average
- $k_1/k_2 = 1$, Two-cell Average
Figure 28  Interactions or Paths of Mixing for Two and Four Cell Configurations.
discussion is about closure \{1\} from Table 1 which was proposed by Brodkey and LeWalle [16]. Figures 29 through 31 are comparisons between closure \{1\} simulation results and the actual simulation results. From these figures the closure does not reproduce the values at any of the kinetic ratios for the three controlling mechanisms. Another important result is that the closure predicts the opposite response to the kinetic ratio that the actual simulation values produce. The result means that as the kinetic ratio is increased the simulation results decrease while the closure results increase. This result suggests along with the discussion in Chapter II that the closure proposed by Brodkey and LeWalle [16] is inadequate for use in solving the mixing problem. The figures and the results were based upon the regular calculation method as discussed earlier in this chapter. Other possible calculation methods such as the Rao and Brodkey modification, reduction to a two-cell mass equivalent system, subtraction of the minimum amount of each component from all cells, and reduction to two-cell mass equivalent system and subtraction of the minimum of each component from both cells yields results which were no better when comparing closure \{1\} to the actual simulation values. For a two-cell simulation the results of all the calculation methods except the regular calculation method were the same. This result is due to the limited averaging and interactions of a single two-cell simulation. The multi-run simulations using ensemble averaging yielded different results for the different calculation methods due to the large number of cells. The results for the multi-run simulations were
Figure 29 Comparison between Closure [1] Calculated $\overline{bp}$ Covariance and Simulation $\overline{bp}$ Covariance Values for $k_1/D_1 = 10^3$. 
Figure 30  Comparison between Closure {1} Calculated \( \bar{b_p} \) Covariance and Simulation \( \bar{b_p} \) Covariance Values for \( k_1/D_i = 10^6 \).
Figure 31 Comparison between Closure (1) Calculated $\overline{b_p}$ Covariance and Simulation $\overline{b_p}$ Covariance Values for $k_1/D_1 = 10^{12}$.
similar to the multi-cell results discussed previously. A short summary of the results comparing the two-cell, the multi-run, and the multi-cell simulations is listed in Table 7.

Table 7
Summary of Results from Comparing the Two-Cell, Multi-Run, and Multi-Cell Simulations

<table>
<thead>
<tr>
<th>Result Number</th>
<th>Description of Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$I_s$ is slightly lower for the multi-cell compared to the multi-run and two-cell due to Interactions of multi-cell</td>
</tr>
<tr>
<td>2</td>
<td>Interaction effect on $bp$ is largest at kinetic and diffusion controlling limits</td>
</tr>
<tr>
<td>3</td>
<td>Closure [1] predicts response to $k_1/k_2$ ratio that is opposite to actual simulation $bp$ values</td>
</tr>
<tr>
<td>4</td>
<td>Closure [1] is better for equal kinetics than for unequal kinetics but still does not adequately predict $bp$ in the simulations (within 100%)</td>
</tr>
</tbody>
</table>

The systems considered so far have been for a simultaneous-consecutive reaction system. This system is important because some experimental data is available for possible comparison. The work done in this section is to examine the step polymerization system described by many simultaneous-consecutive reactions. Therefore the simulation
program was used with more than two reactions. The simulations performed used the multi-cell method to determine the interaction effects and the multi-run technique. The reaction system is given as

\[
\begin{align*}
&w_{1} \\
&A + B \longrightarrow A_1B_1 + Z \\
&w_{3} \\
&A_1B_1 + A \longrightarrow A_2B_1 + Z \\
&w_{2} \\
&A_1B_1 + B \longrightarrow A_1B_2 + Z \\
&w_{5} \\
&A_1B_2 + A \longrightarrow A_2B_2 + Z \\
&w_{4} \\
&A_2B_1 + B \longrightarrow A_2B_2 + Z \\
&w_{7} \\
&A_2B_2 + A \longrightarrow A_3B_2 + Z \\
&w_{6} \\
&A_2B_2 + B \longrightarrow A_2B_3 + Z \\
&w_{9} \\
&A_3B_2 + A \longrightarrow A_3B_3 + Z \\
&w_{8} \\
&A_3B_2 + B \longrightarrow A_3B_3 + Z
\end{align*}
\]

where all the rate constants are assumed equal and where \(A_1B_1 = P\), \(A_2B_1 = R\), \(A_1B_2 = S\), \(A_2B_2 = T\), \(A_3B_2 = U\), \(A_2B_3 = V\) and \(A_3B_3 = W\) (relating to single letters from previous reactions).
Figures 32 through 40 show the effect of the number of reactions on the various desired second order covariances. These figures are the multi-cell results and provide new information about some of the covariance terms. First, all covariances involving a product species that can be consumed in a reaction in both cell types varies in sign and is approximately zero (Figures 33, 34, 37, and 38). Six repeat simulations using different random number seeds were averaged and resulted in the covariances of products that can be consumed in both types of cells being from one tenth to one hundredth the value of a single simulation.

These covariances for each of the separate simulations showed a random variation about zero and therefore the average value is concluded to be zero. All other covariances had similar values to the single simulation values. Secondly, $I_s$ does not seem to be affected by the number of reactions in the reaction system. Finally, all other covariances have a shape like the $\bar{bp}$ covariance of the simultaneous-consecutive reaction system with the relative minimum increasing as the product term increases in molecular weight. The first set of $\bar{bp}$-like covariance terms have the same relative minima as the $\bar{bp}$ covariance term from the two reaction case. The result follows use by the reactions of the first product species. This result is quite different than the assumption made by MacKinnon [39] for a radical polymerization system that all the covariances are related to $I_s$ as Brodkey and LeWalle [16] related the $\bar{bp}$ covariance to $I_s$. The results of the simulation suggest that if a reaction product is able to be
Figure 32 Intensity of Segregation for Multiple Equal Rate Reactions.
Figure 33 $\bar{a}(a_1b_1)$ Covariance for Multiple Equal Rate Reactions.
Figure 34  $\mathbf{b}(a_1b_1)$ Covariance for Multiple Equal Rate Reactions.
Figure 35 \( b(a_2b_1) \) Covariance for Multiple Equal Rate Reactions.
Figure 36 $a(a_1b_2)$ Covariance for Multiple Equal Rate Reactions.
Figure 37 \( b(a_2b_2) \) Covariance for Multiple Equal Rate Reactions.
Figure 38 $a(a_2b_2)$ Covariance for Multiple Equal Rate Reactions.
Figure 39 \( \text{b}(a_3 b_2) \) Covariance for Multiple Equal Rate Reactions.
Figure 40  $\overline{a(a_2b_3)}$ Covariance for Multiple Equal Rate Reactions.
consumed in another reaction in both types of cells or by both initial reactants, A and B, then all of this products' covariances should be zero. Other covariance terms, except $ab$, are similar to the $bp$ covariance term of the simultaneous-consecutive reaction system. These covariances have increasing minima as the molecular weight of the product term increases.

The differences between the multi-cell technique and the multi-run technique (using 100 runs) are: 1) $I_s$ is minutely different, 2) all the $bp$-like covariances are slightly greater for the multi-run case compared to the multi-cell case and, 3) all other covariances have smaller maxima and larger minima for the multi-cell case than the multi-run case. Thus the results are very similar and the two techniques become less distinguishable when the number of reactions increases.
Integration Techniques and Equations

The analysis of the turbulent mixing problem with appropriate closures requires integration of the coupled averaged turbulent component mass conservation equations. The approach to solving these equations was twofold. First, for the simpler simultaneous-consecutive reaction system case a computer program utilizing quadrature was used. For more than two reactions, the solution program utilized Gear's method for stiff partial differential equations. This program was written in ACSL (advanced computer simulation language). Both programs were tested as proposed by Brodkey and LeWalle [16]. The programs have been written for the reaction system

\[ A + B \rightarrow \text{product} + \text{by-product} \]  

(84)

where a by-product, called Z previously, is given in each step. This type of reaction is representative of step polymerization reactions. MacKinnon [39] developed an ACSL computer program for the radical polymerization case utilizing the Brodkey-LeWalle closure. The use of this closure for all product components was described in Chapter III as invalid. Product species that are subsequently reactive in both
types of streams should result in covariance terms that are approximately zero, as previously discussed in Chapter III.

The averaged turbulent component mass conservation equations consist of equation (13), the desired closures, and the appropriate kinetic expressions. These equations are usually rewritten in terms of fractional conversion and \( I_s \). For the simultaneous-consecutive reaction system given by reaction equations (22) and (23), the equations are

\[
\beta U_x \frac{dF_A}{dx} = -k_1 \bar{A}_0 (F_A F_B - I_s) \tag{85}
\]

\[
\bar{U} \frac{dF_B}{dx} = (-k_1 \bar{A}_0 - k_2 \bar{A}_o F_p/F_A)(F_A F_B - I_s) \tag{86}
\]

\[
\beta U_x \frac{dF_P}{dx} = (k_1 \bar{A}_o - k_2 \bar{A}_o F_p/F_A)(F_A F_B - I_s) \tag{87}
\]

\[
\beta U_x \frac{dF_S}{dx} = k_2 \bar{A}_0 (F_A F_B - I_s) \tag{88}
\]

The equations for the more complex polymerization reaction systems were developed as follows: 1) equation (13) was written for each component, 2) closure equations were supplied for the covariance terms, 3) common terms were collected, and 4) conversion was made to the fractional conversion form. The resulting equations for the five-reaction system of equations (75) through (79) are
These equations have assumed that the Brodkey-LeWalle closure is correct. The equations utilizing the new idea that the covariance term for products that are not cell specific is zero results in equations

\[
\frac{dF_A}{dx} = (-k_1/\beta - k_3F_p/F_B - k_5F_S/F_B)(F_{AB} - I_s)A_0 - k_3F_pA_0
\] (95)

\[
\frac{dF_B}{dx} = (-k_1 - k_2F_p/F_A - k_4F_R/F_A)(F_{AB} - I_s)A_0 - k_2F_pA_0
\] (96)

\[
\frac{dF_P}{dx} = (k_1/\beta - k_2F_p/(F_A\beta) - k_3F_p/F_B)F_{AB}A_0
\] (97)

\[
\frac{dF_R}{dx} = (-k_4F_R/(\beta F_A))(F_{AB} - I_s)A_0 + k_3F_pA_0
\] (98)
for the same reaction system. The equations given are no different for the simultaneous-consecutive reaction case. The difference arises when at least three reactions are present and the three are of the form of equations (75), (76), and (77). Both methods have been incorporated into the ACSL routine and a comparison of the results will be given later in this chapter.

Discussion of Results

The quadrature program was used to examine the fourteen closure equations listed in Table 8 (repeating Table 1). The experimental data of Li [37] was used to compare with the closures. This data had a $k_1/k_2$ ratio of approximately 2000:1. No data was available with a ratio of 1:1. The results of the numerical integrations are given in Figures 41 through 43. In these figures the homogeneous solution refers to the solution of the equations when the intensity of segregation is zero; i.e., when complete mixing is always present. The Brodkey-LeWalle closure [1] is inadequate for the range of Reynolds numbers given although it represents the high Reynolds number regime. Another problem with this closure besides the inability to satisfy the

\[ \bar{U}_x \frac{d\xi}{dx} = \left( -k_s F_B / F_B \right) \left( F_A F_B - I_s \right) \bar{\alpha} + k_2 F_B F_B / \beta \]  

(99)

\[ \bar{U}_x \frac{d\xi}{dx} = \left( -k_s F_R / (\beta F_A) - k_s F_S / F_B \right) \left( F_A F_B - I_s \right) \bar{\alpha} \]  

(100)
Table 8
Closure Forms Tested

<table>
<thead>
<tr>
<th>Closure Number</th>
<th>Equation relating $bp$ to $ab$ or $I_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\overline{bp} = \overline{ab} \frac{P}{A}$ (101)</td>
</tr>
<tr>
<td>2</td>
<td>$\overline{bp} = 0$ (102)</td>
</tr>
<tr>
<td>3</td>
<td>$\overline{bp} = \overline{B} \overline{P}$ (103)</td>
</tr>
<tr>
<td>4</td>
<td>$\overline{bp} = \overline{B} \overline{P}$ (104)</td>
</tr>
<tr>
<td>5</td>
<td>$\overline{bp} = - \overline{ab} \frac{P}{A}$ (105)</td>
</tr>
<tr>
<td>6</td>
<td>$\overline{bp} = - \overline{ab} \frac{P}{A}$ $N_1 &gt; 1$ (106)</td>
</tr>
<tr>
<td></td>
<td>$\overline{bp} = \overline{ab} \frac{P}{A}$ $N_1 &lt; 1$ (107)</td>
</tr>
<tr>
<td></td>
<td>$\overline{bp} = 0$ $N = 0$ (108)</td>
</tr>
<tr>
<td>7</td>
<td>$\overline{bp} = \overline{ab} \frac{P}{A}$ $N_2 &gt; 1$ (109)</td>
</tr>
<tr>
<td></td>
<td>$\overline{bp} = - \overline{ab} \frac{P}{A}$ $N_2 &lt; 1$ (110)</td>
</tr>
<tr>
<td></td>
<td>$\overline{bp} = 0$ $N_2 = 0$ (111)</td>
</tr>
<tr>
<td>8</td>
<td>$\overline{bp} = \overline{ab} \frac{P}{B}$ (112)</td>
</tr>
<tr>
<td></td>
<td>( \bar{b}p = \frac{ab}{A} \frac{\bar{P}}{\bar{B}} ) &amp; (113)</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>9</td>
<td>( \bar{b}p = ab \frac{N_{Nm_1,2}^i}{N_{Nm_1,1}^i} ) where ( C_x = \bar{B}, C_y = \bar{P}, ) and ( C_z = \frac{(\bar{B} + \bar{P})}{2} ) &amp; (114)</td>
</tr>
<tr>
<td>10</td>
<td>( \bar{b}p = ab \frac{N_{Nm_1,2}^i}{N_{Nm_1,1}^i} ) where ( N_{Nm_1,2}^i ) same as above and ( N_{Nm_1,1}^i ) has ( C_x = \bar{A}, ) ( C_y = \bar{B} ) and ( C_z = \frac{(\bar{A} + \bar{B})}{2} ) &amp; (115)</td>
</tr>
<tr>
<td>11</td>
<td>( \bar{b}p = ab \frac{N_{Nm_1,2}^i}{N_{Nm_1,1}^i} ) &amp; (116)</td>
</tr>
<tr>
<td>12</td>
<td>( \bar{b}p = ab \frac{N_{Nm_1,2}^i}{N_{Nm_1,1}^i} = \frac{k_2P}{k_1A} ) &amp; (117)</td>
</tr>
<tr>
<td>13</td>
<td>( \bar{b}p = abk_2B \frac{P}{(k_1A \bar{B} + k_1ab - k_2ab)} ) &amp; (118)</td>
</tr>
<tr>
<td>14</td>
<td>( \bar{b}p = ab \frac{P}{A} ) ( K = ) constant at each ( N ) Re</td>
</tr>
</tbody>
</table>
Figure 41  Comparison between the First Five Closures and Li's Experimental Data.
Figure 42  Comparison between the Second Five Closures and Li's Experimental Data.
Figure 43  Comparison between Closures {11}, {12}, and {13} and Li's Experimental Data.
molar averaged fluctuation balance equation is the apparent insensitivity of the calculated values to different Reynolds numbers compared to the actual experimental data. The insensitivity is a problem with many of the closures to be discussed. Closure (1) alone is not an adequate representation of the covariance relationship for the entire Reynolds number range for a $k_1/k_2$ ratio of approximately 2000:1. No conclusions can be drawn about the adequacy of this closure for different kinetic ratios since experimental data is not available. The statistical simulation results from Chapter III suggest that the closure (1) is not adequate for a kinetic ratio ranging from one to 2000. The result obtained for a kinetic ratio of about 2000:1 is in agreement with the discussion on the failure of this closure to satisfy the molar fluctuation balance equations. All further results and comparisons assume that the kinetic ratio for the simultaneous-consecutive reaction is about 2000:1. The rate constants for the multiple reaction system involving more than two reactions are all assumed equal since data is unavailable.

The intensity of segregation used in the numerical integrations was obtained from Singh and Toor [57]. They present equations which describe the change in the intensity of segregation with respect to the distance away from the mixing module face. One modification to their equations was used. This modification was basically a parabolic curve fit between three points. The points were initial point were complete segregation exists, the intersection point of their two curves, and a point 0.15 inches from the mixing module face. The
equations of Singh and Toor [57] will be compared to experimental data in Chapter V.

Closure (2) was used to determine if the second covariance term, which is smaller in size than $\bar{a}\bar{b}$, should be zero throughout the reaction. This closure is also inadequate for the range of Reynolds numbers. This closure is almost identical to the homogeneous case over most of the range. The difference is negligible if the jet Reynolds number is greater than about 800 (point A). Closure (3), $\overline{B\overline{P}}$, and closure (5), the negative of the Brodkey-LeWalle closure, have indistinguishable results. Closure (5) was used to determine if the Brodkey-LeWalle closure could be modified by changing sign. This would describe a premixed system with respect to the first product component, $P$; such a system might be considered premixed (in a two component type case). The results are adequate only at low Reynolds numbers (see region B in Figure 41). An interesting point is that closure (3), which is a limit on the second covariance term, cannot be greater than the product of the average components concentrations for a unpremixed system (corresponds to slow mixing). Thus the experimental data ranges from slow mixing described by closure (3), the product of the component averages, to fast mixing (high Reynolds numbers) described by closure (1) of Brodkey and LeWalle [16]. The reason that the Brodkey-LeWalle closure (1) describes the high Reynolds number data because the deviation from segregation is determined in terms of $\bar{a}\bar{b}$ or $I_s$ and this closure relates the deviation of $\overline{B\overline{P}}$ from the segregated value of $\overline{B\overline{P}}$. Closure (3) is equivalent to the
negative of the Brodkey-LeWalle closure as shown in Figure 41. The results imply that the reactor streams can be considered segregated or unpremixed for this low range of Reynolds numbers. One can conclude that the experimental data goes from the limit where the covariance is equivalent to the product of the respective average component concentrations (poor mixing) to the limit of fast mixing where the covariance is related via the Brodkey-LeWalle relationship to the intensity of segregation.

The curves of closure \( \{4\}, \overline{E_0F} \), are inadequate for describing the experimental data but it does produce the proper sensitivity to Reynolds number over the range covered. This closure is simply the absolute maximum (unrealistic) which a system might attain if one component did not react and was not allowed to diffuse (always a constant fluctuation at the initial value) and the other component’s fluctuations were equated to its average concentration. This limit is unrealistic since the covariance always involves two reactive species and this closure takes one as being inert.

Figure 42 contains five more closure equations that were tested against the experimental data of Li. Closures \( \{6\}, \{7\} \) and \( \{8\} \) all used the knowledge that the Brodkey-LeWalle closure \( \{1\} \) was adequate at high Reynolds numbers while closure \( \{5\} \) was adequate at low Reynolds numbers. These new closures used zero as the connecting value and changed from one closure to another based upon either the first or second average Damköhler number value. The curves show that the covariance is not simply related through the Damköhler to the
covariances that solve the equations at a particular range of Reynolds numbers since the experimental data is not reproduced using these closures.

Closures \{9\} through \{13\} involve relating the second covariance term to the first via one of the Damköhler numbers. There are more than two relationships since various methods of averaging the concentration terms are available. The results from all of these closures are inadequate since they do not predict the experimental data. The reasoning behind these closures was that the covariance for the first reaction should be related to the covariance of the second reaction by the ratio of the Damköhler numbers. The closures which involve just the second reaction's Damköhler number were chosen because the scale of the reaction system is dependent upon the Reynolds number and therefore some sensitivity to the Reynolds number should occur. The proper scale might produce the correct value for the Damköhler number such that the \( \bar{b}p \) covariance term is related to the \( \bar{ab} \) covariance term by the Damköhler number but the results of using the various physical scales such as the scalar microscale, macroscale, and the Kolmogoroff scale were inadequate.

The closures all have failed to predict the experimental data adequately. The Brodkey-LeWalle closure was further used with an adjustable constant. This closure \{14\} must reproduce the data as shown in Figure 44 since it is an empirical fit. The constant ranges from a value of minus one to one as shown in Figure 45. This closure \{14\} can be used to show the conversion to component S versus time as in Figure 46. This figure shows that not only does the maximum value
of S change with Reynolds number but the slope of the curve (the rate) is also dependent upon the Reynolds number. Another possible closure tried was a simple linear Reynolds number relationship between closure \(1\) and closure \(3\). Closure \(3\) was used at low Reynolds numbers, closure \(1\) was used at high Reynolds numbers, and fractional amounts of both were used in between. Results from this linear closure were inadequate. This result shows that the differential equations are not linear.

Figures 47 and 48 are the response curves of closure \(14\) for two Reynolds numbers. These curves show that the large rate constants of the reaction system of Li [37] produce large changes in the reactants and products early in a reaction. The modified closure suggests that the theories behind the development following Toor's hypothesis are not totally incorrect but that the proposed closure should satisfy the following criteria: 1) molar fluctuation balances, 2) correct sign of covariance, and 3) limits of very fast reaction and pure mixing (no reaction). These limits have never been satisfied by any of the closures proposed to date.

**Conclusions**

The extension of the Brodkey-LeWalle closure to more than two reactions has been studied by MacKinnon [39] and by Brodkey and LeWalle [16]. MacKinnon [39] examined a radical polymerization system. The results previously obtained from the simulation program suggest that certain covariance terms should be zero. This information will be used to compare, for a step polymerization system, the
Figure 44 Comparison between Closure {14} and Li's Experimental Data.
Figure 45  Empirical Constant of Closure \{14\} Versus Reynolds Number.
Figure 46 Conversion of $S$ Versus Time for Closure [14] for Various Reynolds Numbers.
Figure 47  Conversion of A, B, P, and S Versus Time for Closure (14) for a Reynolds Number of 500.
Figure 48 Conversion of A, B, P, and S Versus Time for Closure (14) for a Reynolds Number of 4900.
results using the Brodkey-LeWalle closure extended to all covariance terms (similar to MacKinnon [39] work) to the extension applied only to the non-zero covariance terms. The comparison will be on a system of five reaction equations as previously listed in equations (75) through (79). The initial concentration of reactants A and B was equal as were all the rate constants. Figures 49 through 54 show that over the Reynolds number range considered the final values of the curves are not affected by the new information. A comparison of the curves shows that they are minimally different. Thus the methods can not be differentiated and without experimental data no conclusion can be drawn determining which is correct.
Figure 49  Conversion Versus Time for Components of Five Reactions for a Reynolds Number of 490 and Utilizing Closure \{1\}.
Figure 50  Conversion Versus Time for Components of Five Reactions for a Reynolds Number of 2500 and Utilizing Closure [1].
Figure 51  Conversion Versus Time for Components of Five Reactions for a Reynolds Number of 4900 and Utilizing Closure [1].
Figure 52 Conversion Versus Time for Components of Five Reactions for a Reynolds Number of 490 and Utilizing Closure [1] and New Concept about Reactive Products.
Figure 53  Conversion Versus Time for Components of Five Reactions for a Reynolds Number of 2500 and Utilizing Closure [1] and New Concept about Reactive Products.
Figure 54 Conversion Versus Time for Components of Five Reactions for a Reynolds Number of 4900 and Utilizing Closure \{1\} and New Concept about Reactive Products.
Batch Kinetic Equipment and Operating Information

The equipment for the batch kinetic experiments must produce the kinetic controlled limit given by Mao and Toor [42]. This requirement means that even for very fast reactions (one's with large rate constants), the second Damkohler number must be small. This in turn requires that diffusion or mixing be fast. This requirement was satisfied by using a stirred tank reactor. Figure 55 is a schematic of the batch reactor system. The tank was a 400 milliliter pyrex beaker. Stainless steel baffles were placed inside the reactor to ensure that adequate mechanical mixing occurred. The baffles were used to prevent vortex flow within the reactor. The reactor was placed in a constant temperature reservoir to ensure isothermal operation. The stirrer motor had an operating range of 500 to 7500 rpm, but the speed used was kept near 3800 rpm. A higher speed was not used since a vortex, which dispersed air bubbles into the reaction media, formed around the impeller. The amount of reactant solution was 100 milliliters of a solution of piperazine with triethylamine in chloroform and 100 milliliters of a solution of sebacoyl chloride in chloroform. This reaction system is discussed in Chapter VI. The reaction times were measured by a stop watch. The diethylamine was added to the mixture at
Figure 55  Batch Kinetics Equipment Schematic.
the desired time to terminate the reaction.

The experimental procedure was: 1) solutions with the desired concentrations were made and were allowed them to reach thermal equilibrium, 2) 100 milliliters of both solutions were measured, 3) the desired amount of diethylamine which depends upon concentration of initial reactants was measured, 4) the stirrer was lowered into the reactor and the motor was set to the desired speed, 5) the stop watch was started and the reactants were poured into the reactor, 6) after the desired time interval had occurred diethylamine was poured into the reactor, 7) the solution set for a short time, 8) the motor was stopped, and 9) the solution was stored for subsequent measurement. This procedure was used so that estimates of the limiting rate constant could be obtained. If the exact rate constant value were desired a more sophisticated system could be devised that could inject the reactants at the exact same time and measure the time of reaction more accurately.

Another problem with the mixing method occurred when the solutions were not poured into the reactor at the right speed and the stirrer sprayed a mist of reactant solution. The spraying was minute if the reactants were injected into the reactor within about a second and in a direction away from the stirrer. The heat of reaction was negligible for the low concentration experiments but was perceivable for higher concentration experiments. This prompted the use of a constant temperature bath. The batch kinetic equipment was used with the initial reactant concentrations shown in Table 9. The evaluation
Table 9
Batch Kinetic Experiment Initial Concentrations

<table>
<thead>
<tr>
<th>Experiment Times (sec)</th>
<th>Concentration of Piperazine (moles/liter)</th>
<th>Concentration of Sebacoyl Chloride (moles/liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.095, 0.0245, 0.0095, 0.00245</td>
<td>0.100, 0.025, 0.010, 0.0025</td>
</tr>
<tr>
<td>5</td>
<td>0.095, 0.0245, 0.0095, 0.00245</td>
<td>0.100, 0.025, 0.010, 0.0025</td>
</tr>
<tr>
<td>10</td>
<td>0.095, 0.0245, 0.0095, 0.00245</td>
<td>0.100, 0.025, 0.010, 0.0025</td>
</tr>
<tr>
<td>15</td>
<td>0.095, 0.0245, 0.0095, 0.00245</td>
<td>0.100, 0.025, 0.010, 0.0025</td>
</tr>
<tr>
<td>30</td>
<td>0.095, 0.0245, 0.0095, 0.00245</td>
<td>0.100, 0.025, 0.010, 0.0025</td>
</tr>
<tr>
<td>45</td>
<td>0.095, 0.0245, 0.0095, 0.00245</td>
<td>0.100, 0.025, 0.010, 0.0025</td>
</tr>
<tr>
<td>∞</td>
<td>0.095, 0.0245, 0.0095, 0.00245</td>
<td>0.100, 0.025, 0.010, 0.0025</td>
</tr>
</tbody>
</table>
of the results and the method used to determine the concentrations are discussed in Chapter VI.

**Multi-jet Tubular Reactor Equipment**

The turbulent mixing multi-jet tubular reactor system consisted of feed tanks, pressure cylinder, pressure regulator and relief valve, flow valves, drain valves, in-line mixers, two-way solenoid valves, packed bed, mixing module, tubular reactor, and either a thermocouple measurement probe or a reactor in-line mixing device. A schematic of the flow system is shown in Figure 56. The equipment and flow system were designed to handle corrosive chemicals such as sebacoyl chloride, HCl, and piperazine. The tubular reactor, mixing module tubes, connecting tubing, valves, were all made of stainless steel. Previous work with water systems used polymethyl methacrylate (PMMA) tubing for the reactor and for the mixing modules' frame. PMMA was not used because it is slightly soluble in chloroform. The system was changed to stainless steel and chloride resist epoxy to solve the solubility problem. The mixing module had the dimensions given by Singh and Toor [57] and by Zakanycz [64] and the design used by Zakanycz [64] is shown in Figure 57.

The new module was constructed from stainless steel hypodermic tubing and a chemical resistant epoxy compound (Eccobond 285 with Catalyst 11 made by W. R. Grace). The compound Eccobond 285 supposedly does not swell in, is not soluble in, and does not react with chlorinated solvents. The epoxy was easy to apply at room temperature, since the cure time was more than a day at room temperature.
Figure 56 Multi-jet Reactor Equipment Schematic.
Figure 57 Mixing Module.
Therefore the module could be formed and then cured in an oven at the desired temperature and for the required time. The faces of the module were smoothed with 280 grit sand paper to ensure that no flow restriction was left from the manufacturing. The in-line mixers were designed so that the acid acceptor, triethylamine, would be mixed with the reactants, sebacoyl chloride and piperazine, just prior to introduction of the solutions to the mixing module. This procedure was necessary to prevent reaction of the sebacoyl chloride and triethylamine as described by Morgan [45]. Figure 58 shows the in-line mixers that were designed. The glass bead produced large scale mixing and the stainless steel mesh produced fine scale mixing.

The mixing module was preceded by a packed bed to even the flow into the longer tubes of the mixing module. The short tubes had a restricted flow volume and cross-flow to produce equal flow in each. The feed tanks were steel tanks coated with a chloride resistant and corrosion resistant epoxy. The feed tanks were pressurized by nitrogen from a gas cylinder. The tanks were rated for pressures up to 200 psig at 450°F. The experiments that were performed on the multi-jet tubular reactor in this preliminary study were used to measure the intensity of segregation. These experiments involved measuring the fractional conversion of an almost infinitely fast reaction at various positions away from the mixing module face.

Hydrochloric acid and sodium hydroxide were reacted. This reaction was used by Vassilatos and Toor [62] and Mao and Toor [41, 42] to determine the mixing characteristics of various reactors. The reaction was used to check the reactor system design and to provide
Figure 58  In-line Static Mixer Diagram.

Figure 59  Thermocouple Probe Diagram.
necessary data for future work using this reactor. The reaction was followed by measuring the temperature rise of the solution at various locations away from the mixing module. Thus, a thermocouple measurement probe was needed. Figure 59 shows the thermocouple probe system. The probe was made of 30 gauge chromel/alumel thermocouple wire connected to 24 gauge chromel/alumel thermocouple wire. One lead of the 24 gauge thermocouple wire was connected to one lead of a 30 gauge chromel/alumel thermocouple and then both remaining leads were connected to copper wire and put in an ice bath for referencing. The 0.25 inch support tube contained centering veins to ensure that the thermocouple was located at the centerline of the reactor. This tube also housed the thermocouple leads. The probe was sealed with silicon rubber to the end of the support tube. Rubber insulation was used to isolate the reactor electrically from the rest of the equipment and to insure that all ground loops were eliminated. The reactor was also thermally insulated to insure adiabatic operation.

The reactor in-line mixing device is shown in Figure 60. This device is needed for future work involving the polymerization reactions. The device is used to inject the polymerization terminator into the restricted flow region where large scale mixing occurs followed by fine scale mixing caused by the stainless steel mesh. A sample tube withdrew some of the terminated reaction product solution. This device also had veins for centering purposes. Not included in the figure was a pump which caused the flow of the terminating species.
Figure 60 Reactor In-line Mixing Device.
The reactor system as shown in Figure 56 did not use any pumps. The system was so designed because pumps produce periodic flows which are undesirable. Thus the use of pressure to produce the desired flow conditions was examined. An analysis of the flow system showed for a Reynolds number of 3600 that the pressure required by the system would be approximately 145 psig. This pressure set limits upon the feed tank specifications which were met by a 200 psig tank limit. The actual obtainable Reynolds number was about 2500 at 200 psig. This value corresponded to a flow of about seven gallons of water per minute.

The procedure for the infinitely fast reaction experiments was:
1) make desired concentrations, 2) let solutions remain at room temperature for twelve to twenty-four hours to reach thermal equilibrium, 3) fill feed tank one with acid solution, 4) fill feed tank two with base solution, 5) fill feed tank three with water, 6) open nitrogen cylinder valve, 7) set feed tank pressure with pressure regulator, 8) position thermocouple probe at desired height, 9) open valve from tank one to measure feed inlet temperature then close tank, 10) purge system of feed by opening valve on tank three, 11) repeat step (9) for feed two, 12) repeat step (10), 13) open valves from tank one and tank two, 14) measure temperature of system, 15) close valves and purge system with water and, 16) return to step (8) if another position is desired or stop. The temperature data obtained from the experiments were related to the fractional conversion of the acid. The fractional
conversion was related to $I_\text{s}$. Therefore from the temperature measurements information about mixing could be determined.

**Discussion of Results for Multi-jet Reactor**

The analysis of the infinitely fast reaction system has been shown by Vassilatos and Toor [62] to result in equation (8) for streams in stoichiometric proportions. This result is used with the temperature-concentration relationship to relate $I_\text{s}$ to the temperature rise from the reaction. The temperature-concentration relationship was also derived by Vassilatos and Toor [62]. They started with the one dimensional steady-state turbulent mass balance equation for a component and used an eddy diffusivity to express the velocity-concentration fluctuation terms. The equation is

$$\bar{U}_x \frac{d\bar{C}_i}{dx} = \frac{d}{dx} (D_i + \epsilon_x) \frac{d\bar{C}_i}{dx} + R_i$$ (119)

Next, they wrote an adiabatic reactor heat equation using a heat eddy diffusivity. This equation is

$$\bar{U}_x \frac{d\bar{T}}{dx} = \frac{d}{dx} (\alpha + \epsilon_{hx}) \frac{d\bar{T}}{dx} + \frac{R_A}{\rho C_p} \Delta H$$ (120)

They assumed that the axial eddy diffusivities were equal and were much larger than the molecular values. The two equations are similar
and have similar boundary conditions and therefore they explained that the solutions to the two equations must satisfy

$$\Delta C_A = \frac{\rho C_p}{\Delta H} \Delta T$$

(121)

Therefore, the temperature rise measurements are related to the conversion which is related to \(I_s\). The assumption concerning the neglect of the axial diffusion terms is justified by Vassilatos and Toor [62] who held that these terms were small and were not critical in the analysis. Vassilatos and Toor [62] also pointed out that equation (121) is valid in a non-uniform field if the total diffusivities of mass and heat are equal and if the bulk average values are used in place of the overbarred terms. Li [37] related the fractional conversion directly to the millivolt readings from the thermocouple by

$$F = \frac{(V - V_o)}{(V_f - V_o)}$$

(122)

where \(V_o\) is the initial inlet temperature voltage and \(V_f\) is the voltage after complete conversion had occurred.

The experiments input conditions are initial hydrochloric acid concentration of 0.15 M ± 0.0015 M, initial sodium hydroxide concentration of 0.15 M ± 0.0015 M and a jet Reynolds number of 1500. Measurements were made one, five, ten, fifteen, twenty, thirty, and
ninety millimeters away from the face of the mixing module. Ninety millimeters defined \( V_f \). The results of the experiments are given in Table 10 and in Figure 61.

Table 10
Experimental Results for Intensity of Segregation

<table>
<thead>
<tr>
<th>Position (mm)</th>
<th>Fractional Conversion</th>
<th>Intensity of Segregation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.080</td>
<td>0.8464</td>
</tr>
<tr>
<td>5</td>
<td>0.261</td>
<td>0.5461</td>
</tr>
<tr>
<td>10</td>
<td>0.629</td>
<td>0.1376</td>
</tr>
<tr>
<td>15</td>
<td>0.811</td>
<td>0.0357</td>
</tr>
<tr>
<td>20</td>
<td>0.935</td>
<td>(4.225 \times 10^{-3})</td>
</tr>
<tr>
<td>30</td>
<td>0.957</td>
<td>(1.849 \times 10^{-3})</td>
</tr>
<tr>
<td>90</td>
<td>1.000</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The selection of the Reynolds number of 1500 corresponds to the Reynolds numbers with available flow data of Zakanycz [64], McKelvey [43], Yieh [63], and McKelvey et al. [44]. The results of the experiments should be comparable to the data given in Toor [60] and in Mao and Toor [42]. A comparison of the experimental data and the equations
\[ I_s = 3.52 \times 10^7 (\sqrt{N_{Re} Y})^{-3.45} \]  

\[ I_s = (23.48 - 0.050Y)N_{Re}^{-0.47} \]  

\[ Y = x/d_{jet} \]

which describe the data given in Singh and Toor [57] is shown in Figure 61. The experimental data is described adequately by the equations (123) and (124). Therefore the equations are adequate in describing \( I_s \) as a function of Reynolds number and position from the mixing module (downstream).
Figure 61  Comparison between Experimental Conversion Data of Mao and Toor [42], Experimental Conversion Data of Heeb, and Curvefits of Singh and Toor [57] for a Reynolds Number of 1500.
Requirements for the Polymerization Reaction System

Previous work on reaction kinetics has shown for water soluble component systems that reactions can be classified according to the reaction rate constants. The classifications must be normalized to be used with other systems. Normalization by the diffusivity or more appropriately by using the second Damköhler number will allow the classifications to be applicable to other reaction system. The original classifications of Mao and Toor [42] are listed in Table 11.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Rate Constant (1/mole/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very Fast or Diffusion Controlled</td>
<td>$&gt; 10^6$</td>
</tr>
<tr>
<td>Rapid</td>
<td>$&lt; 10^6$ and $&gt; 500$</td>
</tr>
<tr>
<td>Slow or Reaction Controlled</td>
<td>$&lt; 500$</td>
</tr>
</tbody>
</table>
Important information still not considered by the classifications is possible inertial and viscous effects on the reaction rates. Such information could be necessary for relating reaction systems that use different flow characteristics and compounds. The simple simultaneous-consecutive reaction data of Li [37] were used to compare to the mixing theories in previous chapters. The multiple reaction turbulent mixing problem was of concern and was examined by this investigator. A more complex reaction system involving more than two reactions was desired to allow more information to be obtained about turbulent mixing effects on selectivity. This prompted a search for a polymerization reaction system which met the following conditions: 1) single phase system, 2) high reaction rates, 3) solution polymerization, 4) step polymerization, 5) two reactive monomers, 6) second order irreversible reactions, 7) reacts at room temperature, and 8) non-toxic.

The desire for the polymerization reaction system to be single phase was that this would be a simpler case which still has not been adequately solved using current turbulent mixing theories. The kinetics of a two phase polymerization system would be more difficult to establish than those for a single phase system due to the changes in the reactivity of the solid phase compared to the components in the liquid phase. This change in reactivity has been demonstrated by Morgan [45] by dissolving a solid precipitate of a polymerization reaction in another solvent and measuring the change in the average molecular weight. Another example is the interfacial polymerization
system which proceeds at very fast rates as long as the polymer product is removed from the interface. If the polymer is not removed then the reaction slows and little polymer is formed. These examples show effects that occur when a two phase system is used and these effects would make analysis more difficult.

The need for a polymerization reaction system with high rates is evident from Table 11 which shows that rate constants around $10^6$ liter/mole/second provide a very fast reaction. The reason a very fast reaction is desired is that by changing the concentration of reactants, the rate falls into different controlling mechanisms. This concentration effect is another reason for classifying the controlling mechanisms according to the second Damköhler number which includes a reactant concentrations effect.

A solution polymerization system is desired to minimize the effects of the heat generated by the reaction and the change of viscosity that occurs as polymers are formed. The need for a room temperature polymerization is that costs of equipment are lower and the overall reactor system is simpler. The reaction system must produce many different product species early in the reaction to be applicable for study with the multi-jet tubular reactor equipment. This requirement is best satisfied by a step polymerization system since this reaction system produces many short chain products early in the reaction. A radical polymerization produces a few long chain reaction products early in the reaction and thus would not be effective for the reactor system. An added benefit of producing many short chained
products initially is that the viscosity does not change significantly. Step polymerization does not show a large viscosity change until high conversions and long reaction times are attained. The viscosity will not change significantly in the multi-jet reactor because the components are only in the reactor for a short period of time. The reaction will convert only a few percent of the initial reactants in this short time period. Thus the change in average molecular weight will be small as will the change in viscosity. This allows the energy balance equation to be eliminated from analysis since the conversion is low and the system is in solution so that the changes in temperature are a minimum and all physical properties are constant.

Two monomers are desired to react since the multi-jet mixing module is designed to inject two different types of streams. Other systems that are possible are to inject a catalyst (initiator or accelerator) in one stream and the reactive component in the other. This is how a radical polymerization reaction would be examined. The main problem with using a single reactant are that there are no products which can only be produced in one component stream. When two monomers (A and B) are reacting, products ABA and BAB can be produced. These two products are different and can each be produced in one stream initially. Thus a two monomer system allows more products to be differentiated and more selectivities to be determined. This allows more information on turbulent mixing to be determined. Another advantage of the two monomer system is that the reactive groups are on separate components and therefore no reaction occurs between the two monomers before the two are mixed together while for the single monomer case it
is possible that some reaction occurs before injection into the reactor.

The reaction mechanism consists, hopefully, of single second order irreversible reactions. This is desired since previous work on simultaneous-consecutive reactions involved second order irreversible reactions. Thus, if second order reactions are involved, then use can be made of the existing information available on the simultaneous-consecutive reaction systems. More complicated reaction systems can be evaluated as long as the appropriate rate equations are available.

Discussion on the Polymerization Reaction Mechanism

From the conditions previously cited a select group of reaction systems are possible. These reactions satisfied other criteria before any experimental work was performed. The additional criteria were cost of reaction components, cost of the materials of manufacturing for the reactor as well as the manufacturability of these materials, availability of the components and materials, purity needed for the reaction components, and techniques to analyze the products and reactants. These criteria narrowed the possible reactions down to piperazine (and derivatives) reacting with a diacid chloride in the presence of an acid acceptor. The best systems used triethylamine as the acid acceptor and are listed in Table 12.

The most promising system with regard to all available information is the first one listed. This system has one problem which was discovered by experimentation. The polymer produced forms a supersaturated solution in the solvent. Therefore after a certain amount
Table 12

Reaction Systems With Highest Potential for Experimental Work

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Diamine</th>
<th>Diacid Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>trans 2,5-Dimethyl-Piperazine</td>
<td>Terephthaloyl Chloride</td>
</tr>
<tr>
<td>Dichloro-Methane</td>
<td>Piperazine</td>
<td>Terephthaloyl Chloride</td>
</tr>
<tr>
<td>Dichloro-Methane</td>
<td>Piperazine</td>
<td>Sebacoyl Chloride</td>
</tr>
<tr>
<td>Chloroform</td>
<td>Piperazine</td>
<td>Sebacoyl Chloride</td>
</tr>
</tbody>
</table>
of time the polymer products begin to precipitate out of solution. This system could still be used if analysis were performed before any precipitation occurred or if the chloroform was evaporated and a better solvent such as m-cresol used for storage and analysis. Another problem of this system was the need for a very specific derivative of piperazine. This derivative was limited in availability and had a high cost. The main reason that it is considered the best reaction system was that its rate was very high. The third reaction system involving piperazine and sebacoyl chloride in dichloromethane also formed a supersaturated solution. Both of these reaction systems were therefore considered inadequate. The second system precipitated polymer almost immediately and thus was also inadequate. The fourth system was the only one examined experimentally that produced product which was soluble for an indefinite period of time.

The disadvantages of the fourth reaction are lower rate than the first and the use of aliphatic monomer. The aliphatic diacid chloride was somewhat more susceptible to reaction with the acid acceptor than an aromatic diacid chloride. The analysis of the reaction products was difficult in the solvent chloroform. Chloroform is a good liquid chromatography solvent for ultraviolet detection as long as the components to be measured absorb above a wavelength of approximately 250 nanometers. An aromatic ring in the polymer might insure that the products absorb at a higher wavelength. The high refractive index of chloroform made refractive index detection less sensitive than for other common organic solvents. Another possible analysis technique involved using a Fourier transform ion cyclotronic resonant
mass spectrometer. This machine was an experimental measurement system which was capable of determining molecular weights over the range from zero to approximately 5000. The mass spectrometer could also be both quantitative as well as qualitative. The use of the Ohio State University's mass spectrometer was limited by equipment failures but could be considered further for analysis when stable operation is obtained.

The use of liquid chromatography required that the appropriate column be chosen to separate the components of the reaction system. The components to be separated had low molecular weights compared to most polymers. The difference in the product species molecular weights were a minimum of about eighty. This low molecular weight difference could require more than a single column to obtain complete separation or the use of slow flow rates. The type of column which separated the different components is a size exclusion column. The column was packed with ten micron diameter styrene-divinylbenzene copolymer beads with 100 Å pores. The separation was affected by trapping the smaller sized molecules in the pores while the larger molecules passed by the pores. Thus the largest molecules were eluted from the column first followed by progressively smaller ones. As the components eluted from the column they were measured by a detection device. Both refractive index and UV detectors were used to produce usable results but since UV standards were not available only the refractive index results were used in analysis.

The reaction system was composed of second order irreversible reactions. A general reaction mechanism for the diamine and diacid
chloride reacting in the presence of an acid acceptor was given by Morgan [45] and is

\[
\text{Diacid Chloride + Diamine } \rightarrow \text{ Amide Hydrochloride } \quad (126) \\
\text{Amide Hydrochloride } \rightarrow \text{ Amide + HCl } \quad (127) \\
\text{Diamine + HCl } \rightarrow \text{ Diamine Mono-HCl } \quad (128) \\
\text{Diamine Mono-HCl + HCl } \rightarrow \text{ Diamine Di-HCl } \quad (129) \\
\text{Acid Acceptor + HCl } \rightarrow \text{ Acceptor Salt } \quad (130) \\
\text{Diamine Salts + Acceptor } \rightarrow \text{ Diamine + Acceptor Salts } \quad (131) \\
\text{Diacid Chloride + Acceptor } \rightarrow \text{ Complex } \rightarrow \text{ By-Products } \quad (132)
\]

Polymer was produced by reactions involving the amide with the appropriate reactant. The general mechanism is reduced to the desired second order reaction mechanism system by utilizing assumptions and information available in Morgan [45] and Morgan and Kwolek [46].

Reaction (132) was considered negligible since a sterically hindered acid acceptor was used and the contact time between the diacid chloride and acid acceptor were kept to a minimum. The acid acceptor chosen was triethylamine which provided the necessary steric hindrance. The acid acceptor provided the necessary base strength to be preferentially used in reaction (130) instead of reactions (128) and (129) which use the diamine to consume the by-product acid. The acid acceptor, triethylamine, had a base strength that was about one pKa unit greater than piperazines' pKa base strength and five pKa units greater than diamine monohydrochlorides. This difference caused
reaction (130) to be favored over reactions (128) and (129). Reac-
tions (128) and (129) could use some of the diamine but the diamine
was regenerated by reaction (131) with triethylamine. Thus reactions
(128) and (129) were much slower than reaction (130) and even when
they did occur reaction (131) reversed their effects as long as tri-
ethylamine was present. Thus reactions (128), (129), and (131) were
neglected in the rate equation analysis and the mechanism reduced to

Diacid Chloride + Diamine $\longrightarrow$ Amide Hydrochloride \hspace{1cm} (133)
Amide Hydrochloride $\longleftarrow$ Amide + HCl \hspace{1cm} (134)
Acid Acceptor + HCl $\longleftarrow$ Acceptor Salt \hspace{1cm} (135)

This system was still not second order unless reaction (135)
is not reversible and reaction (134) is much faster than reaction
(133). Morgan and Kwolek [46] have shown for a diamine diacid chlo-
ride reaction system that the reaction (134) was essentially irrevers-
able and that its rate constant was much greater than the rate con-
stant for reaction (133). Thus the two reactions are essentially one
single second order reaction. Reaction (135) is described by Morgan
[45] as being irreversible since the reactions involving a diamine and
diacid chloride have such high rates and produce high molecular weight
polymers. Thus the reaction mechanism is reduced to two reactions

Diacid Chloride + Diamine $\longrightarrow$ Amide + HCl \hspace{1cm} (136)
Acid Acceptor + HCl $\longrightarrow$ Acceptor Salt \hspace{1cm} (137)
This reaction mechanism describes the generation of the first amide oligomer and is second order with respect to the basic reactant components.

The mechanism is continued by reactions involving the various amide products with the appropriate reactant as the following listing shows

\[
\begin{align*}
\text{Amide}(1) + \text{Diacid Chloride} & \rightarrow \text{Amide}(2) + \text{HCl} \\
\text{Amide}(1) + \text{Diamine} & \rightarrow \text{Amide}(3) + \text{HCl} \\
\text{Amide}(3) + \text{Diacid Chloride} & \rightarrow \text{Amide}(4) + \text{HCl} \\
\text{Amide}(2) + \text{Diamine} & \rightarrow \text{Amide}(4) + \text{HCl} \\
\text{Amide}(4) + \text{Diacid Chloride} & \rightarrow \text{Amide}(5) + \text{HCl} \\
\text{Amide}(4) + \text{Diamine} & \rightarrow \text{Amide}(6) + \text{HCl} \\
\text{Amide}(6) + \text{Diacid Chloride} & \rightarrow \text{Amide}(7) + \text{HCl} \\
\text{Amide}(5) + \text{Diamine} & \rightarrow \text{Amide}(7) + \text{HCl}
\end{align*}
\]

etc.

A reaction between two amides is also possible and eventually will occur to help increase the molecular weight of the product mixture.

The termination of the reaction system has not been discussed. The reaction system continued until one type of reactive group had been completely consumed. Thus a termination step was needed to stop the reaction so that reaction kinetics could be measured and so that the kinetics could be stopped in the reactor system. The termination step used diethylamine to scavenge available HCl, any acid chloride reactive end groups, and any diacid chlorides. Morgan [45] stated
that monofunctional secondary amines were useless as acid acceptors because of their rapid reaction with the acid chlorides. He also stated that chain termination was brought about by monofunctional secondary amines unless they were severely sterically hindered. Thus diethylamine was chosen as the chain terminator. The reaction between diethylamine and the acid chloride groups was essentially instantaneous. Morgan [45] also stated that the reaction rate constants for the acylation of piperazine with not more than one methyl substituent adjacent to each nitrogen were in the range of $10^2$ to $10^6$ l/mole/sec. Thus the fastest of these reactions was near the very fast reaction range given by Mao and Toor [42]. The reported values for the rate constant range also supported the reduction of the mechanism to second order reactions. The rate limiting step of the reaction system was the reaction involving production of the various amides (propagation type reactions).

**Discussion on Analysis and Results**

Size exclusion chromatography using a Phenomenex Phenogel 100 A pore size and 10 micron particle size column packed in chloroform was used to determine the amounts of various components in the reaction mixture. Figure 62 shows the conversions of the diamine and diacid chloride as a function of time for one initial concentration. These curves were obtained by normalizing the area percent values from the chromatographs at the specific retention time by the same value obtained from the infinitely long reaction experiment. This procedure
allowed the concentration fractions of components A and B to be determined based on the assumption that all the reactants were consumed in the infinitely long reaction experiment (time was approximately ten days). These concentration versus time curves were used to determine the rate constants. The evaluation of the rate constants depended upon the number of product species produced. From the chromatographs the number of products for the low initial concentration case was one while for the high initial concentration case the number of products was four. The concentration versus time values obtained for the reactants was assumed more accurate than the values obtained for the products since the product species always resulted in area percent values less than seven percent and frequently below one percent. The analysis assumed that reaction between two product amides did not occur early in the polymerization. This assumption should be valid because early in the reaction the concentration of the various amides was much less than the concentration of the diamine and diacid chloride.

The evaluation of separate rate constants would have involved large amounts of data to obtain accurate estimates for each rate constant. The evaluation technique for this type of system would have involved numerical integration of the equations with estimates for the rate constant values followed by updating the estimates until some error criterion on the concentrations would have been met. This procedure would have assumed that the concentration versus time data would have been exactly correct and any slight errors in the data would have resulted in errors in the rate constants. Inherent errors would also have been introduced in the numerical integration. This
Figure 62 Conversion of Piperazine and Sebacoyl Chloride Versus Time for Initial Piperazine Concentration of 0.095M and Initial Sebacoyl Chloride Concentration of 0.100M.
technique was not used since the limiting rate constant for the polymerization would have been from a propagation step and all propagation steps would have had approximately equal rate constants. Therefore, the approach in determining the rate constants was to obtain an estimate for the rate constant of the rate limiting step.

The analysis was simplified greatly since all the rate constants were assumed to have the same value. The amount of rate data needed to obtain an accurate value for the rate constant was drastically less for one rate constant evaluation than for the multiple rate constant case. The value of the rate constant was needed to solve the turbulent mixing scalar balance equations. The numerical procedure used to calculate the rate constant was: 1) assume only one reaction occurred between the first two reactants and estimate the rate constant for this reaction with the assumption that the value obtained should approximate the correct rate constant value and 2) run an ACSL simulation program with the approximate value of the rate constant obtained in step 1) and the correct number of reactions to produce the desired number of products and make new estimates of the rate constant until the concentration versus time curves for the initial two reactants were satisfactorily fitted by the program predictions. The range of values obtained (from all the measured batch experiments) is 10 to 120 liter/mole/second. A single value was not obtained for the rate constant because many different effects occurred when the concentration of the monomers was changed. Some of the effects were the impurities effects, the solvent effect, and the accuracy of the analysis and concentration of the solutions used. The impurities in the
solvent, diamine, and diacid chloride could react with the diamine and diacid chloride. With higher initial concentrations of reactants, the percentage of the reactants being consumed in unwanted side reactions was less. Thus the higher initial concentration reactions should have provided more accurate values for the rate constant (larger values) as long as the assumption of equal rate constants for all reactions was acceptable. The higher initial concentration reactions produced up to four product species.

The assumption of equal rate constants for all reactions allowed determination of a single rate constant but no verification and validation will be given to determine if the rate constants of the first few reaction steps is different from those of the propagation-type steps. Thus the values obtained at the higher concentrations could also be in error. The upper portion of the range was found to be within the range for the diacid chloride-diamine reaction range given by Morgan [45], $10^2$ to $10^6$ liter/mole/second. The size of the value places the polymerization system in the slow reaction region of Mao and Toor [42]. Therefore, this reaction system did not warrant further examination in the multi-jet tubular reactor.

Conclusions

The reaction system that best satisfied the rate constant criterion was shown to be expensive and to form a supersaturated polymer solution from which the polymer products precipitated after about a day. The system was not examined since analytical equipment was not
available within a few hours of the batch kinetic experiments. The system chosen reacted piperazine and sebacoyl chloride with triethylamine as the acid acceptor and chloroform as the solvent. The products remained soluble indefinitely. The system did not have rates as high as the trans 2,5-dimethylpiperazine and terephthaloyl chloride polymerization. The problems of measurement of the product species produced by the piperazine-sebacoyl chloride stemmed from the solvent chloroform and the non-aromaticity of the polymer backbone. The list of possible reactions presented previously in this chapter did not consider the reactions in which the reactants were not available from chemical suppliers.

If chemicals, such as ethylene bischloroformate, were more readily available then other reactions such as piperazine and ethylene bischloroformate become possible as choices for examination. The system chosen was examined experimentally in a batch reactor to determine the rate constant of the rate limiting step. The range of values obtained for the rate constant is within the range given by Morgan [45] and falls in the slow reaction range of Mao and Toor [42]. Thus this reaction should not be studied in the multi-jet reactor to evaluate the turbulent mixing theories capabilities of predicting the product distribution.
CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The work presented here has examined the turbulent mixing and reaction problem. This work has produced the following results

(1) The Brodkey-LeWalle closure is simply an extension of Toor's hypothesis applied to the second reaction as was demonstrated in Chapter II.

(2) The failure of the Brodkey-LeWalle closure for the entire Reynolds number range is due to its inability to satisfy all the criteria necessary for a closure to adequately describe the relationship between the covariance terms. This failure means that Toor's hypothesis fails when extended to the multiple reaction case as was demonstrated for a kinetic ratio of about 2000:1.

(3) The Brodkey-LeWalle closure was shown to be valid for the high Reynolds number region for the kinetic ratio of 2000:1. For the low Reynolds number region either \( \overline{B} \overline{P} \) or the negative of the Brodkey-LeWalle closure was shown to be valid. These results suggest that for poor mixing the \( \overline{bp} \) covariance is equal to the product of the \( \overline{B} \) and \( \overline{P} \).
The fast mixing case was examined by writing the Brodkey-LeWalle closure as

\[ \bar{bp} = \bar{ab} \frac{BP}{AB} \]  

(146)

This equation shows that for poor mixing the \( \bar{ab} \) covariance is equal to the product of \( \bar{A} \) and \( \bar{B} \) and this results in the equality of the \( \bar{bp} \) covariance with the product of \( \bar{B} \) and \( \bar{P} \). The fast mixing limit did not allow \( \bar{AB} \) to equal the product of \( \bar{A} \) and \( \bar{B} \) and therefore \( \bar{bp} \) did not equal the product of \( \bar{B} \) and \( \bar{P} \) but \( \bar{bp} \) was now dependent upon \( \bar{ab} \) as described by the Brodkey-LeWalle closure relationship.

(4) The failure of closures involving the Damköhler numbers was considered to be due to the use of average values in the definitions and the unknown scale that these numbers required.

(5) All other closures examined failed.

(6) The development of improved closures depended upon use of three criteria: the molar fluctuation balance must be satisfied, the sign on the covariance term must be correct, and the limits of infinitely fast reaction and pure mixing (no reaction) must be satisfied.
(7) The simulation program adequately represented qualitatively the expected physical results. This program should provide insights into possible new closure formulations.

(8) The chemical system studied for rate constants did not fulfill the objectives as was anticipated. The use of the trans 2,5-dimethyl-piperazine reaction system should fulfill the needs as long as analysis is made within one day of the reaction.

(9) The reactor system was successfully tested using the very fast reaction between hydrochloric acid and sodium hydroxide. The results are in agreement with published values given by Toor [60], Mao and Toor [42], and Singh and Toor [57].

(10) The simulation program results for a multiple reaction case show that some of the covariance terms should be zero. This result was then used in the numerical integration routines and was shown to minimally change the results from those obtained by using the Brodkey-LeWalle closure. Without experimental data no determination can be made concerning which is correct or more valid.

(11) The two cell volume averaged simulation results are equivalent to the multiple run simulation results. However, the multiple cell simulation runs showed that interactions occurred which were not accounted for by the simple two cell case or the multiple two cell run case. The difference could be as great as twenty-five percent.
The results of this work have demonstrated that previous theories are not sufficient for analyzing real experimental data. This failure suggests that the basis for a single second order reaction system was only partially correct and that revisions are necessary to accommodate more reactions.

**Recommendations**

The work described in this dissertation is the necessary preliminary research that is needed to begin exploring new avenues of turbulent mixing with multiple second order chemical reactions. Future work should contain the following:

(1) Analysis equipment such as a liquid chromatograph should be purchased along with refractive index and ultraviolet light detectors. An automatic sampler would also be advisable due to the length of time required to separate a sample. Other possible equipment that could be needed are the accessories that are used when preparative chemistry is performed on the liquid chromatograph. This equipment might be needed to separate the product species so that standards can be made from them. This separation would also allow other analysis techniques to verify the exact molecular weight of the compound. Another important analysis technique (the ion cyclotronic mass spectrometer) should be used for high precision work if its operation becomes more reliable. The ion cyclotronic mass spectrometer supposedly can determine both qualitative and quantitative results on samples that have molecular weights less than about 5000.
(2) An analysis for various rate constant ratios should be made of the kinetic terms that are assumed zero (for all values of the rate constants) in the Toor type derivation. The possibility exists that the no reaction and infinitely fast reaction limits imposed upon the kinetic terms in the covariance continuity equations described a minimum and that some curve with a maximum value described the region between the limits.

(3) Experimental equipment utilizing either a smaller mixing module or larger feed tanks than were used in this work is suggested. With the current system the amount of time before refilling the tanks is about 120 seconds. This suggestion requires little experimental work if larger tanks are used but if a new module is designed then the necessary flow measurements and intensity of segregation measurements must be made.

(4) Reaction systems involving three and four reactions should probably be examined prior to experimentation with a polymerization system. More preliminary information could be obtained on the intermediate covariance terms (if they could be established) which then could be used in the polymerization study.

(5) The kinetic experiments which are used to obtain the rate constants need to utilize more precise equipment. A possible reaction system in manufactured by Update Instrument, Incorporated. This system is called the system 1000 Chemical/Freeze Quench Apparatus. The
quenching operation of this system would allow the reaction to be terminated at a specified time. This system is computer controlled which provides higher precision time measurements compared to the current method. The total cost of this system with suggested accessories is about $28000. The equipment would need to be made of materials that do not swell or are not soluble in the solvent to be used in the experiments (chloroform in this study).
LIST OF REFERENCES


APPENDIX

Computer Program Names
The computer routines (and a short functional description) used in the two-cell and multi-cell statistical simulations were:

- **BASE.FOR**: selected base cells
- **CALC2.FOR**: calculated the average and fluctuating components of the instantaneous values
- **CEQN2.FOR**: calculated the closure predictions and other related equations
- **CFIG.FOR**: set up the configuration array and was used to determine cells with common borders
- **CONC.FOR**: readjusted the component amounts for the chosen event
- **DELTA.FOR**: calculated the rates of mass transfer and reaction and corresponding fractions or probabilities of these events
- **DET.FOR**: calculated the number of component A and B in product species
- **DRAT.FOR**: calculated the diffusivities for the components
- **GETNAME.FOR**: opened the desired output/input files
- **INPUT1.FOR**: acquired the desired input data from the appropriate file or device
- **IREP.FOR**: randomly selected the events
- **MOLW.FOR**: calculated the molecular weight of the product species
The multi-run computer programs were: PHDN4.FOR, BASE.FOR, CFIG.FOR, CONC.FOR, DELTA.FOR, DET.FOR, DRAT.FOR, INPU3.FOR, IREP.FOR, NOSET.FOR, PHDWOR1.FOR, and SUMT.FOR. The description of most of these routine was previously given. A description of the remaining routines is:

INPU3.FOR  functions as INPU1.FOR
PHDN4.FOR  controls the flow of information and determines when output is saved

The programs used for the calculations were TIMCALC.FOR, CALCTIM.FOR, CEQNTIM.FOR, and DET.FOR. A short description of these routines is:

CALCTIM.FOR  calculated the average and fluctuating components of the instantaneous values
CEQNTIM.FOR  calculates the closure predictions and other desired equations
TIMCALC.FOR  opens the input files (output from multi-run simulations) and randomly selects
cells

The quadrature numerical integration program consisted of:

KNEW.FOR solved the simultaneous-consecutive reaction case coupled mass balance equations

SCALE.FOR calculated the characteristic dimension

Incorporated into this program were the $I_s$ equations developed by Singh and Toor as well as the exponential decay law and the ability to use a table of $I_s$ values. This program also allowed the average velocity to be expressed as a constant or as a table of data which varied along the reactor length. The multiple reaction system required that ACSL routines be developed. The names of the ACSL routines that were used to simulate multiple reactions were:

RLE.CSL multiple second order reaction solution routine that used Brodkey-LeWalle type closures

RLLE.CSL same as above except that the new ideas about certain covariance terms being zero was incorporated
The last program used in this work was called RATE.CSL. This program was used to predict better estimates of the rate constant for the rate limiting step of the sebacoyl chloride and piperazine reaction system.