INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.
Numerical studies of chemical selectivity and heat transfer in decaying homogenous turbulence

Chakrabarti, Mitali, Ph.D.
Iowa State University, 1991
Numerical studies of chemical selectivity and heat transfer in decaying homogenous turbulence

by

Mitali Chakrabarti

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

Department: Chemical Engineering
Major: Chemical Engineering

Approved:

Signature was redacted for privacy.
In Charge of Major Work
Signature was redacted for privacy.
For the Major Department
Signature was redacted for privacy.
For the Graduate College

Members of the Committee:

Signature was redacted for privacy.

Iowa State University
Ames, Iowa
1991

Copyright © Mitali Chakrabarti, 1991. All rights reserved.
# TABLE OF CONTENTS

**GENERAL INTRODUCTION** ................................................. 1  
Explanation of dissertation format .................................. 3  

**PART I. CHEMICAL SELECTIVITY IN HOMOGENOUS DECAYING TURBULENCE**  
1. **INTRODUCTION** .......................................................... 5  
2. **BACKGROUND** ............................................................ 10  
   2.1 Mixing and chemical reaction .................................... 12  
   2.2 Models for turbulent reacting flows ......................... 14  
   2.3 Experiments .......................................................... 21  
   2.4 Numerical methods ................................................ 24  
   2.5 Other work .......................................................... 28  
3. **METHOD** ............................................................... 30  
4. **RESULTS AND DISCUSSION** ..................................... 44  
   4.1 Effect of physical parameters ................................. 48  
   4.2 Evaluation of closure theories ............................... 59  
5. **CONCLUSIONS** ....................................................... 116
APPENDIX A: BACKGROUND ON TURBULENCE 201

The physics of turbulence 201
Characteristics of turbulence 201
Approaches to the turbulence problem 205

APPENDIX B: LITERATURE REVIEW ON MIXING AND REACTION 211

Mixing and chemical reaction 211
Mixing 211
Turbulent mixing 212
Turbulent mixing and fast chemical reactions 215
Multiple chemical reactions 219
Reactions in parallel 219
Reactions in series 219
Series-parallel reactions 220
Micromixing and selectivity 222
Models 229
Mechanistic models 230
Direct turbulence models 236

APPENDIX C: SPECTRAL METHODS 247

Introduction 247
The spectral (Galerkin) method 248
Pseudospectral method 250
Recent developments 254

APPENDIX D: SOME DERIVATIONS 256
LIST OF FIGURES

Figure 1.1: Examples of reactants A and B which undergo parallel-consecutive reactions (Bourne, 1984) ............................................ 9
Figure 3.1: Schematic diagram of a plug flow reactor ........................................ 39
Figure 3.2: Schematic sketches of scalar initial fields (a) striped initial scalar field (b) stirred initial scalar field ........................................ 40
Figure 3.3: Effect of random number generators on statistical quantities (a) Kinetic energy (b) Mean concentration of A, \( \overline{C_A} \) (c) concentration fluctuation covariance \( \overline{c_B c_R} \) ........................................ 41
Figure 4.1: Time history of reactants and products for code A and an initial scalar field U (a) single reaction (b) series-parallel reaction 71
Figure 4.2: Local values of reaction rate, \( k_1 C_A C_B(x,0,0) \), for a single reaction for code K and initial scalar field U ................................. 73
Figure 4.3: Local values of reaction rate, \( k_1 C_A C_B(x,0,0) \), for series-parallel reactions for code A and initial scalar field U ................................. 74
Figure 4.4: Local values of reaction rate, \( k_2 C_B C_R(x,0,0) \), for series-parallel reactions for code A and initial scalar field U ................................. 75
Figure 4.5: Comparison of local values of $k_1 C_A C_B(x,0,0)$ for a single reaction (code K) and $k_1 C_A C_B(x,0,0)$ and $k_2 C_B C_R(x,0,0)$ for a series-parallel reaction (code A) at time, $t=3.0$.

Figure 4.6: Schematic of concentration profiles of A, B, R and S for the case with no velocity: (a) initial distribution (b) distribution after a finite time, (Levenspiel, 1972).

Figure 4.7: Comparison of the intensity of segregation $I_s$ for code A and striped initial scalar field U and stirred initial scalar field V: $I_s$ for A and B is $\frac{A_{cc} B}{C_A C_B}$, $I_s$ for B and R is $\frac{B_{rc} C}{C_B C_R}$.

Figure 4.8: Effect of turbulence intensity on selectivity: codes A, B and C for an initial scalar field U.

Figure 4.9: Effect of viscosity on selectivity: codes A, F and G for an initial scalar field U.

Figure 4.10: Effect of viscosity on scalar microscale: codes A, F and G for an initial scalar field U.

Figure 4.11: Contour plot of reaction rate, $k_1 C_A C_B(x,y,0)$ for different viscosities and Schmidt numbers for an initial scalar field U at $t=3.0$ (a) $k_1 C_A C_B$ for code A (b) $k_1 C_A C_B$ for code E (c) $k_1 C_A C_B$ for code G.

Figure 4.12: Contour plot of reaction rate $k_2 C_B C_R(x,y,0)$ for different viscosities and Schmidt numbers for an initial scalar field U at $t=3.0$ (a) $k_2 C_B C_R$ for code A (b) $k_2 C_B C_R$ for code E (c) $k_2 C_B C_R$ for code G.
Figure 4.13: Perspective plot of $k_1 C_A C_B(x, y, 0)$ for code E and an initial scalar field $U$ at $t=3.0$ ......................................................... 88

Figure 4.14: Perspective plot of $k_1 C_A C_B(x, y, 0)$ for code A and an initial scalar field $U$ at $t=3.0$ ......................................................... 89

Figure 4.15: Effect of Schmidt number on selectivity: codes H, I, A and J and an initial scalar field $U$ ......................................................... 90

Figure 4.16: Effect of viscosity and $Sc$ on selectivity: codes A, D and E and an initial scalar field $U$ ......................................................... 91

Figure 4.17: Effect of rate constants on selectivity: codes A, L, M, N and O and an initial scalar field $U$ ......................................................... 92

Figure 4.18: Time history of reactants and products for code O, different $k_1/k_2 = 0.5$ and an initial scalar field $U$ ......................................................... 93

Figure 4.19: Effect of non-stoichiometry on selectivity: codes P, Q, A, R and S and an initial scalar field $U$ ......................................................... 95

Figure 4.20: Effect of initial conditions on the evolution of R and S: code A with striped (1-d, scalar field $U$) and stirred (3-d, scalar field $V$) distribution of reactants A and B ......................................................... 96

Figure 4.21: Effect of initial conditions on selectivity: code A with striped (1-d, scalar field $U$) and stirred (3-d, scalar field $V$) initial distribution of reactants A and B ......................................................... 97

Figure 4.22: Perspective plots of reaction rates for code A for an initial isotropic scalar field $V$ at $t=3.0$ (a) $k_1 C_A C_B(x, y, 0)$ (b) $k_2 C_B C_R(x, y, 0)$ ......................................................... 98
Figure 4.23: Evolution of scalar concentration microscales for code A and A striped initial scalar field U ......................... 100
Figure 4.24: Evolution of scalar concentration microscales for code A for an initial isotropic scalar field V ......................... 101
Figure 4.25: Comparison of scalar concentration microscales for code A for isotropic and anisotropic initial scalar fields ............. 102
Figure 4.26: DNS results for covariance of concentration fluctuations $\overline{c_A c_B}$ and $\overline{c_B c_R}$ for code A ......................... 103
Figure 4.27: Comparison of DNS and model predictions of $\overline{c_B c_R}$ values for code A (a) striped initial scalar field U (b) stirred initial scalar field V .............................................. 104
Figure 4.28: Predictions of mean quantities for code A: DNS ........... 106
Figure 4.29: Predictions of mean quantities for code A: Bourne-Toor closure compared with DNS ................................. 107
Figure 4.30: Predictions of mean quantities for code A: Brodkey-Lewalle closure with DNS ........................................... 108
Figure 4.31: Predictions of mean quantities for code A: Li-Toor closure compared with DNS ........................................... 109
Figure 4.32: Predictions of mean quantities for code A: Dutta-Tarbell closure compared with DNS ....................................... 110
Figure 4.33: Comparison of $X_s$ values (DNS with closure theories) for code A and a striped initial scalar field U ..................... 111
Figure 4.34: Comparison of $\overline{c_A c_B}$ for 1 and 2 reactions and $\overline{c_A c_A}$ for mixing 112
Figure 4.35: Comparison of Brodkey-Lewalle closure and DNS results for
different values of $k_1/k_2$ ........................................ 113

Figure 4.36: Comparison of the "unproposed non-closure" with DNS re-
results for code A for a striped initial scalar field ............. 114

Figure 4.37: Comparison of the "unproposed non-closure" with DNS re-
results for code A and an initial isotropic scalar field .......... 115

Figure 2.1: Toaster and mandoline configurations ................. 138

Figure 4.1: Evolution of Reynolds number for decaying isotropic turbulent
scalar field for DNS runs B1 and B4 ................................. 154

Figure 4.2: Evolution of velocity and scalar derivative skewness for decay-
ing isotropic turbulent scalar field for DNS runs B1, B2 and
B3 - scalars 1, 2 and 3 refer to initial length scale ratios of 1,
0.5 and 1.5 respectively ............................................ 155

Figure 4.3: Evolution of scalar variance for isotropic turbulent scalar for
DNS runs B1, B2 and B3 (a) linear scale (b) log-log scale .... 156

Figure 4.4: Evolution of integral velocity and scalar length scales for de-
caying isotropic turbulent scalar field - DNS and DIA with
initial Gaussian spectra ............................................ 158

Figure 4.5: Evolution of Taylor velocity and scalar length scales for de-
caying isotropic turbulent scalar field - DNS and DIA with
initial Gaussian spectra ............................................ 159

Figure 4.6: Evolution of length scale ratios for decaying isotropic turbu-
 lent scalar field - DNS and DIA with initial Gaussian spectra 160
Figure 4.7: Evolution of velocity and scalar dissipation for decaying isotropic turbulent scalar field for DNS runs B1, B2, B3

Figure 4.8: Evolution of kinetic energy for the toaster for DNS runs C1, C2, and C3

Figure 4.9: Evolution of scalar variance for the toaster for DNS runs C1, C2, and C3 (a) linear scale (b) log-log scale

Figure 4.10: Evolution of the scalar transport correlation coefficient $\rho_{\theta}$ for the toaster for DNS runs C1, C2, and C3

Figure 4.11: Evolution of the integral velocity and scalar length scales for the toaster for DNS run C2

Figure 4.12: Evolution of the integral length scale ratios for the toaster for runs C1, C2, and C3

Figure 4.13: Evolution of the eddy diffusivity ratio $\epsilon_H/\alpha$ for the toaster for DNS runs C1, C2, and C3

Figure 4.14: Comparison of evolution of the length scale ratios for the toaster for conditions of DNS run C4

Figure 4.15: Comparison of the evolution of the scalar transport correlation coefficient $\rho_{\theta}$ for the toaster for conditions of DNS run C4

Figure 4.16: Comparison of the evolution of the eddy diffusivity ratio $\epsilon_H/\alpha$ for the toaster for conditions of DNS run C4

Figure 4.17: Evolution of turbulent Reynolds number for the mandoline for DNS run D4

Figure 4.18: Evolution of kinetic energy for the mandoline for DNS runs D3 and D4
Figure 4.19: Evolution of velocity derivative skewness for the mandoline for DNS runs D3 and D4 175

Figure 4.20: Evolution of scalar derivative skewness for the mandoline for DNS runs D3 and D4 176

Figure 4.21: Evolution of scalar variance for the mandoline for DNS runs D3, D4, D5 and D6 (a) linear scale (b) log-log scale 177

Figure 4.22: Evolution of scalar transport correlation coefficient $\rho_{uv\theta}$ for the mandoline for DNS runs D3, D4, D5 and D6 179

Figure 4.23: Evolution of ratio of integral length scales for the mandoline for different mandoline configurations, DNS runs D4, D5 and D6 180

Figure 4.24: Evolution of eddy diffusivity ratio for the mandoline for different mandoline configurations for DNS runs D3, D4, D5 and D6 181

Figure 4.25: Comparison of evolution of kinetic energy for the the mandoline for conditions of DNS run D7 182

Figure 4.26: Comparison of evolution of the velocity derivative skewness for the mandoline for conditions of DNS run D7 183

Figure 4.27: Comparison of evolution of the length scale ratios for the mandoline for conditions of DNS run D7 184

Figure 4.28: Comparison of the evolution of the scalar transport correlation coefficient $\rho_{uv\theta}$ for the mandoline for conditions of DNS run D7 185

Figure 4.29: Comparison of the evolution of the eddy diffusivity ratio $\epsilon_H/\alpha$ for the mandoline for conditions of DNS run D7 186
Figure 4.30: Comparison of the evolution of the correlation coefficient $\rho_{v\theta}$
for the toaster and mandoline .......................... 187

Figure 4.31: Comparison of the evolution of the correlation coefficient $\rho_{v\theta}$
for the toaster and mandoline, DIA and DNS ............. 188

Figure 6.1: Schematic diagram of vortex stretching showing the compression and stretching of fluid elements (Frost and Bitte, 1977) . 210

Figure 6.2: Mechanism of turbulent mixing, Brodkey (1975) ........... 244

Figure 6.3: Bourne's diffusion-reaction model, Bourne (1984): A, B, C,
show large scale deformations of a blob of B-rich fluid surrounded by A-rich fluid, D, E show fine scale deformations . 245

Figure 6.4: Fine scale concentration profiles for a series-parallel reaction
as explained in Bourne and Toor's (1977) closure model .... 246
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Summary of some first-order closure theories</td>
<td>17</td>
</tr>
<tr>
<td>3.1</td>
<td>Initial energy spectra</td>
<td>36</td>
</tr>
<tr>
<td>3.2</td>
<td>Conditions for the simulations</td>
<td>37</td>
</tr>
<tr>
<td>3.3</td>
<td>Initial scalar field</td>
<td>38</td>
</tr>
<tr>
<td>4.1</td>
<td>Summary of concentration covariance values</td>
<td>48</td>
</tr>
<tr>
<td>4.2</td>
<td>Damköhler numbers for the striped and stirred initial fields</td>
<td>48</td>
</tr>
<tr>
<td>4.3</td>
<td>Effect of turbulence Reynolds number</td>
<td>51</td>
</tr>
<tr>
<td>4.4</td>
<td>Effect of viscosity</td>
<td>52</td>
</tr>
<tr>
<td>4.5</td>
<td>Effect of Schmidt number</td>
<td>53</td>
</tr>
<tr>
<td>4.6</td>
<td>Coupled effect of $\nu$ and $D$</td>
<td>54</td>
</tr>
<tr>
<td>4.7</td>
<td>Effect of coupled $\nu$ and $D$ changes for different initial energy spectra</td>
<td>55</td>
</tr>
<tr>
<td>4.8</td>
<td>Effect of rate constants</td>
<td>56</td>
</tr>
<tr>
<td>4.9</td>
<td>Effect of initial stoichiometric ratio</td>
<td>57</td>
</tr>
<tr>
<td>4.10</td>
<td>Effect of initial scalar field</td>
<td>58</td>
</tr>
<tr>
<td>4.11</td>
<td>Time development of the square of the concentration microscales relative to $\lambda_0$</td>
<td>60</td>
</tr>
</tbody>
</table>
Table 4.12: Evaluation of individual terms in the evolution equation for $c_A c_B$ .......................... 66

Table 2.1: Heat transfer results from previous work ......................... 135

Table 3.1: Parameters for the pre-simulation run .......................... 142

Table 3.2: Initial conditions for isotropic scalar turbulence ............... 143

Table 3.3: Parameters for the toaster run (initial $\theta_l = 0$) ............. 144

Table 3.4: Parameters for the velocity field for the mandoline ............. 145

Table 3.5: Parameters for the scalar field for the mandoline ............... 145

Table 4.1: Asymptotic values of derivative skewnesses for isotropic scalar
and velocity fields ............................................. 149

Table 4.2: Asymptotic values of integral length scale ratio for isotropic
velocity and scalar fields ........................................ 150

Table 6.1: Theoretical values of length scales for different initial spectra 267
GENERAL INTRODUCTION

Turbulence takes place in a majority of flow situations. It occurs on geo- and astro-physical scales (Corrsin, 1961). Its ability to mix transported quantities much more efficiently and quickly than if only molecular diffusion were involved is used frequently in industrial applications. Any description of turbulent flow must include its unpredictable nature and also take into account the presence of vorticity distributed in all three dimensions (Hinze, 1975). The understanding of turbulent flows is thus one of the most important but difficult problems in the field of fluid mechanics. The presence of a wide range of length and time scales and the nonlinearities in the governing equations make the problem even more complex. It is still difficult to visualize a solution to the turbulence problem or even a generalized approach to the problem, even though the equations governing turbulent flow have long been known.

Corrsin (1961) described the analytical study of turbulent flow as the attempt to predict the history of a velocity field whose behavior at each point in space-time is given by the Navier-Stokes equations. Since the flow is random, an explicit account of the motion of every particle of fluid cannot be given. Consequently, statistical methods are resorted to, and the flow is described in terms of various averaged functions. But, due to non-linearities in the equations, the resulting system of averaged governing equations is not closed, in that the number of unknowns turns out to be
more than the number of equations, and so there is a need to establish auxiliary relations between some unknowns. Several closure models have been proposed in the literature, but none of them works very well.

In direct numerical simulations, the nonlinear dynamical equations are solved using time-dependent, three-dimensional, full turbulence simulations, with no turbulence modeling and with all time and length scales well resolved. The use of direct numerical simulations has enabled researchers to probe, model turbulent flows numerically and has made it possible to measure quantities that are difficult to measure in the laboratory and to test useful or practical statistical theories of turbulence by examination of the dynamical variables and their statistics. The pseudo-spectral method was made popular with the development of fast Fourier transforms, and Patterson and Orszag (1972) were the first to carry out direct numerical simulations of homogenous isotropic turbulent flow using these methods. Pseudo-spectral methods have since been widely used for simulations of turbulent flows.

In the present study, direct numerical simulations using a pseudo-spectral method were used to study two problems – turbulent flows with multiple chemical reactions and turbulent flow with heat transfer.

Explanation of dissertation format

This dissertation consists of two parts, each part dealing with a separate problem. The tables have been included within the text but the figures are at the end of the respective chapters. The first part of this dissertation is a paper entitled “Chemical Selectivity in Decaying Homogenous Turbulence” to be submitted to the AIChE Journal. It addresses the problem of chemical selectivity in turbulent reacting flows
with multiple chemical reactions. This work is an extension of the studies on turbulent reacting flows with a single step reaction made by Leonard and Hill (1988, 1989, 1991) in that complex chemistry has been introduced into the reaction scheme. Many complex chemical reactions are involved in combustion, air pollution problems, and industrial applications. Those reactions are often a combination of several series-parallel reaction schemes. In an attempt to provide a fundamental understanding of the interaction of turbulence, mixing, and complex chemistry, simulations were made for a series-parallel reaction pair. The effect of turbulence Reynolds number and other physical parameters on selectivity was determined. Simulations were also made to test simple first order closure theories for the covariance of the concentration fluctuations of reactants and products.

The second part, entitled “Gradient Transport of a Passive Scalar in Homogeneous Turbulence”, deals with the problem of heat transfer in homogenous turbulent flow. The evolution and transport of a passive scalar by a uniform mean scalar gradient were studied using direct numerical simulations, and the results were compared with predictions of a statistical theory (the direct-interaction-approximation of Kraichnan, 1959, 1964) and with laboratory measurements by Sirivat and Warhaft (1983). The experiments being simulated correspond to the “mandoline” (heated wires to introduce the temperature fluctuations) and “toaster” (uniform temperature gradient existing upstream of the turbulence grid) cases. The evolution of various statistical quantities was compared for cases with and without a mean scalar gradient, to understand the effect of a scalar gradient on the transport of the scalar.
PART I.

CHEMICAL SELECTIVITY IN HOMOGENOUS DECAYING TURBULENCE
1. INTRODUCTION

Many industrial processes involve chemical reactions in turbulent flow as important steps. As is well known, the vast majority of chemical reactors operate in the turbulent flow regime (Hill, 1976). Turbulence is often preferred over laminar flow because it enhances heat and mass transfer rates. The kinetics of reactions involved in industrial chemical processes are often complex, with multiple steps and many intermediate products. The results of manufacturing the wrong distribution of products are a waste of raw materials and also an increased load on the separation stages to extract the desired product in pure form. Such considerations are particularly important in air-pollution, propulsion, and combustion problems, which involve a wide range of complex multiple reactions, and also in chemical processing using, for example, polymerization and co-polymerization reactions. Figure 1.1, (Bourne, 1984), gives a list of reactants A and B which would undergo series-parallel reactions. The chlorination of hydrocarbons, the hydration of ethylene oxide, the formation of ethanolamines (Nauman, 1975), the nitration of aromatic hydrocarbons with nitronium salts (Pfister et al, 1975) are some examples of reaction schemes exhibiting series-parallel behavior. Carmichael et al (1986) show the multitude of reactions in a simple model of photochemical smog. Attempts to reduce the production of undesirable by-products that occur in parallel-consecutive reactions make the study of
chemical selectivity important.

A turbulent flow with complex chemistry involves a complicated interaction of fine scale turbulent mixing, large scale fluid motion, and multiple reactions. The difficulties encountered in conducting turbulent reacting flow experiments under controlled conditions have limited the scope of experimental work on the effect of multiple reactions in a turbulent flow field. The simulation of chemical reactions in a turbulent flow presents difficulties more than just the addition of conservation equations to be integrated for chemical species (Oran and Boris, 1987), because new time and length scales are introduced into the problem. Also, highly exothermic reactions can influence the velocity field by causing large variations in density and other physical quantities.

Except for combustion studies, the principal experimental work on turbulent reacting flows with complex chemistry has been carried out by Bourne and his coworkers (Bourne et al, 1981) who studied a particular series-parallel reaction system—the diazo-coupling reaction, now referred to as Bourne's reaction. Several subsequent experimental studies (Li and Toor (1986), Mehta and Tarbell (1987)) have made use of Bourne's reaction. It should be noted that in Bourne's reaction, the first reaction is very fast compared to the second. Since most experimental studies were limited to just this particular reaction system, knowledge about turbulent flow with multiple reactions has been extremely limited.

Because of the wide range of length and time scales in turbulent flow problems, statistics, such as moments or probability distributions of the velocity, temperature, and composition of the fluid are usually used to describe the flow. Statistical treatments of turbulent flow are based on averaging the governing equations, but since the
equations are nonlinear, the number of unknowns becomes more than the number of
equations as a result of the averaging. This is referred to as the “closure problem”.
In turbulent reacting flows, the averaged rate expressions for the scalars are also un­
closed, leading to the need for closure theories for covariances of the concentration
fluctuations. Some closure theories have been proposed by Bourne and Toor (1977),
Brodkey and Lewalle (1985), Li and Toor (1986), and Dutta and Tarbell (1989), but
these proposed closure methods are not well-founded and do not work very well.

Advances in the power and speed of computers have now made it possible to
solve directly the equations for turbulent reacting flows at moderate Reynolds num­
bers. In direct numerical simulations (DNS), the nonlinear dynamical equations are
solved with no turbulence modeling and with all time and length scales well-resolved.
DNS ensures complete reproducibility and very good control of “experimental” con­
ditions and also allows calculation of quantities that are difficult to measure in the
laboratory. Consequently, DNS serves as a very useful supplement to laboratory
experiments. Direct numerical simulations of three-dimensional chemically reacting
homogenous turbulent flow for unmixed reactants in a single step reaction have been
Riley, Metcalfe and Orszag (1986) have made direct numerical simulations for chem­
ically reacting turbulent mixing layers. Some preliminary investigations on the effect
of various physical parameters for the series-parallel reaction case have been made
by Chakrabarti and Hill (1990) and are presented more completely here. Gao and
O’Brien (1991) have also made preliminary studies on the effect of rate constants for
the series-parallel reaction. Among other work on turbulent reacting flows with com­
plex chemistry, Heeb and Brodkey (1990) have critically evaluated the Brodkey and
Lewalle closure and have studied the covariance term for complex chemical reactions using a statistical simulation program.

In the present study, DNS of a series-parallel reaction pair in a decaying, homogenous turbulent flow was used to help provide a fundamental understanding of the problem of chemical selectivity. The effect of turbulence, compared to the case with no motion, was studied by examining the variations of product distributions with turbulence intensity and viscosity, i.e., by varying the turbulence Reynolds number. The effects of other physical parameters such as Schmidt numbers, diffusivities, reaction rate constants, initial stoichiometric ratios, and initial scalar field conditions were also studied. Comparisons between the single reaction and the parallel-consecutive reaction systems were made to better understand the complexity introduced by more complicated and realistic chemistry. Since closed forms of the averaged rate expressions are needed for reactor modeling, various closure models for covariances of concentration fluctuations such as the first order closure models of Bourne and Toor, Brodkey and Lewalle, Li and Toor, and Dutta and Tarbell were tested by comparing predictions of the models with results of the direct numerical simulations in order to select an appropriate model.
Figure 1.1: Examples of reactants A and B which undergo parallel-consecutive reactions (Bourne, 1984)
2. BACKGROUND

Parallel-consecutive reactions are among the simplest forms of complex chemistry schemes, and so they are studied in the preliminary investigation reported here. A simple model series-parallel reaction scheme for chemical species A, B, R and S is

\[
A + B \xrightleftharpoons[k_1]{k_2} R + B \rightarrow S, \tag{2.1}
\]

where R, the intermediate product, will be considered the desired product and S will be considered the undesired product. The measure of selectivity used here is the ratio of the amount of B that reacts to form by-product S to the total amount of B reacted (Bourne et al, 1981) and is represented by \(X_S\). This definition translates to

\[
X_S = \frac{2C_S}{(2C_S + C_R)}, \tag{2.2}
\]

where \(C_R\) and \(C_S\) are the concentrations of R and S respectively. Appendix D has the details of the material balance which leads to equation (2.2). When R is the desired product, attempts are made to increase the formation of R and suppress the formation of S, in order to reduce \(X_S\).

Another common definition of selectivity is the ratio of the amount of the limiting reagent, B, that reacts to form the desired product to the amount that reacts to form the undesirable product, S. \(i.e., C_R/2C_S\). The yield of R, \(i.e., C_R/C_{A0}\), where \(C_{A0}\)
is the initial concentration of A, is also sometimes used to characterize the product distribution.

The rate expressions for the series-parallel reaction scheme are

\[
\begin{align*}
  r_A &= \frac{dC_A}{dt} = -k_1 C_A C_B \\
  r_B &= \frac{dC_B}{dt} = -k_1 C_A C_B - k_2 C_R C_B \\
  r_R &= \frac{dC_R}{dt} = k_1 C_A C_B - k_2 C_R C_B \\
  r_S &= \frac{dC_S}{dt} = k_2 C_R C_B.
\end{align*}
\]

If Reynolds' decomposition is applied to the concentration fields,

\[ C_i = \overline{C_i} + c_i, \]  

where \( \overline{C_i} \) is the average concentration and \( c_i \) the fluctuating component of species \( i \),
then the averaged rate expression for \( R \) would be

\[ \overline{r_R} = k_1 (\overline{C_A \overline{C_B}} + \overline{c_A c_B}) - k_2 (\overline{C_R \overline{C_B}} + \overline{c_R c_B}), \]

where \( \overline{c_i c_j} \) is the covariance of the concentration fluctuations of species \( i \) and \( j \).

The equation (2.8) is not closed because of the appearance of correlations \( \overline{c_A c_B} \) and \( \overline{c_B c_R} \). There is thus a need for closure models to relate higher order moments to lower order moments (i.e., relating covariances to means). Some investigators have proposed closure models for the covariances of concentration fluctuations, and so a brief overview of the closure models available in literature will be given. A short description of turbulent mixing with chemical reaction is first presented in this chapter to highlight the physics behind it. A summary of experimental work and numerical studies on turbulent reacting flows with complex chemistry will also be presented.
2.1 Mixing and chemical reaction

It is important to understand mixing and the interaction of mixing, chemical reaction, and turbulence in order to be able to design turbulent flow chemical reactors. After a brief description of turbulence-enhanced mixing, the interaction of mixing and chemical reaction will be discussed, and the discussion will be extended to include multiple reactions. Hill (1976) gives examples of chemically reacting flows in which turbulent mixing is important.

In a turbulent flow field, vortex stretching and distortion of fluid elements by turbulence causes the concentration gradients of the two species to increase, increases the area of the interface of the unmixed components, and draws the regions of the two species closer together (Patterson, 1985). Turbulent diffusion reduces the scale of segregation to a considerable degree, and molecular diffusion ultimately mixes the two fluids on a molecular level. Thus the rate of mixing is greatly enhanced by turbulence.

If chemical reaction takes place as the fluids mix, then the scenario is more complicated. The most useful single parameter for describing the role of turbulence on chemical reactions, according to O'Brien (1975), is the ratio of the time scale characteristic of the chemical kinetics scheme ($\tau_k$) to the time scale characteristic of turbulent mixing ($\tau_m$). Hill (1976) has defined three groups $N_T = \tau/\tau_m$, $N_D = \tau/\tau_D$ and $N_R = \tau/\tau_k$, where $\tau_m = L_0/u_0$, $\tau_D = L_0^2/D$, $\tau_k = \Gamma_0/R_0$, $\tau$ is either $\tau_m$, $\tau_D$ or $\tau_k$, and $L_0$, $u_0$, $\Gamma_0$, $R_0$ are characteristic turbulent length scale, velocity, concentration and reaction rate respectively. $N_T$, $N_D$ and $N_R$ are measures of the relative ease of achieving mean uniformity by turbulent mixing, of attaining detailed uniformity by molecular diffusion, and of reaching chemical equilibrium,
respectively. O'Brien (1975) used Toor's (1969) analysis and defined slow reactions as those for which \( \tau_k/\tau_m \gg 1 \), moderately fast reactions as those for which \( \tau_k/\tau_m \approx 0(1) \) and very fast reactions as those for which \( \tau_k/\tau_m << 1 \). Hill (1976) recognized the importance of the diffusion time for non-premixed reactants, and so very slow reactions are defined as those for which \( \tau_k >> \tau_D \) and \( \tau_m \), and very fast reactions are defined as those for which \( \tau_k << \tau_m \) and \( \tau_D \). In slow reactions turbulence will induce chemical homogeneity before any significant reaction occurs, and the fluctuations in concentration do not affect the rate of reaction. In fast reactions complex coupling between the turbulence and the reaction is to be expected even under statistically homogenous conditions. In this case, concentration gradients are increased by reaction, and the reaction rate is increased by the mixing rate. For very fast reactions, the rate of molecular diffusion enhanced by turbulence, controls the rate of progress of the reaction.

If more than one reaction occurs simultaneously, then interactions between turbulence enhanced mixing and reaction become very important, since it is recognized that selectivity to specific products is a strong function of mixing rate (Patterson, 1985). That complex reactions are strongly affected by the mixing intensity has been noted by other investigators such as Paul and Treybal (1971) and Cheng and Tookey (1978). Patterson (1975) compared results of a hydrodynamic model for stirred tanks and experimental data obtained in agitated tank reactions.

In the case of a simple single step reaction, reactants A and B react to form the product R. But series-parallel reactions are more complicated: A and B first react to form R by the first reaction, B then further reacts with the R formed to produce S. When a substantial amount of R has been formed, both A and R compete for the
B present in the system to form either more R or S, respectively. And the outcome of this competition determines the product distribution. Consecutive-competitive reactions constitute an important class of mixing-sensitive reactions, where the yield of the intermediate R ranges from a maximum in the chemical regime (slow reaction) through intermediate values in the diffusion-reaction regime (fast reaction) to zero in the diffusional regime (instantaneous reaction) (Bourne, 1982). A more detailed account of the interaction of mixing, reaction and turbulence is presented in Appendix B.

2.2 Models for turbulent reacting flows

The design of chemical reactors using multiple chemical reactions in turbulent flow should account for the complicated interaction of macromixing, micromixing and complex chemistry. Models for turbulent reacting flows are often simplified representations of the physical process but can approximately describe the reaction rate and product distribution. Hill (1979a) had proposed a classification of models of mixing and multiple chemical reactions in turbulent flows as (i) Mechanistic Models and (ii) Direct Turbulence Models. This classification has been adopted and widely used by other investigators, such as Mehta and Tarbell (1987), Dutta and Tarbell (1989) etc. and will be used in this dissertation.

Mechanistic models are based on idealized mechanisms, are simple in form, and are modest in computational demands. But they do not necessarily describe correctly the underlying physics of the problem (Dutta and Tarbell, 1989). All of these models have adjustable parameters which must be fit to experimental data. Some of these models are:
1. Slab diffusion model (Mao and Toor, 1971)

2. Interaction by exchange with mean (IEM) model (David and Villermaux, 1975)

3. Three environment model (Ritchie and Togby, 1979)

4. Four environment model (Mehta and Tarbell, 1983)

5. Diffusion-reaction model (Belevi, Bourne and Rys, 1981)

6. Engulfment-deformation-diffusion (EED) model (Baldyga and Bourne, 1984)

7. Coalescence-dispersion model (Curl, 1963)

8. Mixing-reaction model (Nabholz, Ott and Rys, 1978)

9. Stretch or lamellar mixing model (Ou and Ranz, 1983a,b, Chella and Ottino, 1984, Ranz, 1985)

10. Engulfment (E) model (Baldyga and Bourne, 1989)

11. Linear eddy model (Kerstein, 1991)

12. Turbulent stochastic molecular mixing model (Fox, 1991)

**Direct Turbulence Models** are based on the Navier-Stokes equations and component continuity equations and thus are claimed to have some physical basis. However, in order to arrive at a closed system of equations, the fundamental equations of direct turbulence modeling must be supplemented by closure models which relate higher order statistics to lower order statistics of the concentration distribution (Patterson, 1981).
First order closures provide relationships between second-order correlations and the mean concentrations $\overline{C_A}$, $\overline{C_B}$ or $\overline{C_R}$. Toor (1969) was the first to propose a first-order closure method for reacting systems with finite rate chemistry. He suggested a closure of $\overline{c_A c_B}$ for a single step reaction which has been widely used, although its validity is questionable as described later. First-order closure schemes for $\overline{c_B c_R}$ for a parallel-consecutive reaction have been proposed by Bourne and Toor (1977), Brodkey and Lewalle (1985), Li and Toor (1986) and Dutta and Tarbell (1989). A summary of the closures is given in Table 2.1. A brief description of the closure models follows. A more detailed discussion is given in Appendix B.

Toor (1962) claimed that data from a mixing experiment can be used for very fast, irreversible second order reactions under identical hydrodynamic conditions. Keeler et al. (1965) showed that experimental data on the mixing of a passive scalar additive in a non-reacting system may be used to accurately predict the yield of a rapid, irreversible, second order reaction when the hydrodynamics and initial conditions on mixing for the reactive system are identical to those of the non-reactive system, thereby verifying Toor’s (1962) theory. In order to extend these ideas to systems with finite reaction rates, Toor (1969) suggested that the covariance of reactant concentrations, $\overline{c_A c_B}$, is independent of the speed of the reaction, that is, the covariance depends only on the hydrodynamics and not on the reaction rate. He showed that the behavior of $\overline{c_A c_B}$ is identical for two limiting cases (very slow and very fast reaction) when the reactant species have the same diffusivities and are fed in stoichiometric proportion, and when a Gaussian distribution of the concentration fluctuations of the conserved scalar is assumed. This is commonly referred to as
Table 2.1: Summary of some first-order closure theories *

<table>
<thead>
<tr>
<th>Closures</th>
<th>$\bar{c}_Ac_B$</th>
<th>$\bar{c}_Bc_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toor (1962, 1969)</td>
<td>$\overline{(c_Ac_B)_0} \left( \frac{c_A^2}{c_A0^2} \right)_m$</td>
<td>—</td>
</tr>
<tr>
<td>Bourne-Toor (1977)</td>
<td>$\overline{(c_Ac_B)_0} \left( \frac{c_A^2}{c_A0^2} \right)_m$</td>
<td>$\approx 0$</td>
</tr>
<tr>
<td>Brodkey-Lewalle (1985)</td>
<td>$\overline{c_A^2}_{Am}$</td>
<td>$\bar{c}_AaB \left( \frac{\bar{C}_R}{\bar{C}_A} \right)$</td>
</tr>
<tr>
<td>Li-Toor (1986)</td>
<td>—</td>
<td>$(\bar{C}_B - \bar{C}_S)(\bar{C}_R - \bar{C}_S)$</td>
</tr>
<tr>
<td>Dutta-Tarbell (1989)</td>
<td>$-I_s(\overline{C}_A \overline{C}_B0 + \overline{C}_B \overline{C}_A0)$</td>
<td>$-I_s\bar{C}_R(\overline{C}_B0 - \overline{C}_B)$</td>
</tr>
</tbody>
</table>

*Note: The subscript 0 refers to initial values, and the subscript $m$ refers to conditions of pure mixing without chemical reaction. The intensity of segregation $I_s$ is the value for a non-reacting scalar, $I_s = \frac{c_A^2}{c_Am/C_A0^2}$. 
Toor's hypothesis. The closed form of $c_Ac_B$ is

$$c_Ac_B = (c_Ac_B)_0(e^{-A^2/c_A0^2})_m,$$  \hspace{1cm} (2.9)

where the subscript $m$ denotes values in the absence of reaction, and 0 denotes initial values. Another form of the same equation (Brodkey and Lewalle, 1985) is

$$c_Ac_B = -IsC_A0C_B0$$ \hspace{1cm} (2.10)

where $C_A0$ and $C_B0$ are the mixed feed concentrations, and $Is$ is the intensity of segregation for an otherwise equivalent non-reacting system. For a reacting system, Danckwerts (1952) defined $Is$ to be

$$Is = -c_Ac_B/C_A/C_B,$$ \hspace{1cm} (2.11)

and for a non-reacting system as

$$Is = \left(\frac{c^2_A/C_A/C_B}{C_A+C_B} \right)_m = \left(\frac{c^2_B/C_A/C_B}{C_A+C_B} \right)_m,$$ \hspace{1cm} (2.12)

where $C_A + C_B = 1$ and $c_A0 = -c_B0$. The form in equation (2.12) is commonly used in the closure models even for reacting systems. For a tubular plug flow reactor, $Is$ can be determined from the decay of concentration fluctuations in nonreactive mixing experiments or from the mean conversion of infinitely fast reactions such as acid-base reactions. Miyawaki et al (1974) carried out experiments in a multi-nozzle injection tubular mixer and tested Toor’s theory. The probability distribution of the concentration fluctuations was measured and proved to be the normal distribution. Toor’s theory concerning the relation between concentration fluctuations and conversion of very rapid reactions was also experimentally proved. Kosály (1987) has shown that the asymptotic behavior of Toor’s model for reactant covariance needs to
be modified for the case of very fast chemistry and non-premixed reactants, where the initial pdf for the conserved scalar is not Gaussian. If it is assumed that the pdf of a conserved scalar approaches a Gaussian form asymptotically, then a simple factor that depends on the shape of the initial pdf is needed to correct Toor's hypothesis for long times (Givi and McMurtry, 1988). If the initial pdf is a bimodal delta function, the correction factor is $2/\pi$. Givi and McMurtry (1988) have used direct numerical simulations of zero rate and infinitely fast chemical reactions to investigate the validity of Toor's hypothesis and claim that the application of Toor's hypothesis is not appropriate for the prediction of the conversion rate in plug-flow type reactors with initially segregated reactants. The assumption of a Gaussian pdf for the final stages of mixing of a non-reacting scalar is justified, but the Gaussian pdf assumption is not justified for infinitely fast chemistry. Leonard and Hill (1989) have tested the validity of Toor's hypothesis by using numerical simulations for finite rate chemistry. They found that Toor's model shows excellent agreement with the DNS results for the moderate Damköhler case and reasonably good agreement for the high Damköhler number case, but the concentration covariance predicted by Toor's theory was not independent of the reaction rate.

Bourne and Toor (1977) estimated qualitatively the influence of partial segregation and feed configuration on selectivity.

For a premixed feed they assumed

$$\overline{c_B c_R} > 0 \text{ (positively correlated)},$$
whereas for a non-premixed feed

$$\overline{c_Rc_B} \approx 0 \text{ (uncorrelated).} \quad (2.13)$$

With segregation the rate of formation of R decreases, whereas the rate of formation of S remains relatively unchanged, and thus the amount of R formed relative to S is reduced.

**Brodkey and Lewalle (1985)** extended Toor's hypothesis to the second reaction. They assumed that \( \overline{c_Ac_B} \) is unaffected by the second reaction. The suggested closure is:

$$\overline{c_Rc_B} = \overline{c_Ac_B} \left( \frac{\overline{c_R}}{\overline{c_A}} \right). \quad (2.14)$$

This model is presumed to be valid to at least within few percent when \( k_1 = k_2 \) but fails for very large \( k_1/k_2 \) ratios and is not valid for the entire Reynolds number range.

**Li and Toor (1986)** used a conserved scalar approach. Their closure applies when the reactants are segregated and the first reaction is almost diffusion controlled (\( k_1 \) is very large compared to \( k_2 \)). The closure states:

$$\overline{c_Bc_R} = (\overline{\dot{C}_B} - \overline{\dot{C}_S})(\overline{\dot{C}_R} - \overline{\dot{C}_S}) - \overline{c_Bc_S}, \quad (2.15)$$

where \( \overline{\dot{C}_B} \) and \( \overline{\dot{C}_R} \) are the time-averaged concentrations for B and R when \( k_2 = 0 \).

**Dutta and Tarbell (1989)** developed a model based on fast and slow reaction asymptotics, and on some mechanistic models (CRD, IEM, 3E and 4E). Micromixing parameters of these models were determined from curve-fitting of experimental results
and were correlated to $I_s$, the intensity of segregation for inert or non-reacting species, by a decay law. The turbulent mixing process is assumed to be unaffected by the presence of chemical reactions. The closure models are:

$$\overline{c_A c_B} = -I_s(\overline{C_A C_B_0} + \overline{C_{A_0} C_B} - \overline{C_A C_B}) \quad (2.16)$$

$$\overline{c_R c_B} = -I_s\overline{C_R (C_{B_0} - C_B)} \quad (2.17)$$

where $I_s$ is the intensity of segregation for the non-reacting system, and $\overline{C_{A_0}}, \overline{C_{B_0}}$ are the initial mean concentrations of A and B, respectively. The model does not have a strong theoretical basis, since the value of the model parameter is determined by curve-fitting.

### 2.3 Experiments

Experimental studies with a parallel-consecutive reaction scheme in turbulent flow have been done predominantly on a single reaction system—the coupling of 1-naphthol (A) with diazotised sulphanilic acid (B) in dilute alkaline solution at room temperature. The two reaction products are a mono-azo dyestuff 4-(4'-sulphophenylazo)-1-naphthol (R), and a bis-azo dyestuff 2,4-bis(4'-sulphophenylazo)-1-naphthol (S). The reaction took place at a temperature of 298 K and pH of 10. The rate constant of the first reaction, $k_1$, is $7300 \, m^3 \, mol^{-1} \, s^{-1}$, and the rate constant of the second reaction, $k_2$, is $3.5 \, m^3 \, mol^{-1} \, s^{-1}$, so the first reaction is very fast compared to the second. This reaction scheme, is commonly known as Bourne's reaction (Bourne, 1982).
(1) Paul and Treybal (1971) studied the product distribution for the homogeneous, liquid phase, series-parallel reaction of iodine (B) with L-tyrosine (A) to form 3-iodo-L-tyrosine (R) and 3,5-diiodo-L-tyrosine (S). The reaction rate and/or the product distribution may be influenced by mixing if the course of the reaction is influenced by concentration. The yield of R was correlated by a dimensionless group $(k_1C_B\tau)(C_{A0}/C_B)$, where $\tau$ is time scale of mixing. The magnitude of this group provides a criterion for predicting the importance of mixing effects on other reaction systems – if the magnitude of the group is less than $10^{-5}$, then mixing effects are not significant.

(2) Bourne and co-workers (Bourne et al, 1978, 1981) carried out an extensive series of experiments using the so-called Bourne's reaction to determine the effect of various physical parameters on selectivity. The product distribution from fast, competitive-consecutive reactions, based on laboratory measurements of the yield of the diazo-coupling reactions in a CSTR, was found to depend upon the stoichiometric ratio, the volumetric ratio of the reagent solution, the location of the feed point, the backmixing into the feed pipe, the operating mode of the reactor, the viscosity of the solutions, the type, diameter and rotation speed of the impeller, and the concentrations of the feed solution and concentrations in the tank. It was observed that secondary product formation can be reduced by one or a combination of the following measures: increasing the agitator input, reducing the solution viscosity, reducing the reaction temperature, avoiding high volume ratios, using dilute reagent solutions, increasing the stoichiometric ratio, etc. The experimental results were used to validate the mechanistic EED model (Baldyga and Bourne, 1984). An extensive review of
Bourne's work is given in Appendix B.

(3) Li and Toor (1986) used Bourne's reaction and carried out experiments in single-jet and multiple-jet devices. The reaction took place in an essentially one-dimensional system in which the micromixing was taking place at a rate determined independently. The yield was found to decrease with a decrease in the Reynolds number in both the single-jet and the multi-jet reactors. At the same Reynolds number, the yield was greater for the multi-jet reactor. The yield decreased as the reactant concentrations increased or as the intrinsic reaction rate increased. Thus, a decrease in yield was observed as the ratio of the mixing speed to intrinsic reaction speed, the inverse of a Damköhler number, increased. Also with both single-jet and multiple-jet feeds, reactive mixing was not sensitive to molecular diffusion. The data from these experiments was compared with predictions of mechanistic models such as the slab diffusion model (Mao and Toor, 1971) and with the closure model of Li and Toor (1986).

(4) Heeb (1986) carried out experiments with a polymerization reaction, but the experiments have not been very successful. He chose a polymerization reaction system such that the system would be single phase, the reactions would be second order, irreversible reactions with very high reaction rates, two reactive monomers would be involved in solution polymerization and step polymerization, the reactions would take place at room temperature, and the system could be examined easily experimentally. The reaction system was piperazine reacting with a di-acid chloride in the presence of an acid acceptor. The work was rather inconclusive, however, but
led to suggestions of potentially better systems.

(5) Mehta and Tarbell (1987) used Bourne's reaction in an unmixed feedstream multijet tubular reactor. The ratio $\frac{C_{B0}}{C_{A0}}$ was varied from 0.39 to 1.54. The concentration profiles (particularly the S profile) showed large deviations from the perfect mixing limit corresponding to a plug-flow reactor. Mechanistic models such as the three-environment model and four-environment model (Mehta and Tarbell, 1983) use data from these experiments to determine the value of the micromixing parameter for the models (Tarbell and Mehta, 1986) and Dutta and Tarbell (1989) have used results from these experiments to validate their closure.

2.4 Numerical methods

An excellent discussion on simulations of turbulent reacting flows has been given in the review article by Givi (1989). Model-free simulations for turbulent reactive flows have been classified as (i) Direct Numerical Simulations and (ii) Large Eddy Simulations. In the direct numerical simulations of reacting flows, the conservation equations for mass, momentum, energy, and density of each reacting species are solved without resorting to any models, and all the length and time scales are well resolved. In large eddy simulations, the transport variables are decomposed into a "large-scale" component which is related to the large-scale eddies in the turbulent field and a "sub-grid-scale" component which is related to the small-scale fluctuations. Only the large scale motions are explicitly computed and the sub-grid scales, which are assumed to be more or less universal, are modeled. This approach lies between the extremes of
direct simulation, in which all fluctuations are resolved and no model is required, and the classical statistical approach, in which only mean values are calculated and all fluctuations are modeled (Rogallo and Moin, 1984). Leonard and Hill (1989) have discussed some of the methods used in direct numerical simulations of turbulent reacting flows. Some of the more popular techniques used in making direct numerical simulations of reacting turbulent flows are briefly discussed in this section.

(1) Finite-difference Methods: In finite-difference calculations, a continuous variable is approximated at a set of discrete points, and Taylor series expansions are used to approximate the derivatives at each grid point, using the discrete representation of the function (Anderson et al, 1984). Though finite-difference techniques are most commonly used for general fluid flow problems, they are not very well suited for turbulence simulations because of the high dispersive and diffusive errors. In fact there are very few applications of finite-difference methods to the direct numerical simulations of reacting flows. Since finite-difference techniques cannot resolve sharp gradients properly, flux corrected transport algorithms are sometimes used to treat steep gradients correctly. Fujiwara et al (1986) have reported a calculation on the transition to turbulence in a spatially-developing, two-dimensional mixing layer using finite-difference methods.

(2) Spectral Methods: In these methods, the fundamental variables are approximated by a finite series of orthogonal basis functions (Oran and Boris, 1987). The methods most commonly used with full turbulence simulations are of the spectral type. According to Orszag (1971), for flows within three-dimensional simple
boundaries, the spectral methods require less computer time and storage to achieve reasonable accuracy than do finite-difference methods. Spectral methods provide very accurate estimates of the derivatives of functions if the functions are sufficiently smooth. Also for a given number of independent degrees of freedom (Galerkin basis functions or space-grid mesh points), infinite-order accurate Galerkin approximations give considerably more accurate results than finite-difference approximations. Givi (1989) demonstrated the latter point with an example. A major disadvantage of the spectral methods is that the non-linear terms cannot be computed efficiently. Pseudo-spectral methods overcome this shortcoming; here the nonlinear terms are calculated in physical space and then transformed back to Fourier space or other transform space. The pseudo-spectral method is much faster than the spectral method and for incompressible flows is faster than other methods for a comparable accuracy in a simulation, primarily because a Poisson equation does not need to be solved at each time step (Leonard and Hill, 1989). The evaluation of nonlinear products produces aliasing errors, that is, the bilinear products of the variables in physical space generate wave numbers higher than those retained in the original orthogonal series expansion (Givi, 1989). These spill over into the lower wave numbers because of the periodic discrete transform. Several procedures are available for dealiasing, and for most flows the aliasing errors can be almost eliminated. The use of global basis functions in spectral methods limits the resolutions of discontinuities and steep gradients and the range of length and time scales which can be accurately resolved are limited by computational constraints. Still, pseudo-spectral methods are considered to be currently the best choice for the full simulation of incompressible, homogenous turbulent flows. A detailed description of this method is given in Appendix C.
Several studies have been made of direct numerical simulations of turbulent flow with a single step irreversible reaction using pseudo-spectral methods. Riley, Metcalfe and Orszag (1986) made simulations of chemically reacting turbulent mixing layers. Givi and McMurtry (1988) have made simulations on homogenous turbulent reacting flows with unmixed reactants, and their observations are briefly summarized in the section on Toor's hypothesis. Leonard and Hill (1988, 1989, 1991) have made extensive studies of the problem of a single reaction in decaying turbulent flow.

However, very little work has been done on turbulent reacting flows involving complex chemistry. Some preliminary work has been done by Chakrabarti and Hill (1990) investigating the effect of various physical parameters on the product distribution for a series-parallel reaction scheme. Gao and O'Brien (1991) have looked at the effect of rate constants on mean concentrations and have compared the time history of reactants and products for the single reaction and series-parallel reaction cases.

(3) Spectral element methods: In these methods, developed by Patera (1984), the accuracy of the spectral method is combined with the versatility of the finite element methods, and the approach is more flexible than either spectral methods or finite element methods alone. The computational domain is broken into a series of finite elements, and within these elements the variables are approximated by high-order Lagrangian interpolant through Chebyshev collocation points. By using an appropriate time differencing scheme, the differential equation governing the transport of the variable is decomposed into a non-linear hyperbolic and a linear elliptic equation. The hyperbolic part is solved using a a pseudo-spectral method, and finite element techniques are used for the the elliptic equations (Givi, 1989). This method is espe-
(4) **Lagrangian methods**: These methods describe the transport of the flow variables in a Lagrangian sense and the velocity field, induced by a discrete number of vortex elements, is calculated. They may be classified as vortex methods and random vortex methods. The vortex methods are based on a model of the vortex and the vorticity-stream function transport equations of fluid flow. Vorticity is considered as a transport variable and is represented by an ensemble of discrete packets which carry a finite amount of circulation. The vortex methods are particularly useful for simulations of flows with large localized velocity gradients. Random vortex methods include the viscous transport of the vortex elements. The main difficulties with these methods lay in the modeling of viscous and diffusive effects. Random vortex methods have been used in the study of two-dimensional turbulent pre-mixed flames by Ashurst et al (1987) and in the study of two-dimensional turbulent diffusion flames by Ghoneim and Givi (1987) among others. Givi (1989) gives a more complete review of Lagrangian methods applied to turbulent reacting flows.

### 2.5 Other work

Tichacek (1963) analyzed several hypothetical reaction schemes to show the effects of axial mixing on the production of an intermediate. The effects of axial mixing are negligible in most commercial or large-scale equipment but are important in experimental or pilot-scale apparatus, so knowledge about the effects of axial mixing are important for successful scale-up of a process. Some guidelines for the design of a
reactor has been provided and an example calculation for the series-parallel reaction scheme has been given.

Heeb and Brodkey (1990) developed a statistical simulation program to study the covariance terms involved in the mass balance equations for complex chemical reactions during mixing. The Brodkey and Lewalle (1985) closure was examined critically, and alternative closures were also evaluated but found to be inadequate. Some limits on the covariance of concentration fluctuation $\bar{c}_B \bar{c}_R$ were suggested and these are zero, $\bar{C}_{B0} \bar{C}_R$, and $\bar{C}_B \bar{C}_R$. Heeb and Brodkey (1990) found that an increase in the ratio $k_1/k_2$ caused $\bar{c}_B \bar{c}_R$ to approach zero.
3. METHOD

The model parallel-consecutive reaction system being studied is equation (2.1),

\[ \begin{align*}
A + B & \xrightarrow{k_1} R \\
R + B & \xrightarrow{k_2} S,
\end{align*} \]

where R is the desired product and S is the undesired product. The reaction rates are assumed to be second order with known constant reaction rate coefficients that are of the same order of magnitude for each reaction in order to avoid a set of stiff differential equations. The effective binary Fickian diffusion coefficient and all physical properties are assumed to be constant. The fluid is incompressible, and the scalar field is assumed passive with respect to the velocity field. A decaying, homogenous turbulent velocity field with no mean gradients is assumed, and averages (as indicated by overbars) are evaluated as volume averages over the entire domain.

The problem is equivalent to that in which the observer follows the flow in a turbulent plug flow reactor with the mean velocity, as shown in Figure 3.1. An initial turbulence level is specified, and then the velocity fluctuations decay in time as viscous dissipation reduces the velocity gradients. The physical space domain for the simulation is a transparent cube with sides of length L (=2\pi), with periodic boundary conditions for all variables and the units used are arbitrary. The square box in the reactor in Figure 3.1 is a face of the cube. Initially the reactants A and B
are spatially segregated, and no products R or S are present. For most simulations, alternating slabs of reactant species are used as initial conditions for concentration values in order to make visualization of the reaction zones easier. Some simulations were done for the case where the scalar field (reactants A and B) is isotropic. Sketches of these conditions are shown in Figure 3.2.

The velocity field is governed by the Navier-Stokes equation
\[ \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} = -\frac{\nabla p}{\rho} + \nu \nabla^2 \mathbf{u}, \] (3.1)
and the incompressibility condition,
\[ \nabla \cdot \mathbf{u} = 0. \] (3.2)

The concentration \( C_i \) of species "i" = A, B, R, S, is governed by the mass conservation equation
\[ \frac{\partial C_i}{\partial t} + \mathbf{u} \cdot \nabla C_i = D_i \nabla^2 C_i + r_i, \] (3.3)
where \( r_i \) is the rate expression for the creation of species "i" and \( D_i \) is the molecular diffusivity of species "i". The diffusivities of all species are assumed to be equal in this work.

In the present work, the governing equations are solved with a pseudo-spectral method using a code adapted from Kerr (1985). The fluid velocity field is represented by the Fourier expansion
\[ \mathbf{u}(x, t) = \sum_{n=1}^{N} \hat{u}(n, t) e^{in \cdot x}, \] (3.4)
and the concentration field by
\[ C_i(x, t) = \sum_{n=1}^{N} \hat{C}_i(n, t) e^{in \cdot x} \] (3.5)
for a wave-number domain of $N^3$ Fourier modes. The rotational form of the Navier-Stokes equation,

$$\frac{\partial \mathbf{u}}{\partial t} = \mathbf{u} \times \omega - \nabla \left( \frac{p}{\rho} + \frac{u^2}{2} \right) + \nu \nabla^2 \mathbf{u},$$  \hspace{1cm} (3.6)

is used because it conserves kinetic energy in the absence of time-stepping errors and viscous dissipation (Orszag, 1971). The conservative form of the mass conservation equation,

$$\frac{\partial C_i}{\partial t} + \nabla \cdot \mathbf{u} C_i = D_i \nabla^2 C_i + r_i,$$  \hspace{1cm} (3.7)

is used, where "i" is A, B, R or S. The Fourier components of the dynamical variables are integrated forward in time using a third-order Runge-Kutta algorithm designed to minimize memory requirements. The equations are given by Hamlen (1984) in his detailed description of an earlier version of the code. The time integration uses a variable time step based on a Courant-Friedrichs-Lewy (CFL) stability criterion or Courant number, modified to include the effects of a finite reaction rate. The modified Courant number $C$ is set to 1.5 where $C$ is defined as

$$C = \max \left( \sum \frac{u_i}{\Delta x_i} + k_1 \max(C_A, C_B, C_R, C_S) \right) \Delta t,$$

and where $u_i$ is the fluctuating component of the velocity in the $i$-direction, $\Delta x_i$ is the grid spacing in the $i$-direction, and the maximum value is evaluated over the entire domain (Leonard, 1989). Increasing the Courant number corresponds to increasing the time step, so the computer time for the simulation is reduced but time-stepping errors become significant. The nonlinear terms are evaluated in physical space and then transformed back to wave number space using fast Fourier transforms (FFT). The pressure term is evaluated in wave number space by using the solenoidal property of the velocity field. Pseudo-spectral methods introduce aliasing
errors, so partial de-aliasing is done by spherical truncation of wave-numbers outside a spherical shell of radius 8K/9. The initial energy spectrum for the velocity field has been chosen to be “Gaussian” \(a k^4 e^{-bk^2}\), “exponential” \(a k^3 e^{-bk}\), or of the form \(a(kb)^4/(1+(kb)^2)^3\) (eqn. 3-151, Hinze, 1951) where \(a\) and \(b\) are given in Table 3.1. The theoretical and actual (measured in simulations) values of the integral length scale, Taylor microscale and Kolmogorov microscale for the different spectra are shown in Table 3.1. The details of the derivations of the theoretical forms of the length scales are given in Appendix D, and Table 6.1 in Appendix D has a summary of the theoretical expressions for the length scales for different spectra. In the present study, the simulations used an initial Gaussian energy spectrum \((X)\), unless otherwise mentioned.

Two types of initial scalar fields, shown in Figure 3.2, are used in this study. One corresponds to the striped case where the initial concentration distribution of reactant species is similar to that used by Leonard and Hill (1989), in which the initial scalar field corresponds to spatially segregated slabs of reactants parallel to the \(x_1\) plane, such that B lies in the center half of the domain and A lies to the sides.

The other type of initial scalar field corresponds to the pre-stirred case, where the scalar field is preconditioned to create realistic spatial structures for the concentrations of A and B. For this case, both the velocity and scalar fields are preprocessed. An initial energy spectrum of the form

\[ E(k, 0) \propto \frac{(kL)^4}{(1 + (kL)^2)^3} \tag{3.8} \]

was specified for the presimulation. To generate a statistically isotropic scalar field, the scalar field is preconditioned as follows. The Fourier coefficients of a Gaussian
random variable $\phi$ are scaled to fit a prescribed concentration spectrum of the form

$$E_\phi(k, 0) \propto \frac{(kL)^3}{(1 + (kL)^2)^2}. \quad (3.9)$$

The function $\phi$ is allowed to convect and diffuse for some time (till $t = 0.4$, that is, about one-half of an eddy turnover time) while the velocity field is being pretreated. In regions where $\phi$ is positive, the concentration of $A$ is assigned a value of 2 and in regions where $\phi$ is negative, $B$ is assigned the value 2. The Fourier transform of this concentration field is used as initial values for the scalar field. Diffusive damping of the initial conditions ($Dt^* = 0.02$) was used at the beginning of the simulation for both initial scalar fields to avoid negative concentrations produced by Gibb’s ringing.

Simulations in this study were carried out in decaying isotropic turbulence on a grid of $64^3$ Fourier modes. The calculations were done on the Cray X/MP and Cray Y/MP at the National Center for Supercomputer Applications, Illinois and on the Cray Y/MP at the Ohio Supercomputer Center. The computational or 'cpu' time per time step for the simulations was about 12 seconds on the Cray Y/MP, and a typical simulation needed about 250 time steps.

The turbulence Reynolds number ($R_\lambda$) and other physical parameters were varied for the different calculations performed. The turbulence Reynolds number $R_\lambda$ is a measure of turbulence and is defined as $u'\lambda/\nu$, where $u'$ is the turbulence intensity, $\lambda$ is the Taylor microscale for the velocity field, and $\nu$ is the viscosity. The velocity field description is given in Table 3.1, the initial conditions and parameters for the simulations along with the corresponding "labels" or "condition codes" are given in Table 3.2, and the scalar field description is given in Table 3.3. The condition code, the velocity field code and the scalar initial field code completely describe the exact conditions of the simulations. The same initial conditions for the velocity field (that
is, the same seed for the random number generator) were used for all runs except for three runs which were done with three different random number seeds. Statistical quantities such as $R_\lambda$, $\overline{C_A}$, and $\overline{c_B c_R}$ are shown for the three different cases in Figure 3.3. The statistical quantities are almost identical for the three cases and so the calculations presented here are a realistic representative sample.
Table 3.1: Initial energy spectra *

<table>
<thead>
<tr>
<th>Label</th>
<th>$E(k,0)$</th>
<th>$a$</th>
<th>$b$</th>
<th>$\Lambda_f$</th>
<th>$\lambda_g$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X$</td>
<td>$ak^4 e^{-bk^2}$</td>
<td>$\frac{16 u^2}{k_0^3} \sqrt{\frac{2}{\pi}}$</td>
<td>$\frac{2}{k_0^2}$</td>
<td>Th. $\S$: 1.00</td>
<td>Th.: 0.8</td>
<td>Th.: 0.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ac. $^\parallel$: 0.99</td>
<td>Ac.: 0.78</td>
<td>Ac.: 0.07</td>
</tr>
<tr>
<td>$Y$</td>
<td>$ak^3 e^{-bk}$</td>
<td>$\frac{81 u^2}{4 k_0^4}$</td>
<td>$\frac{3}{k_0}$</td>
<td>Th.: 0.94</td>
<td>Th.: 0.6</td>
<td>Th.: 0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ac.: 0.82</td>
<td>Ac.: 0.58</td>
<td>Ac.: 0.06</td>
</tr>
<tr>
<td>$Z^{**}$</td>
<td>$\frac{a(kb)^4}{(1 + (kb)^2)^3}$</td>
<td>$\frac{8 \sqrt{2} u^2}{\pi k_0}$</td>
<td>$\frac{\sqrt{2 \pi}}{k_0}$</td>
<td>Ac.: 0.94</td>
<td>Ac.: 0.3</td>
<td>Ac.: 0.05</td>
</tr>
</tbody>
</table>

* $u'$ is the turbulence intensity and $k_0$ is the peak wave number=2.5. $\Lambda_f$ is the initial longitudinal integral length scale, $\lambda_g$ is the initial Taylor microscale, and $\eta$ is the Kolmogorov length scale.

† Derivations are given in Appendix D.

‡ For conditions of Run A on Table 3.2.

§ Evaluated from theoretical expressions given in Appendix D.

∥ Measured from simulations.

¶ For conditions of Table 3.2 $\Lambda$ should be multiplied by 0.74 and $Da_1$ and $Da_2$ should be multiplied by 0.83.

** For conditions of Table 3.2 $\Lambda$ should be multiplied by 0.38 and $Da_1$ and $Da_2$ should be multiplied by 0.95.
### Table 3.2: Conditions for the simulations*

<table>
<thead>
<tr>
<th>Label</th>
<th>Parameters</th>
<th>Dimensionless groups</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\nu$, $D$, $k_1$, $k_2$, $u'$, $\frac{C_{A0}}{C_{B0}}$, $R_\lambda$, $Sc$, $Da_1$, $Da_2$</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.025, 0.036, 5, 1, 0.96, 1</td>
<td>29.93, 0.7, 5, 1</td>
</tr>
<tr>
<td>B</td>
<td>0.025, 0.036, 5, 1, 1.06, 1</td>
<td>33.12, 0.7, 5, 1</td>
</tr>
<tr>
<td>C</td>
<td>0.025, 0.036, 5, 1, 1.45, 1</td>
<td>45.07, 0.7, 5, 1</td>
</tr>
<tr>
<td>D</td>
<td>0.04, 0.057, 5, 1, 0.96, 1</td>
<td>18.70, 0.7, 5, 1</td>
</tr>
<tr>
<td>E</td>
<td>0.10, 0.143, 5, 1, 0.96, 1</td>
<td>7.48, 0.7, 5, 1</td>
</tr>
<tr>
<td>F</td>
<td>0.04, 0.036, 5, 1, 0.96, 1</td>
<td>18.70, 1.12, 5, 1</td>
</tr>
<tr>
<td>G</td>
<td>0.10, 0.036, 5, 1, 0.96, 1</td>
<td>7.48, 2.8, 5, 1</td>
</tr>
<tr>
<td>H</td>
<td>0.025, 0.25, 5, 1, 0.96, 1</td>
<td>29.93, 0.1, 5, 1</td>
</tr>
<tr>
<td>I</td>
<td>0.025, 0.0625, 5, 1, 0.96, 1</td>
<td>29.93, 0.4, 5, 1</td>
</tr>
<tr>
<td>J</td>
<td>0.025, 0.025, 5, 1, 0.96, 1</td>
<td>29.93, 1.0, 5, 1</td>
</tr>
<tr>
<td>K</td>
<td>0.025, 0.036, 5, 0, 0.96, 1</td>
<td>29.93, 0.7, 5, 0</td>
</tr>
<tr>
<td>L</td>
<td>0.025, 0.036, 5, 2.5, 0.96, 1</td>
<td>29.93, 0.7, 5, 2.5</td>
</tr>
<tr>
<td>M</td>
<td>0.025, 0.036, 5, 5, 0.96, 1</td>
<td>29.93, 0.7, 5, 5</td>
</tr>
<tr>
<td>N</td>
<td>0.025, 0.036, 1, 2, 0.96, 1</td>
<td>29.93, 0.7, 1, 2</td>
</tr>
<tr>
<td>O</td>
<td>0.025, 0.036, 2.5, 5, 0.96, 1</td>
<td>29.93, 0.7, 2.5, 5</td>
</tr>
<tr>
<td>P</td>
<td>0.025, 0.036, 5, 1, 0.96, 0.67</td>
<td>29.93, 0.7, 4.1, 0.82</td>
</tr>
<tr>
<td>Q</td>
<td>0.025, 0.036, 5, 1, 0.96, 0.9</td>
<td>29.93, 0.7, 4.7, 0.95</td>
</tr>
<tr>
<td>R</td>
<td>0.025, 0.036, 5, 1, 0.96, 1.2</td>
<td>29.93, 0.7, 5.5, 1.1</td>
</tr>
<tr>
<td>S</td>
<td>0.025, 0.036, 5, 1, 0.96, 1.5</td>
<td>29.93, 0.7, 6.1, 1.2</td>
</tr>
<tr>
<td>T</td>
<td>0.036, 5, 1, 0.0, 1.0</td>
<td>0.0, --, --, --</td>
</tr>
</tbody>
</table>

*Note: $R_\lambda$ is the initial turbulence Reynolds number, $u'/\lambda/\nu$, where $\lambda$ is the Taylor microscale, $u'$ the turbulence intensity, and $\nu$ the kinematic viscosity. $Sc$ is the Schmidt number $\nu/D$, where $D$ is the molecular viscosity. The rate constants for the first and second reactions are $k_1$ and $k_2$, respectively and $Da_1$ and $Da_2$ are the Damköhler numbers (of the first kind) for the corresponding reactions, defined as $Da_1 = k_1\sqrt{C_{A0}C_{B0}A_f/u'}$ and $Da_2 = k_2\sqrt{C_{A0}C_{B0}A_f/u'}$. $A_f$ is the initial longitudinal integral length scale, and $C_{A0}$ and $C_{B0}$ are the initial stoichiometric concentrations of A and B, respectively. The values of $R_\lambda$, $Da_1$ and $Da_2$ correspond to an initial Gaussian energy spectrum, X.
Table 3.3: Initial scalar field

<table>
<thead>
<tr>
<th>Code</th>
<th>Scalar field description</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>Striped (slab initial conditions)</td>
</tr>
<tr>
<td>V</td>
<td>Isotropic (stirred initial conditions)</td>
</tr>
</tbody>
</table>
Figure 3.1: Schematic diagram of a plug flow reactor: adapted from Hill (1976)
Figure 3.2: Sketches of scalar initial fields (a) striped initial scalar field (b) stirred initial scalar field
Figure 3.3: Effect of random number generators on statistical quantities (a) Kinetic energy (b) Mean concentration of $A$, $\bar{c}_A$ (c) Concentration fluctuation covariance $\bar{c}_B \bar{c}_R$.
Figure 3.3 (Continued)
Covariance of concentration fluctuation, $br$
4. RESULTS AND DISCUSSION

Results of the numerical simulations of turbulent reacting flows with complex chemistry are presented in this chapter. After a brief discussion on the evolution of reactants and products in a series-parallel reaction scheme, the series-parallel reaction system will be compared to the single reaction system. Then the effect of various physical parameters on selectivity will be discussed. Finally, an evaluation of various first-order closure models will be given.

Figure 4.1 shows the time evolution of the reactants A and B and products R and S for the cases of single and multiple reactions in a homogenous decaying turbulent flow field for conditions of code K and code A respectively. The decay of B is faster in the case of the series-parallel reaction because B is being consumed by both reactions. The production of R keeps increasing till A and B are exhausted in the case of a single reaction, whereas with a consecutive-parallel reaction scheme R is formed by one reaction and is consumed by the second. The system reaches an asymptotic state once B is fully consumed.

A point to note about parallel-consecutive reactions is that there are two reaction zones, one for each reaction, although there is considerable overlap. In the presence of a turbulent velocity field, the time evolution and spatial variation of the reaction zone depends on the velocity field as well as on reaction and diffusion. Figure 4.2
shows the spatial variation of the reaction rate $k_1 C_A C_B$ at three different times, for the case of a single reaction. Figures 4.3 and 4.4 show the spatial variation of $k_1 C_A C_B$ and $k_2 C_B C_R$ respectively, for the case of a series-parallel-reaction scheme, also at three different time levels. The value of $k_1 C_A C_B$ is the highest initially, and the peak falls as $A$ and $B$ are consumed by the reactions. The second reaction rate, $k_2 C_B C_R$, is zero initially, because there is no $R$ in the system. Then as $R$ forms, the reaction rate increases but again decreases with time. The reaction rates ($k_1 C_A C_B$ and $k_2 C_B C_R$) for the multiple reaction case and the reaction rate ($k_1 C_A C_B$) for the single reaction case, all at one time, are shown in Figure 4.5. This figure shows that the reaction zone for the first reaction in the multiple reaction case almost coincides with the reaction zone for the single reaction. The reaction zones for the two reactions do not coincide, however, in the multiple reaction case. The reaction zone for the second reaction appears to have migrated towards the $B$-rich region because the second reaction depends on the presence of $B$ in the system and not on $A$. The reaction zone for the first reaction does not migrate with respect to the reaction zone for the single reaction because the first reaction depends on the presence of both $A$ and $B$.

In the absence of a velocity field, the distribution of products for the complex chemistry case will depend on the initial distribution of reactants. If $A$ and $B$ have the same initial concentration distributions, with the same peak values but are merely spatially displaced, or in other words, if $A$ and $B$ are initially anti-correlated, the peak value of the generation rate of $R$ would initially occur in the region of overlap of the two distributions and $R$ would be distributed symmetrically about the peak. The distribution of $R$ will depend on the details of the spatial distribution of $A$ and
B. The generation rate of S resulting from the reaction of B and R will be greatest inside the B rich region. If A is given by $A_0 \exp(-\alpha(x + x_0)^2)$ and B is given by $B_0 \exp(-\alpha(x - x_0)^2)$, then $\delta R$ will be $k_1 A_0 B_0 \exp(-\alpha(x^2 + x_0^2))\delta t$, where $\delta R$ is the incremental amount of R produced in time $\delta t$. The actual value of R after a short interval of time can be found by solving the one-dimensional diffusion equation. The second reaction starts only after some R has formed. The distribution of R would be similar in form to the distribution of the generation rate of R except for the spread caused by diffusion. The generation rate of S in the initial period will be given by $\delta S \propto R_1 B_0 \exp(-\alpha(2x^2 - 2xx_0 + 2x_0^2))$, where $R_1$ is the value of R at time $\delta t$. This shows that the generation for S would initially have a peak value at $x_0/2$. Since the reaction system is closed, that is, A and B are not replenished, the result of the reaction is to cause a reduction in the total values of A and B. The reductions are initially localized. The effect of diffusion would be to cause a redistribution of A and B and can be computed by solving the diffusion equation. The consumption rate of B is higher than A because B takes part in two reactions. Figure 4.6 shows the above scenario. The above picture pertains to the case with no motion, so any deviations observed in the results of the simulations can be attributed to the turbulent velocity field and different initial scalar field distributions.

DNS results have been analyzed for an initially striped scalar field and an initially isotropic scalar field for two typical cases: $k_1/k_2=1$ and $k_1/k_2=5$. The covariance of the concentration fluctuations ($c_A c_B$ and $c_B c_R$) was evaluated, and the intensity of segregation $I_s$ for A and B, defined as $c_A c_B/(c_A c_B)$, and $I_s$ for B and R, defined as $c_B c_R/(c_B c_R)$, were determined.

For the case with an initial striped scalar field and equal rate constants, the
minimum value of \( c_A c_B \) was \(-0.856\) and the maximum value of \( c_A c_B \) was \(-0.0008\), which led to values of \( I_s \) for A and B (\( c_A c_B/(C_A C_B) \)) lying between \(-0.739\) and \(-0.969\). As \( k_1/k_2 \) was increased to 5, the range of \( I_s \) was found to be \(-0.744\) to \(-0.965\). The values obtained for \( I_s \) suggest imperfect mixing as expected, since initially segregated reactants were used. The range of \( c_B c_R \) was \(-0.0002\) to \(-0.041\) for the case of equal rate constants and \(-0.001\) to \(-0.061\) for the case of \( k_1/k_2 = 5\). The results from the simulations show that \( c_B c_R \) becomes more negative as the ratio of the rate constants is increased. The value of \( I_s \) for B and R (\( c_B c_R/(C_B C_R) \)) lies between \(-0.467\) and \(-0.688\) for \( k_1/k_2 = 1\) and between \(-0.297\) and \(-0.474\) for \( k_1/k_2 = 5\).

For the case of an isotropic initial scalar field, DNS results show that the value of \( I_s \) lies between \(-0.377\) and \(-10^{-5}\) for \( k_1/k_2 = 1\) and between \(-0.377\) and \(-10^{-4}\) for \( k_1/k_2 = 5\). \( I_s \) for A and B (\( c_A c_B/(C_A C_B) \)) lies between \(-0.377\) and \(-0.791\) for \( k_1/k_2 = 1\) and between \(-0.377\) and \(-0.757\) for \( k_1/k_2 = 5\). The value of \( c_B c_R \) lies between \(-0.0613\) and \(-10^{-4}\) for \( k_1/k_2 = 5\) and between \(-0.0467\) and \(-10^{-6}\) for \( k_1/k_2 = 1\). Thus, \( c_B c_R \) becomes more negative with an increase in the ratio of rate constants in this case too. \( I_s \) for B and R (\( c_B c_R/(C_B C_R) \)) lies between \(-0.219\) and \(-0.596\) for \( k_1/k_2 = 1\) and between \(-0.184\) and \(-0.317\) for \( k_1/k_2 = 5\). The above information on the range of \( c_A c_B \), \( c_B c_R \) and \( I_s \) is given in Table 4.1 and the time evolution of \( I_s \) for A and B, and \( I_s \) for B and R for the striped and stirred case is shown in Figure 4.7.

For conditions of code A, the first and second Damköhler numbers were evaluated for both striped and stirred initial scalar fields and are given in Table 4.2. The first reaction can be said to be moderately fast while the second reaction is slow.
Table 4.1: Summary of concentration covariance values

<table>
<thead>
<tr>
<th>Scalar field conditions</th>
<th>$-c_A c_B$</th>
<th>$-c_B c_R$</th>
<th>$-c_A c_B/c_A c_B$</th>
<th>$-c_B c_R/c_B c_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>max</td>
<td>min</td>
<td>max</td>
<td>min</td>
</tr>
<tr>
<td>Striped $k_1/k_2 = 5$</td>
<td>0.856</td>
<td>0.002</td>
<td>0.061</td>
<td>0.001</td>
</tr>
<tr>
<td>$k_1/k_2 = 1$</td>
<td>0.856</td>
<td>0.0008</td>
<td>0.041</td>
<td>0.0002</td>
</tr>
<tr>
<td>Stirred $k_1/k_2 = 5$</td>
<td>0.377</td>
<td>$10^{-4}$</td>
<td>0.0613</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td>$k_1/k_2 = 1$</td>
<td>0.377</td>
<td>$10^{-5}$</td>
<td>0.0467</td>
<td>$10^{-6}$</td>
</tr>
</tbody>
</table>

Table 4.2: Damköhler numbers for the striped and stirred initial fields

<table>
<thead>
<tr>
<th>Initial field</th>
<th>First kind, $Da_I$ $k_1 C_{A0} \lambda f/u'$</th>
<th>Second kind, $Da_{II}$ $k_1 C_{A0} \lambda g^2/D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Striped case</td>
<td>5.16</td>
<td>1.03</td>
</tr>
<tr>
<td>Stirred case</td>
<td>5.96</td>
<td>0.945</td>
</tr>
</tbody>
</table>

4.1 Effect of physical parameters

It has been noted by Levenspiel (1972) that for the case of a very fast series-parallel reaction, it is important to achieve homogeneity in A and R in order to favor the formation of the intermediate R. Previous simulations have confirmed the general validity of this observation (Chakrabarti and Hill, 1990). In fact, the effect of turbulence and other physical parameters such as viscosity, Schmidt number, diffusivity,
reaction rate constants, initial stoichiometric ratio and initial conditions on product
distribution may be explained very simply: any mechanism sustaining segregation
of reactants depresses formation of $R$, whereas any mechanism causing homogeniza­
tion (mixing) depresses formation of $S$. The literature on series-parallel reactions
also supports the thesis that segregation depresses the formation of intermediate, $R$
(Levenspiel, 1972, Bourne and Toor, 1977).

For the series-parallel reaction, that is, equation (2.1), the ratio of the rates of
the two reactions is given as

$$
\frac{r_R}{r_S} = \frac{k_1(C_A C_B + c_{AcR}) - k_2(C_B C_R + c_{BcR})}{k_2(C_B C_R + c_{BcR})}.
$$

(4.1)

Since $c_i$ are the fluctuations due to imperfect mixing, $c_{BcR}$ is a measure of the im­
perfections in mixing. Bourne and Toor (1977) have shown that for separate feeds,
imperfect mixing lowers the value of $r_R/r_S$. (Details are given in the discussion on
the Bourne-Toor closure in Appendix B.) According to Levenspiel (1972), if there
is any non-homogeneity in $A$ and $R$, the formation of $S$ is favored, since the reac­
tion zones (zones between regions of high $A$ concentration and high $B$ concentration)
contain higher concentrations of $R$ than the surrounding regions, and there is thus
a steep concentration gradient and $R$ mixes and reacts with $B$ to form $S$. But if $A$
and $R$ are spatially homogenous or are present together, they can compete with each
other for the $B$ present and produce more $R$ or $S$. If they are not spatially homoge­
nous, then $R$ reacts with $B$ to form $S$. These situations are comparable to the case
where $B$ is added slowly to a mixture of $A$ and to the case where $A$ is added slowly
to a mixture of $B$, respectively, as described by Levenspiel (1972). Thus, segregation
of reactants favors formation of $S$, whereas homogenization favors formation of $R$.

Appendix B provides a more detailed discussion on the subject.
Effect of turbulence Reynolds number: The presence of turbulence has a marked effect on product distribution and thus on selectivity. Compared to the case with no velocity, it is found that in a turbulent flow field, the mean values of A and B decrease faster, whereas the mean values of R and S increase faster initially, leading to higher conversions. Thus the presence of turbulence favors formation of the desired product R over undesired product S. The effect of turbulence Reynolds number $R_\lambda \left(= \frac{u'\lambda}{\nu} \right)$ was determined by varying the turbulence level and by varying the viscosity, keeping the length scale constant.

Figure 4.8 and Table 4.3 show that a lower value of $X_S$ is achieved in the presence of turbulence and that, as the turbulence intensity is increased (i.e. $R_\lambda$ is increased), the selectivity $X_S$ decreases. Thus a high level of turbulence produces a better yield of the desired product than does a lower level.

Figure 4.9 and Table 4.4 show that a lower value of viscosity, or in other words, a higher value of $R_\lambda$, favors formation of desired product R over undesired product S. These observations support Bourne's hypothesis that a reduction of solution viscosity reduces the formation of secondary product S (Bourne et al, 1978, Angst et al, 1982).

Physically, as the turbulence intensity $u'$ increases, that is, as $R_\lambda$ increases, there is more stretching and distortion of fluid elements and consequently more folding of isoscalar surfaces. As a result, the reaction surface area increases and concentration gradients are steepened, leading to enhanced mixing. Thus transport is enhanced and improved local homogeneity is achieved. As the viscosity is decreased, the flow structure is more detailed, with smaller scales present. The sizes of small scale structures in the velocity field decrease, and since the scalars are transported with the velocity
Table 4.3: Effect of turbulence Reynolds number

<table>
<thead>
<tr>
<th>Code</th>
<th>$u'$</th>
<th>$\nu$</th>
<th>$R_A$</th>
<th>$X_S$†</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>0</td>
<td>-</td>
<td>0</td>
<td>0.740</td>
</tr>
<tr>
<td>E</td>
<td>0.96</td>
<td>0.1</td>
<td>7.48</td>
<td>0.637</td>
</tr>
<tr>
<td>D</td>
<td>0.96</td>
<td>0.04</td>
<td>18.70</td>
<td>0.638</td>
</tr>
<tr>
<td>A</td>
<td>0.96</td>
<td>0.025</td>
<td>29.93</td>
<td>0.631</td>
</tr>
<tr>
<td>B</td>
<td>1.06</td>
<td>0.025</td>
<td>39.12</td>
<td>0.618</td>
</tr>
<tr>
<td>C</td>
<td>1.45</td>
<td>0.025</td>
<td>45.07</td>
<td>0.577</td>
</tr>
</tbody>
</table>

*Sc=0.7 and striped initial scalar field.
†Corresponding to Table 3.2.
‡Values of selectivity @ t=10.0.

field, there is also a decrease in the size of the scalar field structure. Figure 4.10 shows that the scalar microscale, which is a measure of the size of structures in the scalar field, decreases as viscosity is decreased. The isoscalar surface is wrinkled as a result of the small scale structures in the scalar field, and thus the rate of diffusion of the smaller scales is increased, leading to enhanced transport rates and increased homogenization of the smaller scales. So an increase in turbulence Reynolds number caused by either an increase of turbulence intensity or by a decrease of viscosity enhances homogeneity and favors the formation of $R$ over the formation of $S$.

The effect of changes in viscosity on the reaction rates $k_1C_AC_B$ and $k_2C_BC_R$ is shown in Figures 4.11, 4.12, 4.13 and 4.14. Figures 4.11 and 4.12 show contour plots and Figures 4.13 and 4.14 show perspective plots of the two reaction rates for two different values of viscosity. Figures 4.11a and 4.12a correspond to a lower value
of viscosity and thus a higher value of $R_\Lambda$ compared to Figures 4.11b and 4.12b. The contour plots show more fine scale structure for the lower viscosity case, and the perspective plots, which provide a better visualization of the reaction rates, show that the plots of the reaction rate are smoother for the higher viscosity cases. When the viscosity is high, small scale structures are dissipated more quickly, and hence fewer of those are present than in the case for which the viscosity is low and more scales are present. Thus a lower value of the viscosity produces more detail in the scalar field.

**Effect of Schmidt number:** The Schmidt number ($Sc$) is the ratio of viscosity ($\nu$) to diffusivity ($D$), and thus the effect of Schmidt number on selectivity (keeping $\nu$ constant) is essentially the effect of diffusivity on selectivity; a low value of Schmidt number reflects a high value of diffusivity. It is observed from Figure 4.15 and Table 4.5 that $X_S$ decreases with a decrease in the value of the Schmidt number, which
means if diffusivity is increased, more R is formed compared to S.

### Table 4.5: Effect of Schmidt number *

<table>
<thead>
<tr>
<th>Code</th>
<th>$\nu$</th>
<th>$D$</th>
<th>$Sc$</th>
<th>$R_\lambda$</th>
<th>$X_S$ ‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.025</td>
<td>0.25</td>
<td>0.1</td>
<td>29.93</td>
<td>0.565</td>
</tr>
<tr>
<td>I</td>
<td>0.025</td>
<td>0.0625</td>
<td>0.4</td>
<td>29.93</td>
<td>0.616</td>
</tr>
<tr>
<td>J</td>
<td>0.025</td>
<td>0.025</td>
<td>1.0</td>
<td>29.93</td>
<td>0.639</td>
</tr>
<tr>
<td>A</td>
<td>0.025</td>
<td>0.036</td>
<td>0.7</td>
<td>29.93</td>
<td>0.631</td>
</tr>
<tr>
<td>F</td>
<td>0.04</td>
<td>0.036</td>
<td>1.12</td>
<td>18.70</td>
<td>0.652</td>
</tr>
<tr>
<td>G</td>
<td>0.1</td>
<td>0.036</td>
<td>2.8</td>
<td>7.48</td>
<td>0.695</td>
</tr>
</tbody>
</table>

* $\nu' = 0.96$, striped initial scalar field.

† Corresponding to Table 3.2.

‡ Asymptotic values of selectivity $\theta t=10.0$. 

An increase of diffusivity directly decreases the size of the scalar field structure. Figures 4.11b and 4.11c show contour plots of the reaction rate $k_1C_AC_B$ for two different values of Sc whereas Figures 4.12b and 4.12c show contour plots of $k_2C_BC_R$. As Sc is decreased, $D$ is increased, there is more transport, hence more homogeneity, and the first reaction is favored over the second.

**Coupled effect of viscosity and diffusivity:** When the viscosity is decreased for constant Schmidt number the diffusivity is also decreased. Whereas the effect of a decrease in $\nu$ is to decrease $X_S$, the effect of a decrease in $D$ is to increase $X_S$. As a result of these competing effects, the selectivity $X_S$ remains relatively unchanged, as is evident from Figure 4.16 and Tables 4.6 and 4.7.
Table 4.6: Coupled effect of $\nu$ and $D^*$

<table>
<thead>
<tr>
<th>Code</th>
<th>$\nu$</th>
<th>$D$</th>
<th>$R_A$</th>
<th>$X_S^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Initial energy spectrum$^5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$X$</td>
</tr>
<tr>
<td>A</td>
<td>0.025</td>
<td>0.036</td>
<td>29.93</td>
<td>0.631</td>
</tr>
<tr>
<td>D</td>
<td>0.04</td>
<td>0.057</td>
<td>18.70</td>
<td>0.638</td>
</tr>
<tr>
<td>E</td>
<td>0.1</td>
<td>0.143</td>
<td>7.48</td>
<td>0.637</td>
</tr>
</tbody>
</table>

* $u'=0.96$, $Sc=0.7$, striped initial scalar field.
† Corresponding to Table 3.2.
‡ Asymptotic values of selectivity @ $t=10.0$.
§ Corresponding to Table 3.1.

**Effect of rate constants:** As the ratio of the rate constants $k_1/k_2$ is increased, the formation of both $R$ and $S$ is increased, but the formation of $R$ is favored over the formation of $S$. That observation is reflected in the decrease in the value of $X_S$ with an increase in the ratio of the rate constants, as is shown in Figure 4.17 and Table 4.8.

When $k_1 > k_2$ or $Da_1 > Da_2$, where $Da_1 = k_1\sqrt{C_{A0}C_{B0}A_f/u'}$ and $Da_2 = k_2\sqrt{C_{A0}C_{B0}A_f/u'}$, as defined by Gao and O'Brien (1991) for the series-parallel reaction, the first reaction proceeds faster than the second reaction. Thus the initial formation of $R$ by the first reaction is favored. Since both $R$ and $A$ compete for the available $B$, whether $R$ or $S$ will be preferentially formed depends on the relative rates of the two reactions. As $k_1/k_2$ increases, the rate of the first reaction increases...
Table 4.7: Effect of coupled $\nu$ and $D$ changes for different initial energy spectra

<table>
<thead>
<tr>
<th>Initial energy spectrum</th>
<th>Selectivity Values $^\dagger$</th>
<th>$\nu=0.025$</th>
<th>$\nu=0.04$</th>
<th>$\nu=0.10$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Code A</td>
<td>Code D</td>
<td>Code E</td>
<td></td>
</tr>
<tr>
<td>$a k_1^4 e^{-bk_2}$</td>
<td>0.535</td>
<td>0.543</td>
<td>0.563</td>
<td></td>
</tr>
<tr>
<td>$a k_1^3 e^{-bk_1}$</td>
<td>0.544</td>
<td>0.554</td>
<td>0.572</td>
<td></td>
</tr>
<tr>
<td>$a (kb)^4/(1+(kb)^2)^3$</td>
<td>0.559</td>
<td>0.568</td>
<td>0.583</td>
<td></td>
</tr>
</tbody>
</table>

$^*\nu'=0.96$, $Sc=0.7$, striped initial scalar field.

$^\dagger$ Intermediate values of selectivity @ $t=3.0$.

Relative to the second, and thus the formation of R is favored over the formation of S, leading to a decrease in the value of $X_5$. But for a given pair of reactions, the ratio $k_1/k_2$ is almost constant and can only be varied slightly by changing the temperature of operation. Another interesting observation is the fact that $X_5$ depends on the absolute values of $k_1$ and $k_2$. As Figure 4.17 and Table 4.8 show, $X_5$ increases as $k_1$ increases for the same $k_1/k_2$ ratio. Our results are in agreement with the findings of Gao and O’Brien (1991) that for the case of $Da_1 > Da_2$, the formation of S depends upon $Da_2$, whereas for the case of $Da_1 < Da_2$, $Da_1$ is the determining factor. The time evolution of the mean concentrations of A, B, R and S for $Da_1 > Da_2$ and for $Da_1 < Da_2$ is shown in Figures 4.1b and 4.18, respectively. The figures illustrate that whereas R is rich for $Da_1 > Da_2$, comparatively less R is present when $Da_1 < Da_2$. This has also been observed by Gao and O’Brien. The case where $k_1 < k_2$ becomes important is when the second reaction is the desirable reaction and S is the desired product.
Table 4.8: Effect of rate constants *

<table>
<thead>
<tr>
<th>Code</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k_1/k_2$</th>
<th>$X_S$†</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>5</td>
<td>0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>O</td>
<td>2.5</td>
<td>5</td>
<td>0.5</td>
<td>0.829</td>
</tr>
<tr>
<td>N</td>
<td>1</td>
<td>2</td>
<td>0.5</td>
<td>0.870</td>
</tr>
<tr>
<td>M</td>
<td>5</td>
<td>5</td>
<td>1</td>
<td>0.733</td>
</tr>
<tr>
<td>L</td>
<td>5</td>
<td>2.5</td>
<td>2</td>
<td>0.688</td>
</tr>
<tr>
<td>A</td>
<td>5</td>
<td>1</td>
<td>5</td>
<td>0.630</td>
</tr>
</tbody>
</table>

*Initial $R_\lambda=29.9$, $Sc=0.7$, striped initial scalar field
†Corresponding to Table 3.2.
‡Values of selectivity @ $t=10.0$.

**Effect of stoichiometric ratio:** The initial stoichiometric amount of B in the case of series-parallel reactions can be interpreted as either the amount of B needed for the first reaction or as the amount of B needed for both the first and second reaction. The stoichiometric ratio is defined as $\frac{C_{A0}}{C_{B0}}$ for the first interpretation and $2\frac{C_{A0}}{C_{B0}}$ for the second interpretation. $\frac{C_{A0}}{C_{B0}}=0.5$ is the minimum initial concentration ratio required for the second reaction to go to completion. Simulations show that as the value of the initial stoichiometric ratio ($\frac{C_{A0}}{C_{B0}}$) is increased, the asymptotic value of $X_S$ decreases. Also, $X_S$ increases to its asymptotic value faster for higher values of $\frac{C_{A0}}{C_{B0}}$. Figure 4.19 and Table 4.9 show the effect of non-stoichiometric ratios on selectivity.

If the initial stoichiometric ratio ($\frac{C_{A0}}{C_{B0}}$) is greater than 0.5, B is the limiting reagent, and R is not fully converted to S as the reactions run to completion, since
Table 4.9: Effect of initial stoichiometric ratio *

<table>
<thead>
<tr>
<th>Code</th>
<th>P</th>
<th>Q</th>
<th>D</th>
<th>R</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{C_{A0}}{C_{B0}}$</td>
<td>0.67</td>
<td>0.90</td>
<td>1.0</td>
<td>1.2</td>
<td>1.5</td>
</tr>
<tr>
<td>$X_S^\dagger$</td>
<td>0.753</td>
<td>0.656</td>
<td>0.638</td>
<td>0.617</td>
<td>0.607</td>
</tr>
</tbody>
</table>

$k_1=5k_2$, $Sc=0.7$, $R_\lambda=18.7$, striped initial scalar field.
$\dagger$Asymptotic value of selectivity @ $t=10.0$.

B becomes exhausted. Thus, to form significant amounts of R, the initial stoichiometric ratio ($\frac{C_{A0}}{C_{B0}}$) should be greater than 0.5 (e.g., around unity). If initial stoichiometric ratios greatly in excess of 1 are used, very little S is formed. Though $X_S$ is very low in such cases, the price is a low conversion of A and hence a waste of raw materials or increased separation costs. According to Bourne (1982), experimental results from a CSTR show that product distribution is not highly sensitive to stoichiometric ratio when this ratio is around 1. Increasing the initial stoichiometric ratio implies decreasing the amount of B available for reaction, so that B is depleted earlier. Thus more R is formed and $X_S$ reaches its asymptotic value faster.

**Effect of initial conditions:** The above results on the effects of turbulence Reynolds number ($R_\lambda$), viscosity, diffusivity and Schmidt number on selectivity shows that homogenization of reactants is the key factor controlling the amount of R and S produced and consequently in determining $X_S$. These results were all for the striped initial scalar field. A study of the effect of different initial fields for the reactants,
however, further supports the above observation.

Two different initial conditions for the concentration fields were used in this study: one corresponds to the striped case where slab initial conditions were used for A and B, and the other corresponds to an isotropic or stirred case. Figure 4.20 shows that the amount of R produced is considerably higher for the isotropic initial scalar field than for the striped initial field. Consequently, a lower value of $X_S$ is obtained for the stirred case compared to the striped case. These observations are evident from Table 4.10 and Figures 4.20 and 4.21.

Table 4.10: Effect of initial scalar field

<table>
<thead>
<tr>
<th>Initial scalar field</th>
<th>Selectivity, $X_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>t=0.6</td>
</tr>
<tr>
<td>Striped (U)</td>
<td>0.315</td>
</tr>
<tr>
<td>Stirred (V)</td>
<td>0.250</td>
</tr>
</tbody>
</table>

For the striped case, the reactants are present as slabs, and so the transport is initially one-dimensional until the other concentration scales parallel to the slab develop (Leonard and Hill, 1991). For the stirred case the initial scalar field is a three-dimensional field, with A and B distributed randomly in all three directions. So the reactants A and B are better mixed in a macroscopic sense, and the reaction surfaces are more extensive compared to the striped case. The initial integral length scale for the scalar field is 0.51 for the stirred case and 1.2 for the striped case, indicating better
transport and hence more homogeneity for the stirred case. Because of homogeneity in A and R, both A and R can compete for B, and as previously explained, the formation of R is favored over the formation of S. Figures 4.22a and 4.22b show perspective plots of the reaction rates $k_1 C_A C_B$ and $k_2 C_B C_R$, respectively. Since there is more homogenization with an initially isotropic scalar field, the perspective plot Figure 4.22a shows smoother contours compared to the contours in Figure 4.14 which is for an initial striped scalar field. It would be desirable to do a multi-stripe case to match the initial $\lambda_A$'s in order to distinguish between one-dimensional and three-dimensional effects (Leonard and Hill, 1991).

Concentration microscales for inert species and reacting species have been discussed by Leonard and Hill (1991). Since reaction increases concentration gradients, the growth of the concentration microscales was found to be somewhat less when chemical reaction is present compared to the case with no reaction, although the difference was small. The growth rate of the concentration microscales was greater for an isotropic scalar field than for an anisotropic scalar field (Leonard and Hill, 1991). The evolution of concentration microscales for reactants and products are shown in Figure 4.23 for the striped case and in Figure 4.24 for the stirred case, for simulations with a series-parallel reaction pair. Table 4.11 compares values of the non-dimensional scalar microscale for the stirred and striped initial scalar fields. Figure 4.25 shows that the growth of the concentration microscales is pronounced for the stirred case and remains almost constant for the striped case, in agreement with the observations of Leonard and Hill (1991) for a single reaction.
Table 4.11: Time development of the square of the concentration microscales relative to $\lambda_0$.

<table>
<thead>
<tr>
<th>Time, t</th>
<th>$\lambda^2_A/\lambda^2_{A0}$</th>
<th>$\lambda^2_B/\lambda^2_{A0}$</th>
<th>$\lambda^2_R/\lambda^2_{A0}$</th>
<th>$\lambda^2_S/\lambda^2_{A0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Striped</td>
<td>Stirred</td>
<td>Striped</td>
<td>Stirred</td>
</tr>
<tr>
<td>0.2</td>
<td>0.744</td>
<td>0.991</td>
<td>0.734</td>
<td>0.929</td>
</tr>
<tr>
<td>1.0</td>
<td>0.245</td>
<td>0.603</td>
<td>0.261</td>
<td>0.588</td>
</tr>
<tr>
<td>3.0</td>
<td>0.260</td>
<td>1.355</td>
<td>0.265</td>
<td>1.141</td>
</tr>
<tr>
<td>6.0</td>
<td>0.459</td>
<td>2.261</td>
<td>0.306</td>
<td>1.822</td>
</tr>
<tr>
<td>8.0</td>
<td>0.565</td>
<td>2.959</td>
<td>0.329</td>
<td>2.156</td>
</tr>
<tr>
<td>10.0</td>
<td>0.661</td>
<td>3.499</td>
<td>0.320</td>
<td>2.328</td>
</tr>
</tbody>
</table>

4.2 Evaluation of closure theories

The results of testing and analyzing the first-order moment closures of Bourne-Toor, Brodkey-Lewalle, Li-Toor and Dutta-Tarbell are presented in this section. Covariances of such concentration fluctuation terms as $c_A c_B$ and $c_B c_R$ (i.e., $\overline{c_A c_B}$, $\overline{c_B c_R}$) were calculated as volume averages using DNS data. A typical plot of $\overline{c_A c_B}$ and $\overline{c_B c_R}$ from the simulations is shown in Figure 4.26. The closure models were tested in three different ways. First, DNS data were used to evaluate the covariance $\overline{c_B c_R}$ for each model, and the model covariances were compared to the actual covariances from the simulations. Second, the moment equations were integrated, using covariances from the models, in order to obtain the time evolution of the mean quantities $\overline{c_A}$, $\overline{c_B}$, $\overline{c_R}$ and $\overline{c_S}$. The predicted mean concentrations were compared to the actual values from the simulations. Third, the selectivity $X_S$ was calculated.
using model predictions for the covariance and mean quantities, and the predicted \( X_S \) was then compared to DNS values.

For the reaction scheme given by equation (2.1) the averaged rate expressions are the averaged forms of equations (2.3), (2.4), (2.5) and (2.6), that is,

\[
\begin{align*}
\frac{dC_A}{dt} &= -k_1 C_A C_B \\
\frac{dC_B}{dt} &= -k_1 C_A C_B - k_2 C_B C_R \\
\frac{dC_R}{dt} &= k_1 C_A C_B - k_2 C_B C_R \\
\frac{dC_S}{dt} &= k_2 C_B C_R.
\end{align*}
\]

Reynolds' averaging is used to determine the integrated forms of the averaged rate equations. The average concentrations of \( A, B, R \) and \( S \) as a function of time may be written as

\[
\begin{align*}
\bar{C}_A(t) &= - \int_0^t k_1(\bar{C}_A \bar{C}_B) \; dt \\
\text{or} \quad \bar{C}_A(t) &= - \int_0^t k_1(\bar{C}_A \bar{C}_B + \bar{C}_A \bar{C}_B) \; dt, \\
\bar{C}_B(t) &= - \int_0^t k_1(\bar{C}_A \bar{C}_B) \; dt - \int_0^t k_2(\bar{C}_B \bar{C}_R) \; dt \\
\text{or} \quad \bar{C}_B(t) &= - \int_0^t k_1(\bar{C}_A \bar{C}_B + \bar{C}_A \bar{C}_B) \; dt - \int_0^t k_2(\bar{C}_B \bar{C}_R + \bar{C}_B \bar{C}_R) \; dt, \\
\bar{C}_R(t) &= \int_0^t k_1(\bar{C}_A \bar{C}_B) \; dt - \int_0^t k_2(\bar{C}_R \bar{C}_B) \; dt \\
\text{or} \quad \bar{C}_R(t) &= \int_0^t k_1(\bar{C}_A \bar{C}_B + \bar{C}_A \bar{C}_B) \; dt - \int_0^t k_2(\bar{C}_R \bar{C}_B + \bar{C}_R \bar{C}_B) \; dt, \\
\bar{C}_S(t) &= \int_0^t k_2(\bar{C}_R \bar{C}_B) \; dt \\
\text{or} \quad \bar{C}_S(t) &= \int_0^t k_2(\bar{C}_R \bar{C}_B + \bar{C}_R \bar{C}_B) \; dt.
\end{align*}
\]
Thus, the expression for selectivity given by (2.2) may be written

\[ X_s(t) = \frac{2 \int_0^t k_2(C_R C_B + \bar{c} R c_R) dt}{\int_0^t k_1(C_A C_B + \bar{c} A c_B) dt + \int_0^t k_2(C_R C_B + \bar{c} R c_R) dt}. \] (4.10)

Equations (4.6), (4.7), (4.8) and (4.9) are used to predict the time behavior of \( \bar{C}_A, \bar{C}_B, \bar{C}_R \) and \( \bar{C}_S \) using \( \bar{c} B c_R \) from the closure models, and equation (4.10) is used to predict the selectivity. Cubic spline interpolation routines from the International Mathematics and Statistics Library (IMSL) were used to determine intermediate values of statistical quantities, and an explicit finite-difference method was used to integrate equations (4.6), (4.7), (4.8), (4.9) to determine the mean values. Figures 4.27a and 4.27b show a comparison of DNS results with the various closure theories for \( \bar{c} B c_R \) for an initially striped scalar field and an initially stirred scalar field, respectively. Figure 4.28 compares the prediction of mean concentrations of A, B, R and S using DNS values for \( \bar{c} A c_B \) and \( \bar{c} B c_R \) and the actual DNS values. The agreement is very good and this figure serves as a basis of comparison for the predictions of mean values for the different closure theories and is a test of the integration scheme used. Figures 4.29, 4.30, 4.31 and 4.32 show the model predictions for the time evolution of the mean quantities for the Bourne-Toor, Brodkey-Lewalle, Li-Toor and Dutta-Tarbell closure models, compared with DNS results, respectively. Figure 4.33 compares values of the integrated quantity, \( X_S \), as predicted by different models, for the striped initial scalar field.

**Bourne-Toor:** The range of values of \( \bar{c} B c_R \) obtained from simulations and shown in Table 4.1 appear to be in fairly good agreement with Bourne and Toor's closure. But a closer look at the expression for \( X_s \) reveals that the ratio of \( \bar{c} B c_R / C_B C_R \)
is more important than the value of $c_Bc_R$ alone. The Bourne-Toor closure can be judged to be a good closure if $c_Bc_R$ and the ratio $c_Bc_R/C_B/C_R$ are both small. DNS results show that even though $c_Bc_R \approx 0$ compared to $C_A^2$, $|c_Bc_R| \ll C_B/C_R$ is not true. So the apparent agreement of DNS results with the Bourne-Toor closure for $c_Bc_R$ is misleading.

The evolution of the mean values of reactants and products, as predicted by the model, is compared with DNS results in Figure 4.29. It is found that the model underpredicts the value of $R$ and overpredicts the value of $S$, and consequently overpredicts the value of $X_S$. The predicted asymptotic state of the system was that more $S$ would be formed compared to $R$, that is $C_{S\infty} > C_{R\infty}$, where $C_{S\infty}$ and $C_{R\infty}$ represent concentrations of $S$ and $R$ respectively when $B$ has been exhausted, and this contradicts the DNS results.

**Brodkey-Lewalle:** This closure was tested using DNS data for the concentrations of $R$ and $A$ ($C_R, C_A$). The covariance term $\bar{c_Ac_B}$ was evaluated from simulations and also from the mixing limit (i.e., assuming Toor's closure). The validity of the closure was evaluated for $k_1$ to $k_2$ ratios of 1, 2 and 5 and was found to work best for $k_1 = k_2$ as suggested by Brodkey and Lewalle (1985). Since this closure is based on an extension of Toor's hypothesis, it is possible to study it in some detail.

Brodkey and Lewalle (1985) claim that the second reaction does not affect $\bar{c_Ac_B}$, or in other words, $\bar{c_Ac_B}$ for the case of a single reaction is the same as $\bar{c_Ac_B}$ for the case of two reactions. Also, they suggest using Toor's closure for $\bar{c_Ac_B}$, which means using $\bar{c_Ac_B}$ for the mixing limit, i.e., with no reaction. We have used DNS to compare $\bar{c_Ac_B}$ for the mixing case and for cases of one and two reactions. Surprisingly, as
Figure 4.34 reveals, $c_Ac_B$ for the case of two reactions is closer to the mixing case than the single reaction case. The minimum and maximum values of $(c_AC_B)_1/c_A^2$ are $-2.52$ and $-0.968$ whereas the minimum and maximum values of $(c_AC_B)_2/c_A^2$ are $-1.38$ and $-0.762$, respectively, where the subscript 1 or 2 denotes the number of reactions. This suggests that $c_Ac_B$ for the mixing limit may be used in place of $c_Ac_B$ for the case of two reactions without introducing much error.

An analysis of the evolution equations for $c_Ac_B$, $c_Bc_R$, $c_Ac_R$, $c_A^2$, and $c_B^2$ suggests that the basis of the Brodkey and Lewalle closure, that is, the interpretation as an extension of Toor's hypothesis to two reactions, can be tested using DNS data. According to the extension of Toor's hypothesis, the evolution of quantities such as $c_Ac_B$, $c_A^2$, etc. should not depend on the rate of the reaction (Brodkey and Lewalle, 1985). This suggests that the terms involving the kinetic rate constants in the evolution equations do not contribute to the evolution of the covariance terms.

As an example, for the case of a single reaction, the kinetics terms in the evolution equation for $c_A^2$ are

$$-2k_1[c_Ac_Bc_A + c_Bc_A^2 + c_A^2c_B], \tag{4.11}$$

and the extension of Toor's hypothesis suggests that

$$-k_1[c_Ac_Bc_A + c_Bc_A^2 + c_A^2c_B] \approx 0 \tag{4.12}$$

in comparison with the molecular dissipation term for $c_A^2$. There is some support for this idea from previous numerical simulations (Leonard and Hill, 1989, 1991). For the case of multiple reactions, such as the parallel-consecutive reaction scheme, the scenario is more complicated, since two rate constants are involved. The evolution
equation for $c_Ae_{cB}$ is

$$\frac{d(c_Ac_B)}{dt} = -2D \frac{\partial c_A \partial c_B}{\partial x_j \partial x_j}$$

(1)

$$- k_1 [C_A \frac{c_B^2}{2} + C_B c_Ac_B + c_Ac_B + C_A \frac{c_B^2}{2} + C_B c_A + c_Bc_A]$$

(2)

$$- k_2 [C_B c_Ac_R + C_R c_Ac_B + c_Ac_Bc_R],$$

(4.13)

and the evolution equation for $c_Bc_R$ is

$$\frac{d(c_Bc_R)}{dt} = -2D \frac{\partial c_B \partial c_R}{\partial x_j \partial x_j}$$

$$- k_1 [C_A \frac{c_Bc_R}{2} + C_B \frac{c_Ac_R}{2} - C_A \frac{c_B}{2} - C_B \frac{c_Ac_B + c_Ac_Bc_R - c_Ac_B}{2}]$$

$$- k_2 [C_B \frac{c_R^2}{2} + C_R \frac{c_Bc_R}{2} + c_Bc_R + C_B \frac{c_Bc_R}{2} + C_R \frac{c_R^2}{2} + c_Rc_B^2],$$

(4.14)

Brodkey’s extension of Toor’s hypothesis is based on Toor’s conjecture that for a single reaction, term(2) in equation (4.13) is negligible, that is,

$$k[c_Ac_B^2 + c_A^2c_B + c_A^2c_B + C_A \frac{c_B^2}{2} + C_B \frac{c_A^2}{2} + c_Ac_Bc_A (C_A + C_B)] = 0$$

(4.15)

is approximately valid for all values of $k$. His interpretation of the extension of Toor’s hypothesis to the second reaction is that the extension can be applied to the second reaction independently, i.e.,

$$k_1[c_Ac_B^2 + c_A^2c_B + C_A \frac{c_B}{2} + C_B \frac{c_A^2}{2} + c_Ac_Bc_A (C_A + C_B)] = 0$$

(4.16)

and

$$k_2[C_B c_Ac_R + C_R c_Ac_B + c_Ac_Bc_R] = 0.$$

(4.17)

In order to test the validity of this extension of Toor’s hypothesis, DNS results were used to compute individual terms in the evolution equations. For example, term
(2), term (3) and the sum of terms (2) and (3) (denoted as term (4)) in equation (4.13) were computed for different values of \( k_1/k_2 \) and for the two different initial scalar fields for the case of two reactions. The results are shown in Table 4.12.

Table 4.12: Evaluation of individual terms in the evolution equation for \( \frac{\partial c_{AB}}{\partial t} \)

<table>
<thead>
<tr>
<th>Rate constants</th>
<th>Term (2)</th>
<th>Term (3)</th>
<th>Term (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1/k_2 )</td>
<td>Max</td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>1</td>
<td>0.106</td>
<td>3.6 \times 10^{-4}</td>
<td>0.07</td>
</tr>
<tr>
<td>5</td>
<td>0.11</td>
<td>5.5 \times 10^{-4}</td>
<td>0.194</td>
</tr>
</tbody>
</table>

The results show that although term (2) is almost invariant to \( k_1/k_2 \), terms (3) and (4) do depend on \( k_1/k_2 \). However, the extension to Toor's hypothesis would still be valid if terms (2) and (3) (i.e., the reaction terms) are much smaller in comparison to term (1) (the diffusive term), and this was tested by evaluating all of the individual terms and their sums in the kinetic expressions in the evolution equations for variances and covariances of the concentration fluctuations. Also, the scalar dissipation term was calculated in the evolution equations to determine if the reaction terms are indeed small compared to the diffusive terms. DNS results suggest that the dissipation term is dominant in the evolution equations and that the reaction terms can be neglected in those equations. For example, the maximum value of the scalar dissipation term (1) is 0.85, whereas the maximum value of the sum of terms
(2) and (3) that is, term (4) is 0.03 for one set of conditions. These observations are in agreement with those of Leonard and Hill (1989).

An analysis of the evolution equations for $c_A c_B$, $c_B c_R$, $c_A c_R$, $c_A^2$, and $c_B^2$ shows that when $k_1$ and $k_2$ are equal, the extension of Toor's hypothesis (that reaction terms have no contribution in the evolution equations for the covariances) leads to the exact analytical form suggested by Brodkey and Lewalle (1985). And as Figure 4.35 shows, the agreement of this closure with DNS results is best when the rate constants are equal. So, any deviations from DNS results observed in the particular case of equal rate constants should be attributable to the failure of the extension to Toor's hypothesis to multiple reactions or to the failure of Toor's hypothesis itself.

The model predictions of the time behavior of the mean values of reactants and products are compared with DNS results in Figure 4.30. The model underpredicts the mean concentration of $S$ and overpredicts the mean concentration of $R$ and consequently underpredicts the value of $X_S$. The model prediction of the amount of $R$ remaining in the system is greater than that observed in simulations.

**Generalized Brodkey-Lewalle closure:** One can generalize the Brodkey-Lewalle closure by basing it on a slightly different interpretation of an extension of Toor's hypothesis. As in the Brodkey and Lewalle closure, it is assumed that the reaction term makes no contribution to the evolution equations for $c_A c_B$, $c_B c_R$, $c_A c_R$, $c_A^2$, and $c_B^2$. The difference between this closure and the Brodkey and Lewalle closure is in the way Toor's hypothesis has been extended to the second reaction. According to Brodkey and Lewalle, an extension of Toor's hypothesis applied to the evolution equation for $c_A c_B$ gives equations (4.16) and (4.17). A slightly different
extension of Toor's hypothesis that generalizes equations (4.16) and (4.17) is

\[ k_1[\overline{c_A c_B^2} + \overline{c_A^2 c_B} + \overline{c_A c_B} \overline{c_B^2} + \overline{c_A} \overline{c_B^2} + \overline{c_B} \overline{c_A^2} + \overline{c_A c_B} (\overline{c_A} + \overline{c_B})] \\
+ k_2[\overline{c_B} \overline{c_A c_R} + \overline{c_R} \overline{c_A c_B} + \overline{c_A c_B c_R}] = 0. \] (4.18)

Using this extension of Toor's hypothesis in the evolution equations for \( \overline{c_A c_B} \), \( \overline{c_B c_R} \), \( \overline{c_A c_R} \), \( \overline{c_A} \), and \( \overline{c_B} \), and using a few simplifying assumptions such as (i) \( \overline{c_A^2} = \overline{c_B} = \overline{c_A} \) (mixing limit), (ii) \( \overline{c_A c_B c_R} = 0 \), and (iii) \( \overline{c_B c_R} = 0 \), algebraic manipulation of the resulting equations yields the following closure:

\[ \overline{c_B c_R} = \frac{k_1[\overline{c_B} (\overline{c_A c_B} - \overline{c_A^2})] + k_2[\overline{c_R} \overline{c_A^2}]}{k_1(\overline{c_A} + \overline{c_B}) - k_2 \overline{c_B}}. \] (4.19)

When \( k_1 = k_2 \), this closure reduces to the Brodkey-Lewalle closure. The closure works well for both striped and stirred initial scalar fields when DNS values of \( \overline{c_A^2} \) are used. When values of \( \overline{c_A^2} \) for the non-reacting case (pure mixing) is used, the agreement with the striped case is reasonably good but deteriorates when stirred initial conditions are used.

**Li-Toor:** This closure is based on a reaction scheme where the ratio of the rate constants is very high that is, \( k_1 \) is very large compared to \( k_2 \). Results from simulations were used for values of the concentration of B and R for the single reaction case \( \overline{c_B}, \overline{c_R} \) and for values of the concentration of B and S for the series-parallel case \( \overline{c_S}, \overline{c_B} \) in order to compute \( \overline{c_B c_R} \) using the closure given in equation (2.15).

The model prediction of both \( \overline{c_B c_R} \) and \( X_S \) does not compare well with DNS data, because the Li-Toor closure is intended for very high \( k_1/k_2 \) ratios, but DNS cannot handle such high \( k_1/k_2 \) ratios. Consequently, simulations could not be done
for the case where this closure is claimed to be valid. Though the performance of the
closure could not be tested for high reaction rate ratios, it does not give satisfactory
results for reaction rates $k_1$ and $k_2$ that are of the same order of magnitude.

The model predictions for the various mean concentrations did not match at
all with DNS results, as is evident from Figure 4.31. The qualitative time behavior
of $R$ and $S$, and consequently $X_\phi$, as predicted by the model, was different greatly
from the time evolution observed from DNS. This model thus should not be used for
purposes of reactor modeling if the rate constants are of the same order of magnitude.

**Dutta-Tarbell:** DNS data were used to evaluate the concentrations of $B$ and $R$
$(\bar{C}_B, \bar{C}_R)$ and the intensity of segregation $I_\phi$ of a non-reacting scalar, $(\bar{C}_A^2/c_{A0}^2)m$ to
test this closure (2.17). The closure provides the best agreement with DNS results for
the striped scalar field among the theories examined here, but the agreement is poorer
for an isotropic initial scalar field. For the stirred case, this closure overpredicts the
magnitude of $\bar{C}_B\bar{C}_R$ by an order of magnitude, and the agreement worsens with time.

This model overpredicts the mean concentrations of $S$ and underpredicts the
mean concentrations of $R$ compared to DNS results, as shown in Figure 4.32. Thus
the predicted $X_\phi$ is greater than DNS values, but still this closure seems to provide
the best agreement, among those tested, for the striped initial scalar field, despite its
lack of a sound physical basis.

**Closure by inspection:** Noting that the DNS results for $\bar{C}_B\bar{C}_R$ are interme-
diate between the results of Dutta and Tarbell and of Brodkey and Lewalle, the
geometric mean of the predictions of those theories was used to estimate $\bar{C}_B\bar{C}_R$. Fig-
Figure 4.36 shows good agreement between the DNS results and this ad-hoc closure for the case of a striped scalar field, but the agreement is not as good for the isotropic scalar field case as shown in Figure 4.37. This shows that even arbitrary closures can work well for some conditions and fail for other conditions.

A brief overview of the closure theories: Among the first order closure theories available in the literature and discussed here, the Brodkey and Lewalle closure gave the best agreement with the simulations. The Brodkey and Lewalle closure underpredicts the value of the concentration covariance $\overline{c_Bc_R}$ by a factor of about 2 for an initially striped scalar field, and underpredicts $\overline{c_Bc_R}$ by a factor of 3 for an initially isotropic scalar field, but the qualitative behavior of $\overline{c_Bc_R}$ closely follows the DNS pattern and approaches zero asymptotically. Li and Toor's prediction for the $\overline{c_Bc_R}$ fares poorly when compared with DNS values and does not even agree qualitatively with DNS results, but that closure was designed for different conditions ($k_1/k_2 >> 1$). Dutta and Tarbell's closure works reasonably well for the striped initial scalar field - it overpredicts the value of $\overline{c_Bc_R}$ by a factor between 1 and 2. But for an isotropic initial scalar field, the closure overpredicts $\overline{c_Bc_R}$ by an order of magnitude.

Kosály (1988) claims that the Bourne and Toor and Brodkey and Lewalle closure schemes are valid if $\tau_m/\tau_{k2} << 1$ and that the Brodkey and Lewalle closure is also valid if $\tau_m/\tau_{k1} >> 1$ and $\tau_m/\tau_{k2} >> 1$ where $\tau_m$ is the characteristic time of turbulent molecular mixing and $\tau_{k1}$ and $\tau_{k2}$ are the characteristic times of the first and second reactions respectively. Our simulations show that $\tau_m/\tau_{k1}$ is about 5 and $\tau_m/\tau_{k2}$ is about 1.
Figure 4.1: Time history of reactants and products for code A and an initial scalar field $U$ (a) single reaction (b) series-parallel reaction
Figure 4.2: Local values of reaction rate, $k_1 C_A C_B(x,0,0)$, for a single reaction for code K and initial scalar field U
Figure 4.3: Local values of reaction rate, $k_t C_A C_B(x,0,0)$, for series-parallel reactions for code A and initial scalar field U.
Figure 4.4: Local values of reaction rate, $k_2C_B'C_H(x,0,0)$, for series-parallel reactions for code A and initial scalar field $U$. 
Figure 4.5: Comparison of local values of $k_1C_A C_B(x,0,0)$ for a single reaction (code K) and $k_1C_A C'_B(x,0,0)$ and $k_2C'_D C'_R(x,0,0)$ for a series-parallel reaction (code A) for an initial scalar field $U$ at time, $t = 3.0$
Figure 4.6: Schematic of concentration profiles of A, B, R and S for the case with no velocity: (a) initial distribution (b) distribution after a finite time, (Levenspiel, 1972)
Figure 4.7: Comparison of the intensity of segregation $I_s$ for code A and striped initial scalar field $U$ and stirred initial scalar field $V$: $I_s$ for A and B is $\overline{c_A c_B} / \overline{C_A C_B}$, $I_s$ for B and R is $\overline{c_B c_R} / \overline{C_B C_R}$.
Figure 4.8: Effect of turbulence intensity on selectivity: codes A, B and C for an initial scalar field U
Figure 4.9: Effect of viscosity on selectivity: codes A, F and G for an initial scalar field U.
Figure 4.10: Effect of viscosity on scalar microscale: codes A, F and G for an initial scalar field U
Figure 4.11: Contour plot of reaction rate, $k_1 C'_A C'_B(x,y,0)$ for different viscosities and Schmidt numbers for an initial scalar field $U$ at $t = 3.0$ (a) $k_1 C'_A C'_B$ for code A (b) $k_1 C'_A C'_B$ for code E (c) $k_1 C'_A C'_B$ for code G.
Figure 4.11 (Continued)
Figure 4.12: Contour plot of reaction rate $k_2 C_B C_R(x,y,0)$ for different viscosities and Schmidt numbers for an initial scalar field $U$ at $t=3.0$ (a) $k_2 C_B C_R$ for code A (b) $k_2 C_B C_R$ for code E (c) $k_2 C_B C_R$ for code G
Figure 4.13: Perspective plot of $k_t C_A C_B(x,y,0)$ for code E and an initial scalar field $U$ at $t=3.0$. 
Figure 4.14: Perspective plot of $k_A C_B(x, y, 0)$ for code A and an initial scalar field $U$ at $t=3.0$
Figure 4.15: Effect of Schmidt number on selectivity: codes H, I, A and J and an initial scalar field $U$
Figure 4.16: Effect of viscosity and Sc on selectivity: codes A, D and E and an initial scalar field U
Figure 4.17: Effect of rate constants on selectivity: codes A, L, M, N and O and an initial scalar field $U$
Figure 4.18: Time history of reactants and products for code O, $k_1/k_2 = 0.5$ and an initial scalar field U
Figure 4.19: Effect of non-stoichiometry on selectivity: codes P, Q, A, R and S and an initial scalar field U
Figure 4.20: Effect of initial conditions on the evolution of R and S: code A with striped (1-d, scalar field U) and stirred (3-d, scalar field V) initial distribution of reactants A and B
Figure 4.21: Effect of initial conditions on selectivity: code A with striped (1-d, scalar field U) and stirred (3-d, scalar field V) initial distribution of reactants A and B
Figure 4.22: Perspective plots of reaction rates for code A for an initial isotropic scalar field \( V \) at \( t = 3.0 \) (a) \( k_1 C_A C_B(x,y,0) \) (b) \( k_1 C_B C_H(x,y,0) \)
Figure 4.23: Evolution of scalar concentration microscales for code A and a striped initial scalar field U
Figure 4.24: Evolution of scalar concentration microscales for code A for an initial isotropic scalar field $V$
Figure 4.25: Comparison of scalar concentration microscales for code A for isotropic and anisotropic initial scalar fields
Figure 4.26: DNS results for covariance of concentration fluctuations $c_{AB}$ and $c_{BR}$ for code A
Figure 4.27: Comparison of DNS and model predictions of $c_{BcR}$ values for code A
(a) striped initial scalar field $U$ (b) stirred initial scalar field $V$
Figure 4.27 (Continued)
Figure 4.28: Predictions of mean quantities for code A: DNS
Figure 4.29: Predictions of mean quantities for code A: Bourne-Toor closure compared with DNS
Figure 4.30: Predictions of mean quantities for code A: Brodkey-Lewalle closure compared with DNS
Figure 4.31: Predictions of mean quantities for code A: Li-Toor closure compared with DNS
Figure 4.32: Predictions of mean quantities for code A: Dutta-Tarbell closure compared with DNS
Figure 4.33: Comparison of $X_s$ values (DNS with closure theories) for code A and a striped initial scalar field $U$
Figure 4.34: Comparison of $c_A c_B$ for 1 and 2 reactions and $c_A^2$ for mixing
Figure 4.35: Comparison of Brodkey-Lewalle closure and DNS results for different values of $k_1/k_2$
Figure 4.36: Comparison of the “unproposed non-closure” with DNS results for code A and a striped initial scalar field
Figure 4.37: Comparison of the "unproposed non-closure" with DNS results for code A and an initial isotropic scalar field.
5. CONCLUSIONS

Full turbulence simulations of the nonlinear dynamical equations have been performed to study the problem of chemical selectivity using a pseudo-spectral method on grids of $64^3$ Fourier modes. Simulations were carried out in decaying, isotropic turbulence with varying $R_\lambda$ and with initially segregated reactant species.

The effect of various physical parameters on selectivity was examined. Comparisons with the case of no velocity show that the presence of turbulence favors formation of the desired product, $R$, over the undesired product, $S$. As the turbulence Reynolds number is increased, mixing is enhanced and the formation of $R$ is favored. A decrease in viscosity decreases the size of the small scale structure of the velocity and scalar fields, thus favoring the formation of primary product, $R$. A decrease in $Sc$ at fixed $R_\lambda$ implies an increase of diffusivity and favors the first reaction over the second. As the ratio of the rate constants ($k_1/k_2$) is increased, more of $R$ is formed compared to $S$, because the relative rate of the two reactions determines the product distribution. When the initial stoichiometric amount of $A$ is more than 0.5 times the initial stoichiometric amount of $B$, the formation of $S$ is suppressed because the limiting reagent $B$ gets exhausted and the second reaction cannot take place. Simulations for the case where the initial scalar field is isotropic show that the amount of $R$ formed is considerably higher than for the case with a
stirred initial scalar field. The isotropic scalar field is three-dimensional and hence more homogenous, and thus transport is better compared to the striped scalar field where the transport is initially two-dimensional.

Comparisons of the local reaction rates for the one and two reaction cases were made. The reaction zones for the first and second reaction in the complex chemistry case do not coincide, as it appears that the reaction zone for the second reaction migrates towards the B-rich region. Examination of the spatial distribution of reaction rate for various values of physical parameters reveals the following details about the structure of the concentration field: (a) the scalar field is more detailed for a lower value of viscosity since more small scale structures are present, and (b) the sizes of the scalar field structures decrease with an increase of diffusivity. Good mixing and homogeneity in A and R favored the formation of the intermediate R, and thus the effect of all the physical parameters can be explained in terms of the part played by the parameters in bringing about homogenization.

Simple first order closure theories for the covariance of the concentration fluctuation terms were also tested by comparisons with results of the simulations. Reasons for the success or failure of the theories were suggested. Among the closures available in the literature, Brodkey and Lewalle's closure worked best for both initial scalar fields, whereas Dutta and Tarbell's closure worked best for the striped scalar field. None of the first-order closures were satisfactory, however, and there is a need to develop better closure models.

The first order closure theories available in the literature do not include any concentration gradients. But based on the knowledge that local transport to the reaction zone is required and on results of other investigators such as Leonard and
Hill (1991), it may be conjectured that concentration gradients are very important in terms of the physics of the problem and thus should be incorporated in the closure models. Possibilities of using other closures such as mapping closures (Pope, 1991) and stochastic closures (Kerstein, 1991) for multiple reactions need to be explored, although their success at dealing with the single reaction case has not yet been demonstrated.

Simulations in this work were limited to moderate $R_A$ flows, and future work should be directed towards simulating more realistic higher Reynolds number flows. More extensive calculations using grids of $128^3$ or $256^3$ Fourier modes need to be made to ensure proper resolution of the flow. The effect of complex chemistry in a stationary turbulent flow field should be investigated and an adequate forcing scheme needs to be developed for simulating stationary turbulence. A combination of the forcing scheme proposed by Eswaran and Pope (1988) and that proposed by Hill (1979b) can be used. The results of such simulations may then be compared with the preliminary results obtained by Gao and O'Brien (1991). Simulations should also be done for higher $k_1/k_2$ ratios and for higher $Sc$. Since spectral methods cannot handle high $k_1/k_2$ ratios, a combination of finite-difference and pseudo-spectral method would need to be used. The flux-corrected algorithm (Oran and Boris, 1987) is a possible choice. More detailed analysis of the kinematics of the reaction zone needs to be made on the lines of Leonard (1989). Introduction of fluid particle tracers would be useful in facilitating visualization of the reaction zone kinematics, and the method used by Yeung and Pope (1989) might be a good starting point.
6. REFERENCES


Ghoniem, A.F., and P. Givi, "Vortex-scalar Element Calculations of a Diffusion Flame,"


Miyawaki, O., H. Tsujikawa, and Y. Uraguchi, "Turbulent Mixing in Multi-nozzle Injection


PART II.

GRADIENT TRANSPORT OF A PASSIVE SCALAR IN DECAYING HOMOGENOUS TURBULENCE
1. INTRODUCTION

The problem of scalar transport by a uniform mean gradient in an isotropic turbulent-flow, first proposed by Corrsin (1952), has been important in theoretical fluid mechanics for a long time. Statistical theories based on small perturbations from the non-turbulent state and theories involving single point closures are not suitable for this problem (Hill, 1981). But statistical theories which are not empirical in nature and model the dynamics of the flow closely are desired. Since theoretical predictions of the enhancement of scalar transport by the presence of turbulence have been difficult to make, it is desirable to carry out laboratory experiments in addition. Wiskind (1962), Sirivat and Warhaft (1983), and Budwig, Tavoularis and Corrsin (1985) among others, have made laboratory experiments, and numerical simulations have been carried out by Sanderson, Leonard and Hill (1990) to study and understand turbulent scalar transport in the presence of a uniform mean scalar gradient.

With the advent of supercomputer technology, direct numerical simulation (DNS) has become an important tool in turbulence research. In this approach, the unsteady three-dimensional non-linear governing equations are solved numerically without any modeling, and instantaneous values of the dynamical variables are then obtained throughout the flow field. Since complete and accurate information of the velocity and scalar fields is made available, DNS serves as a powerful supplement to experimental investigations. The difficulty in extracting detailed information on the scalar field in turbulent flows has constrained experimental studies on the subject of passive scalar transport with a mean gradient, and
so DNS studies are important for a complete understanding of the problem.

In the present study, the evolution and transport of a passive scalar by a uniform mean scalar gradient in decaying isotropic turbulence were examined using DNS and compared both with a statistical theory (the direct interaction approximation of Kraichnan, 1964) and with laboratory experiments of Sirivat and Warhaft (1983).

The experiments of Sirivat and Warhaft (1983) being simulated correspond to the "mandoline" (heated wires to introduce the temperature fluctuations) and "toaster" (uniform temperature gradient existing upstream of the turbulence-generating grid) cases. The results of Sirivat and Warhaft showed that though the evolution of the scalar field was affected by initial conditions, the asymptotic state appeared to be relatively insensitive to them.

In the present study, good qualitative agreement of the results of numerical simulations with experiments has been obtained, in terms of the asymptotic state of the system. The scalar field is decomposed as \( T = \bar{T} + \theta \) where \( \bar{T} \) is the mean and \( \theta \) is the fluctuation about the mean. The time evolution of such quantities as turbulent kinetic energy, scalar variance \( \bar{\theta}^2 \), ratio of integral length scales and Taylor microscales, cross-stream heat-flux \( \bar{\theta}v \), scalar transport correlation coefficient \( \rho_{\theta\theta} \) (\( = \bar{\theta}v / \theta'v' \)), where \( v \) is the velocity fluctuation in the direction of the mean scalar gradient \( \beta \) (\( = d\bar{T} / dy \)), \( \theta' \) is the rms value of \( \theta \), and eddy diffusivity ratio \( \epsilon_H/\alpha \) (\( = -\bar{\theta}vPr/\beta\nu \)), where Pr is the Prandtl number \( \nu/\alpha \) and \( \nu \) is the viscosity, has been computed. The effect of such initial conditions as initial spectra and initial length scale ratio on the evolution and asymptotic behavior of the system has been studied. Simulations have also been made for cases with no scalar gradient in order to study the differences between the cases with isotropic and anisotropic (axisymmetric) scalar fields.
2. BACKGROUND

The problem of scalar transport in an isotropic turbulent flow with a uniform mean scalar gradient was first studied by Corrsin (1952). He theorized that for non-decaying isotropic turbulence flowing with a mean velocity in the $x$-direction, an imposed passive uniform cross-stream temperature gradient $dT/dy (=\beta)$ will maintain itself and be independent of $x$. Corrsin's predictions, that an initially uniform mean scalar gradient would retain its linearity and magnitude in the presence of isotropic turbulence and that the scalar variance would experience a linear growth rate, were subsequently tested by experiments and theoretical studies. A brief overview of relevant experimental, theoretical and numerical work follows.

2.1 Experimental work

Wiskind (1962) was the first to carry out a laboratory experiment on Corrsin's problem and to confirm the predictions by Corrsin. In Wiskind's experiments, as well as those done by Alexopoulos and Keffer (1971), and by Venkataramani and Chevray (1978), the cross-stream temperature gradient $\beta$ was a constant independent of $x$. In their heated grid experiments, the grid bars were differentially heated to produce a cross-stream temperature gradient, but a cross-stream gradient in the scalar variance $\overline{\theta^2}$ was also produced. Warhaft and Lumley (1978) have shown that heating a grid also produces a significant longitudinal heat flux, but the only flux in these experiments without a scalar gradient should be in
the cross-stream direction, that is, down the temperature gradient. Also, there should be no coupling between the temperature fluctuations and the longitudinal velocity; that is, the cross correlation coefficient $\rho_{\theta u}(=-\overline{\theta' u'}/\overline{\theta' \theta'})$ between $u$ and $\theta$ should ideally be zero. In the heated grid experiments, good homogeneity is never attained, and the cross correlation coefficient $\rho_{\theta u}$ is as high as $-0.3$. The conservation equation for $\overline{\theta^2}$ (Equation (1), Sirivat and Warhaft, 1983) suggests that the coupling of the velocity and temperature fluctuations probably also affects the evolution of $\overline{\theta^2}$.

More recent experiments were done by Sirivat and Warhaft (1983) and Budwig, Tavoularis and Corrsin (1985) to obtain better homogeneity than in the heated grid experiments. The temperature profiles in Sirivat and Warhaft's work were produced by two different methods: the "mandoline" and the "toaster". In the "mandoline" arrangement, a parallel array of fine wires was placed downstream from the turbulence generating grid, and the wires were differentially heated by controlling the voltage drop across each wire. This method produced an initial temperature variance as well as the mean temperature gradient, but the temperature field was far more homogenous than that produced by the heated grid experiments. Also, it was possible to vary the input thermal length scale and study its evolution in the presence of a temperature gradient. In the "toaster" configuration, the temperature gradient was produced deep in the plenum chamber upstream of the turbulence generating grid — the nichrome ribbons were placed in a parallel array and were differentially heated by independently controlling the electric current in each ribbon. The temperature gradient was created in the plenum so that any disturbance to the flow would be dampened out in the flow preconditioning section ahead of the grid. Any temperature fluctuations would be due solely to the action of the grid turbulence acting against the uniform temperature gradient. This method produced good transverse homogeneity of the thermal fluctuation field, but the initial thermal length scale could not be independently controlled since it developed naturally. Figure 2.1 shows the two different configurations.
The studies of Wiskind (1962), Sirivat et al. (1983), and Budwig et al. (1985) were performed at moderate Reynolds numbers, whereas Venkataramani et al. (1978) made their measurements at a relatively high Reynolds number. All these studies concerned a passive scalar, that is, the velocity field evolved independently of the scalar field and the passivity in the experiments was achieved by ensuring that temperature differentials were small.

For the "mandoline" case, Sirivat and Warhaft investigated the effect of various initial thermal and velocity length scale combinations upon the evolution and characteristics of the temperature field. In the presence of a temperature gradient, the length scale ratio approached a constant value, independent of the magnitude of the gradient $\beta$. The initial magnitudes of the length scale ratios were affected by varying the "mandoline" configuration, that is, by changing the initial thermal to velocity length scale ratio. Once the equilibrium length and time scale ratios were established, the temperature variance $\overline{\theta^2}$ grew linearly with time. The equilibrium values of the length scale and time scale ratios for the "toaster" and the "mandoline" were nearly the same, and in both cases, the temperature variance grew linearly with time. In the "mandoline" experiment, since the temperature gradient is imposed on a turbulent velocity field, the velocity and temperature fluctuations are initially uncorrelated, and there is an initial temperature variance, since temperature fluctuations have been produced. For the "toaster" experiment, the temperature gradient is imposed long before the velocity field is made turbulent, so that all fluctuations are damped out before the turbulence is generated. So in this case, temperature fluctuations are produced by velocity fluctuations in the direction of $\beta$; hence the cross correlation coefficient $\rho_{\theta \theta}$ is highly correlated initially.
2.2 Theoretical work

Many approaches have been used over the past forty years to deal with the problem of scalar transport by a uniform mean scalar gradient. Corrsin (1952) predicted that for an isotropic turbulent velocity field with a uniform mean scalar gradient, the mean scalar gradient would retain its linearity and strength, and the scalar energy or variance would grow linearly. Other theoretical work before 1980 consisted of Mélesse's (1954) derivation of relationships between statistical functions for an anisotropic scalar field, Dunn and Reid's (1958) final period of decay results using simultaneous-time quasilinear theory, and Deissler's (1963) perturbation calculation in the limit of zero shear. One of the most prominent two-point statistical theories, the so-called direct interaction approximation or DIA (Kraichnan, 1959) has been extended to scalar fields (Kraichnan, 1964). The DIA is a self-consistent theory requiring no arbitrary constants or functions, and no ad hoc statistical assumptions are necessary to describe the interaction between the velocity and scalar fields, but instead the theory predicts these statistics to second order (Hill, 1981). The DIA theory has some well-known defects relating to inaccurate description of spectral energy transfer rates. The chief symptom of this is that the convection of small scales by large scales is inaccurately treated, since the DIA equations are not Galilean invariant with respect to random large scale motions (Hill, 1981). Because spectral energy transfer rate is inaccurate, the theory predicts a $k^{-3/2}$ inertial range at high Reynolds numbers instead of Kolmogorov's $k^{-5/3}$ law.

Several studies have been made using the DIA for transport problems. Hill (1981) made numerical calculations using the direct interaction approximation (DIA), under conditions close to those of Wiskind's experiments. Hill assumed stationary isotropic turbulence and used analytical velocity field statistics to solve the steady state DIA equations for the temperature field and the temperature Green's function. He used a DIA formulation similar
to the random oscillator problem in which the statistics of the velocity field are given, that is, forms of the velocity correlations were assumed. Also, a spherically averaged DIA was used for the temperature correlation. His results gave much better agreement with the experimental results than some other theories such as the quasilinear and final period of decay or weak turbulence theories. The agreement improved when some of the assumptions were changed, for example, an exponential form of the velocity correlation function gave better results. Hill and Petty (1983) developed another formulation for the DIA and used a smoothing approximation first proposed by Kraichnan to obtain simple approximations for the eddy diffusivity suitable for engineering calculations. Sanderson and Hill (1986) have used the full set of DIA equations based on a formulation for the Boussinesq equations (Kraichnan, 1964), for the case of decaying isotropic turbulence under conditions comparable to those of Wiskind. The calculations of Sanderson and Hill were for an anisotropic scalar field with no angular harmonics retained. The values of the diffusivity ratio \( \epsilon_H / \alpha \) and the correlation coefficient \( \rho_{\theta} \) obtained from the full DIA calculation of Sanderson and Hill were considerably higher than those reported by Hill. However, the value of \( \rho_{\theta} \) agreed reasonably well with the experimentally obtained value of Budwig et al. Sanderson has also made a detailed study of the linear equations and has compared the linear results with non-linear results and previous experimental results, so as to isolate the roles of the linear and non-linear parts (Sanderson, Leonard and Hill, 1990). Table 2.1, adapted from Sanderson and Hill (1986) shows a comparison of some heat transfer results from previous work.

The DIA has been used by Sanderson, Hill and Herring (1987) and Sanderson and Hill (1988) and both the DIA and DNS by Sanderson, Leonard and Hill (1990) in an extension of the scalar transport problem to the study of transport of passive and active scalars in a stably stratified turbulent flow. The results of the DIA computations of stably stratified homogenous turbulence performed by Sanderson and Hill (1988) provide approx-
**Table 2.1: Heat transfer results from previous work**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_\lambda$</td>
<td>29.3</td>
<td>64.4</td>
<td>26</td>
<td>28</td>
<td>29.3</td>
<td>33.5</td>
</tr>
<tr>
<td>$\rho_{ed}$</td>
<td>-0.48</td>
<td>-0.58</td>
<td>-0.7</td>
<td>-0.7 to -0.8</td>
<td>-0.39</td>
<td>-0.86</td>
</tr>
<tr>
<td>$\epsilon_H/\alpha$</td>
<td>17.4</td>
<td>149</td>
<td>18</td>
<td>19</td>
<td>25.7</td>
<td>55</td>
</tr>
</tbody>
</table>

*Probe location is at $x/M \approx 102$.

...imrate agreement with previous numerical simulations of Métais and Herring (1988) and with laboratory results of Itsweire et al (1986). The effect of Prandtl number upon such single point quantities as eddy diffusivity and velocity-scalar correlation coefficient was determined and found to be small. Dannevik (1986) has reported approximate solutions of the full DIA equations for thermal turbulence, the Rayleigh-Bernard convection occurring between parallel plates. In his work a Markovianized approximation to the DIA was used. Also, Domaradzki and Orszag (1987) have solved the DIA equations numerically for homogenous shear turbulence and homogenous, anisotropic turbulence in a rotating fluid. The DIA has some computational disadvantages over the Eddy-Damped Quasi Normal Markovianized (EDQNM) Model (Orszag, 1970), the Test Field Model (TFM) (Kraichnan, 1971), and other Markovianized theories since it is non-Markovian and requires time-convolutions to be calculated.

Some theories which are closely related to the DIA, have tried to improve on the limitations imposed by the DIA, and are potentially applicable to the Corrsin problem are the renormalized Lagrangian approximation (Kaneda, 1981) and the local energy transfer theory (McComb, 1978). The renormalized Lagrangian approximation (RLA), developed...
by Kaneda, is a method of renormalized expansions in the theory of turbulence using the Lagrangian position function. The Lagrangian development of the velocity field is expressed using the position function, and a simple truncation of the expansions yields a closed set of approximate equations which resembles Kraichnan's test-field model and predicts Kolmogorov's inertial range energy spectrum. A second theory, the local energy transfer theory (LET), is a two-point, two-time Eulerian closure for the (Fourier-transformed) velocity covariance in terms of a renormalized propagator function. The basic equations for the LET are nearly the same as the corresponding DIA equations. McComb and Shanmugasundaram (1984) have used the LET theory to obtain energy, dissipation and energy-transfer spectra at low-to-moderate microscale Reynolds numbers and at a single large Reynolds number, and McComb et al (1989) have reported calculations of the velocity derivative skewness and of velocity correlations. The LET gave higher values of energy transfer and of evolved skewness factor than the DIA. Neither the RLA nor the LET have been used for the uniform scalar gradient transport problem.

Such closure theories as Kraichnan's Test Field Model (TFM) (Kraichnan, 1971), Kraichnan's Lagrangian History Direct Interaction (LHDI) Approximation (Kraichnan, 1965), Kraichnan's Abridged Lagrangian History Direct Interaction (ALHDI) Approximation, Orszag's Eddy-Damped Quasi Normal Markovianized (EDQNM) Model (Orszag, 1970) and Kraichnan and Herring's Strain-Based Lagrangian History Direct Interaction (SBLHDI) Approximation (Kraichnan and Herring, 1978) and various other closure theories have been used for the passive scalar problem without a gradient and could possibly be extended to apply to passive scalar problems with a uniform scalar gradient. Newman and Herring (1979) have applied the TFM developed by Kraichnan (1971) to the study of an isotropic passive scalar contaminant convected by decaying isotropic turbulence. Larcheveque et al (1980) have used two-point closures such as the TFM and EDQNM model to study the decay of a passive scalar convected by homogenous turbulence. Recently,
Qian (1990) obtained a closed set of equations of isotropic turbulence by the method of non-equilibrium statistical mechanics and a perturbation-variation approach and used it to study the spectral dynamics of a turbulent passive scalar in the viscous-convective range.

2.3 Previous numerical simulations

Numerical simulations of the transport of a passive scalar without a mean scalar gradient have been made by Herring and Kerr (1982), Kerr (1985), Meneguzzi et al (1987) among others. Herring and Kerr (1982) carried out simulations for the convection of a passive scalar in isotropic turbulence for low $R_A$ and for $Pr=0.5$ and found satisfactory agreement with equivalent results for the DIA and the test-field model. Some simulations investigating the problem of scalar transport by a mean scalar gradient have been reported by Sanderson, Leonard and Hill (1990), but the simulations do not have adequate resolution. Calculations for the transport of passive and active scalars in a stably stratified flow were made by Métais and Herring (1988), Gertz et al (1989) and Sanderson et al (1991), the latter of whom compared DNS results with predictions of the DIA.
Figure 2.1: Toaster and mandoline configurations: Adapted from Sirivat and Warhaft (1983)
3. PROBLEM DESCRIPTION

In the present study, numerical computations of passive scalar transport have been made using direct numerical simulations (DNS) under conditions similar to the "mandoline" and "toaster" experiments of Sirivat and Warhaft (1983). The results are compared with computations made using the direct interaction approximation of Kraichnan (Sanderson, 1991) and with the experiments of Sirivat and Warhaft.

In the simulations, the fluctuating scalar field is started up at the same time as the velocity field for the "mandoline" experiments, although the two fields are initially uncorrelated, whereas for the "toaster" experiments the scalar variance develops as a result of the action of the turbulence against the temperature gradient. A homogenous decaying turbulent field with a scalar gradient imposed on it is used in the simulations, with specified initial turbulence levels. In direct numerical simulations the governing equations are solved without resorting to any turbulence models, and all time and length scales are fully resolved. The physical domain is a cube of size $(2\pi)^3$ with periodic boundary conditions.

The statistical theory used in this study is the direct interaction approximation (DIA) described earlier. The triple moments that occur when the governing equations for the two point-two time correlations are formed are re-expressed in terms of Green's response functions and double moments according to the DIA. The statistical functions are represented using an eigenfunction decomposition and the angular dependence of the eigenfunctions is represented using Legendre polynomials for the scalar-scalar and velocity-velocity functions, and associated Legendre functions for the scalar-velocity quantities. The method was
developed for anisotropic turbulence by Herring (1974) and was extended to the present study by Sanderson (1991), who carried out the DIA calculations which are presented in this study. The DIA equations in the eigenfunction representation are quite complex and are presented in detail by Sanderson, Leonard and Hill (1990). The numerical code for the DIA studies uses a predictor-corrector time-stepping algorithm with the linear terms treated exactly using an eigenvector analysis. The time history integrals were evaluated using one dimensional B-splines, whereas the wave-number convolution integrals were evaluated using two dimensional tensor B-splines to approximate the geometric coefficients and the statistical function products. The computational time needed is proportional to $N^3 \times L^4 \times T^3$ where $N$ is the number of wave-numbers, $L$ is the number of Legendre functions, and $T$ is the number of timesteps. The two-time nature of the DIA and its history integrals require storage for all $(t, t')$ points for $t' \leq t$.

3.1 Numerical method

The DNS code used solves the non-linear governing equations using a pseudo-spectral method and a third order Runge-Kutta time integration algorithm. The code, adapted from Kerr (1985), was modified to run on an IBM 3090 and a HDS EX80. The variables were expressed as truncated Fourier series and the ordinary differential equations for the expansion coefficients were then solved. The non-linear terms were evaluated at collocation points in physical space and the Fourier coefficients of the non-linear terms were then evaluated. The rotational form of the Navier-Stokes equation,

$$\frac{\partial \mathbf{u}}{\partial t} = \mathbf{u} \times \boldsymbol{\omega} - \nabla \left( \frac{\rho}{\rho} + \frac{u^2}{2} \right) + \nu \nabla^2 \mathbf{u}$$

(3.1)

was used and the continuity equation

$$\nabla \cdot \mathbf{u} = 0$$

(3.2)
was used to eliminate the pressure term. The conservative form of the heat equation

\[ \frac{\partial u}{\partial t} + \nabla \cdot uT = \alpha \nabla^2 T \]  (3.3)

was solved. Partial dealiasing was done by spherical truncation of wave-numbers outside a spherical shell of radius \(8K/9\). The integration scheme used a variable time step based on an approximate Courant-Friedrichs-Lewy (CFL) stability criterion, \(v\Delta t/\Delta x = C\), where \(v\) is the maximum value of the magnitude of the velocity, \(\Delta t\) is the time step, \(\Delta x\) is the grid spacing, and \(C\) is a constant called the Courant number and is set to 1.5. Time-stepping errors can be minimized by having a sufficiently small time step controlled by the CFL criterion or the Courant number. Whereas high Courant numbers decrease the computer time needed for the simulation by increasing the time step, they introduce significant time-stepping errors. For simulations to be well resolved, the highest wave numbers in the computational box must be large enough to represent the smallest length scales in the flow, and the integral length scale of the velocity field must be sufficiently small so that the periodic boundary conditions do not affect the statistics by altering the dynamics represented.

Calculations for this study with a \(64^3\) and \(80^3\) wave-number grids were made on an IBM 3090 VF at the IBM Palo Alto Research Center, and \(64^3, 128^3\) and \(256^3\) calculations were made on a HDS EX80 computer at HDS Inc., in Santa Clara. The \(256^3\) calculation was done to test the resolution of the \(128^3\) calculations and to ensure that adequate resolution was obtained with a \(128^3\) grid for the flows being simulated.

3.1.1 Conditions for the simulations

Two different initial spectral shapes were used in this study, in order to investigate the effects of different initial spectral conditions upon the evolution of the system. One is a Gaussian-like spectrum,

\[ E(k, t_0) = 16\sqrt{\frac{2}{\pi}} u^2 k^4 \frac{k^6}{k_0^8} \exp \left( -2\frac{k^2}{k_0^2} \right) \]  (3.4)
where $u'$ is the initial turbulence intensity and $k_0$ is the peak wave-number of the spectrum, and the other is an exponential spectrum,

$$E(k, t_0) = \frac{81}{4} u'^2 k^3 \exp \left( -3 \frac{k}{k_0} \right).$$  \hfill (3.5)

For both the "mandoline" and "toaster" experiments, some runs used a velocity field which had been allowed to develop for some time in a pre-simulation. The initial Reynolds number was high, and the velocity field was allowed to decay until $t=0.1$ in the pre-simulation run. That velocity field was then used as the initial velocity field for the subsequent runs. The conditions for the pre-simulation run are given in Table 3.1. A Gaussian initial energy spectrum was used for the pre-conditioning runs.

**Table 3.1: Parameters for the pre-simulation run**

<table>
<thead>
<tr>
<th>Run</th>
<th>Grid</th>
<th>$\nu$</th>
<th>$R_\lambda$</th>
<th>$u'$</th>
<th>$\Lambda_\nu$</th>
<th>Pr</th>
<th>$\frac{dT}{dy}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>128</td>
<td>0.004</td>
<td>83.29</td>
<td>1.00</td>
<td>0.4206</td>
<td>0.7</td>
<td>0</td>
</tr>
</tbody>
</table>

*Conditions correspond to the beginning of the pre-simulation.

Simulations for isotropic scalar turbulence correspond to the case where there is no scalar gradient. Different initial spectra and different initial length scale ratios were used for the calculations. The same spectra were used for both the velocity field and the scalar field. For convenience, different initial scalar spectra corresponding to initial integral length scale ratios of 1, 0.5 and 1.5 are referred to as cases 1, 2 and 3 respectively in the text. In the figures they are referred to as scalars 1, 2, and 3. Initial conditions for these runs are given in Table 3.2.
Table 3.2: Initial conditions for isotropic scalar turbulence *

<table>
<thead>
<tr>
<th>Run</th>
<th>Grid</th>
<th>$R_\lambda$</th>
<th>Pr</th>
<th>$u'$</th>
<th>$\theta$</th>
<th>$k_u$</th>
<th>$\Lambda_u$</th>
<th>$k_\theta$</th>
<th>$\Lambda_\theta$</th>
<th>$\Lambda_\sigma/\Lambda_u$</th>
<th>Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>80</td>
<td>34.7</td>
<td>0.7</td>
<td>0.99</td>
<td>0.166</td>
<td>6</td>
<td>0.39</td>
<td>4</td>
<td>0.39</td>
<td>1</td>
<td>Exp</td>
</tr>
<tr>
<td>B2</td>
<td>80</td>
<td>34.7</td>
<td>0.7</td>
<td>0.99</td>
<td>0.153</td>
<td>6</td>
<td>0.39</td>
<td>8</td>
<td>0.21</td>
<td>0.5</td>
<td>Exp</td>
</tr>
<tr>
<td>B3</td>
<td>80</td>
<td>34.7</td>
<td>0.7</td>
<td>0.99</td>
<td>0.168</td>
<td>6</td>
<td>0.39</td>
<td>2.67</td>
<td>0.55</td>
<td>1.5</td>
<td>Exp</td>
</tr>
<tr>
<td>B4</td>
<td>80</td>
<td>45.0</td>
<td>0.7</td>
<td>1.0</td>
<td>0.166</td>
<td>6</td>
<td>0.42</td>
<td>4</td>
<td>0.42</td>
<td>1</td>
<td>Gauss</td>
</tr>
<tr>
<td>B5</td>
<td>80</td>
<td>45.0</td>
<td>0.7</td>
<td>1.0</td>
<td>0.165</td>
<td>6</td>
<td>0.42</td>
<td>8</td>
<td>0.21</td>
<td>0.5</td>
<td>Gauss</td>
</tr>
<tr>
<td>B6</td>
<td>80</td>
<td>45.0</td>
<td>0.7</td>
<td>1.0</td>
<td>0.167</td>
<td>6</td>
<td>0.42</td>
<td>2.67</td>
<td>0.63</td>
<td>1.5</td>
<td>Gauss</td>
</tr>
<tr>
<td>B7</td>
<td>128</td>
<td>42.8</td>
<td>0.7</td>
<td>1.0</td>
<td>0.167</td>
<td>6</td>
<td>0.39</td>
<td>4</td>
<td>0.39</td>
<td>1.0</td>
<td>Exp</td>
</tr>
</tbody>
</table>

*No pre-simulation was used for these runs.

The initial conditions for the "toaster" are given in Table 3.3 with the initial scalar fluctuation field $\theta$ set equal to zero. Runs C1 and C2 start with the same velocity field, but the scalar gradient is introduced later (at $t=0.1$) in run C2, allowing for correlations in the velocity field to develop in C2 before starting the heat transfer. Similarly, C5 starts with the same velocity field as C4, but the scalar gradient is introduced after the velocity field has developed till $t=0.1$.

For the "mandoline" case, an initial scalar field was defined using a Gaussian (equation 3.4) or exponential spectrum (equation 3.5). The initial conditions for the velocity and scalar fields for the "mandoline" are given in Tables 3.4 and 3.5. Runs D3, D4, D5 and D6 correspond to cases where the velocity field has been preconditioned. The velocity fields for D4, D5 and D6 are identical, but the scalar field corresponds to different initial spectra and are referred to as scalars 1, 2 and 3 in the figures.

In Tables 3.1 – 3.5, $\nu$ is the viscosity, $u'$ is the initial turbulence intensity, $R_\lambda$ is the turbulent Reynolds number defined as $R_\lambda = u'\lambda/\nu$, $\lambda$ is Taylor microscale for the velocity field, $\Lambda_u$ is the integral length scale for the velocity field, $\Lambda_\theta$ is the integral length scale
Table 3.3: Parameters for the toaster run (initial $\theta' = 0$)

<table>
<thead>
<tr>
<th>Run</th>
<th>Pre-sim</th>
<th>Grid</th>
<th>$\nu$</th>
<th>$R_\lambda$</th>
<th>$u'$</th>
<th>$k_v$</th>
<th>$\Lambda_v$</th>
<th>Pr</th>
<th>$\frac{dT}{dy}$</th>
<th>Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>No</td>
<td>128</td>
<td>0.004</td>
<td>83.29</td>
<td>1.00</td>
<td>6.0</td>
<td>0.4206</td>
<td>0.7</td>
<td>6.2832</td>
<td>Gauss</td>
</tr>
<tr>
<td>C2</td>
<td>Yes</td>
<td>128</td>
<td>0.004</td>
<td>65.16</td>
<td>0.979</td>
<td>6.0</td>
<td>0.406</td>
<td>0.7</td>
<td>6.2832</td>
<td>Gauss</td>
</tr>
<tr>
<td>C3</td>
<td>Yes</td>
<td>128</td>
<td>0.003</td>
<td>41.41</td>
<td>0.811</td>
<td>6.0</td>
<td>0.353</td>
<td>0.7</td>
<td>6.2832</td>
<td>Gauss</td>
</tr>
<tr>
<td>C4</td>
<td>No</td>
<td>80</td>
<td>0.007</td>
<td>45.08</td>
<td>0.997</td>
<td>4.76</td>
<td>0.488</td>
<td>0.7</td>
<td>6.2832</td>
<td>Exp</td>
</tr>
<tr>
<td>C5</td>
<td>No</td>
<td>80</td>
<td>0.007</td>
<td>35.22</td>
<td>0.981</td>
<td>4.76</td>
<td>0.485</td>
<td>0.7</td>
<td>6.2832</td>
<td>Exp</td>
</tr>
</tbody>
</table>

for the scalar field, Pr is the Prandtl number, $dT/dy$ or $\beta$ is the scalar gradient in the $y$ direction.
Table 3.4: Parameters for the velocity field for the mandoline

<table>
<thead>
<tr>
<th>Run</th>
<th>Pre-sim</th>
<th>Grid</th>
<th>$R_\Lambda$</th>
<th>$k_\nu$</th>
<th>$\nu$</th>
<th>$u'$</th>
<th>$\Lambda_\nu$</th>
<th>Spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>No</td>
<td>128</td>
<td>47.59</td>
<td>6.0</td>
<td>0.007</td>
<td>1.00</td>
<td>0.4206</td>
<td>Gauss</td>
</tr>
<tr>
<td>D2</td>
<td>No</td>
<td>256</td>
<td>47.59</td>
<td>6.0</td>
<td>0.007</td>
<td>1.00</td>
<td>0.4206</td>
<td>Gauss</td>
</tr>
<tr>
<td>D3</td>
<td>No</td>
<td>128</td>
<td>83.29</td>
<td>6.0</td>
<td>0.004</td>
<td>1.00</td>
<td>0.4206</td>
<td>Gauss</td>
</tr>
<tr>
<td>D4</td>
<td>Yes</td>
<td>128</td>
<td>65.16</td>
<td>6.0</td>
<td>0.004</td>
<td>0.979</td>
<td>0.4056</td>
<td>Gauss</td>
</tr>
<tr>
<td>D5</td>
<td>Yes</td>
<td>128</td>
<td>65.16</td>
<td>6.0</td>
<td>0.004</td>
<td>0.979</td>
<td>0.4056</td>
<td>Gauss</td>
</tr>
<tr>
<td>D6</td>
<td>Yes</td>
<td>128</td>
<td>65.16</td>
<td>6.0</td>
<td>0.004</td>
<td>0.979</td>
<td>0.4056</td>
<td>Gauss</td>
</tr>
<tr>
<td>D7</td>
<td>No</td>
<td>80</td>
<td>52.59</td>
<td>4.76</td>
<td>0.006</td>
<td>0.997</td>
<td>0.488</td>
<td>Exp</td>
</tr>
<tr>
<td>D8</td>
<td>No</td>
<td>80</td>
<td>45.08</td>
<td>4.76</td>
<td>0.007</td>
<td>0.997</td>
<td>0.488</td>
<td>Exp</td>
</tr>
</tbody>
</table>

Table 3.5: Parameters for the scalar field for the mandoline*

<table>
<thead>
<tr>
<th>Run</th>
<th>Grid</th>
<th>$\Lambda_s$</th>
<th>$Pr$</th>
<th>$\frac{dT}{dy}$</th>
<th>$k_s$</th>
<th>$\bar{\phi}^2$</th>
<th>Spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>128</td>
<td>0.4246</td>
<td>0.7</td>
<td>6.2832</td>
<td>4.0</td>
<td>0.166</td>
<td>Gauss</td>
</tr>
<tr>
<td>D2</td>
<td>256</td>
<td>0.4246</td>
<td>0.7</td>
<td>6.2832</td>
<td>4.0</td>
<td>0.166</td>
<td>Gauss</td>
</tr>
<tr>
<td>D3</td>
<td>128</td>
<td>0.425</td>
<td>0.7</td>
<td>6.2832</td>
<td>4.0</td>
<td>0.166</td>
<td>Gauss</td>
</tr>
<tr>
<td>D4</td>
<td>128</td>
<td>0.425</td>
<td>0.7</td>
<td>6.2832</td>
<td>4.0</td>
<td>0.664</td>
<td>Gauss</td>
</tr>
<tr>
<td>D5</td>
<td>128</td>
<td>0.806</td>
<td>0.7</td>
<td>6.2832</td>
<td>2.0</td>
<td>0.689</td>
<td>Gauss</td>
</tr>
<tr>
<td>D6</td>
<td>128</td>
<td>0.211</td>
<td>0.7</td>
<td>6.2832</td>
<td>8.0</td>
<td>0.661</td>
<td>Gauss</td>
</tr>
<tr>
<td>D7</td>
<td>80</td>
<td>0.33</td>
<td>0.7</td>
<td>6.2832</td>
<td>4.76</td>
<td>0.994</td>
<td>Exp</td>
</tr>
<tr>
<td>D8</td>
<td>80</td>
<td>0.478</td>
<td>0.7</td>
<td>6.2832</td>
<td>3.17</td>
<td>1.003</td>
<td>Exp</td>
</tr>
</tbody>
</table>

*Run numbers correspond to those in Table 3.4.
4. RESULTS AND DISCUSSION

Simulations for the problem of passive scalar transport with a uniform mean scalar gradient have been made to study the effect of the scalar gradient on the transport of the scalar in a decaying, isotropic turbulent field. Different values of initial turbulent Reynolds number and different initial energy spectra, such as Gaussian or exponential, have been used to study the effect of initial conditions on the evolution and asymptotic state of the system. Pre-simulations were made in some cases so as to ensure that the velocity field is well developed.

For the “toaster” and “mandoline” configurations, the evolution of the scalar transport correlation coefficient $\rho_{\theta\theta}$ was examined. This quantity gives useful information on the correlation of the velocity and scalar field. The eddy diffusivity ratio $\epsilon_H/\alpha$ was also calculated for those cases. The evolution of integral and Taylor microscales for both velocity and scalar fields was also studied for the case of isotropic scalar turbulence. The integral length scale for the velocity field is evaluated as

$$\Lambda_f = \frac{\pi}{2\sqrt{2}} \int_0^\infty \frac{E(k,t)}{k} dk$$

where $E(k,t)$ is the 3-d energy spectrum function. The integral length scale for the scalar field is evaluated as

$$\Lambda_\theta = \frac{\pi}{2\sqrt{2}} \int_0^\infty \frac{E_\theta(k,t)}{k} dk$$

where $E_\theta(k,t)$ is the 3-d scalar energy spectrum function. The Taylor microscale for the
velocity field is defined as

\[ \lambda_y = \left( \frac{\varepsilon}{15 \nu u'^2} \right)^{-1/2} \]

where \( \varepsilon \) is the energy-dissipation rate. The Taylor microscale for the scalar field is defined as

\[ \lambda_\theta = \left( \frac{\varepsilon_\theta}{6 D \theta'^2} \right)^{-1/2} \]

where \( \varepsilon_\theta \) is the scalar energy-dissipation rate defined as \( -d\theta^2/dt \) and \( D \) is the molecular diffusivity of the scalar.

The behavior of quantities such as turbulence Reynolds number, kinetic energy, scalar variance, and dissipation were also studied for the different cases. Real space derivative skewnesses, such as the velocity derivative skewness, \( S_u \), defined as

\[ S_u = \left( \frac{\partial u_1}{\partial x_1} \right)^3 \left( \frac{\partial u_1}{\partial x_1} \right)^2 \]

the mixed derivative skewness, \( S_{u\theta} \), defined as

\[ S_{u\theta} = \left( \frac{\partial u_1}{\partial x_1} \right) \left( \frac{\partial \theta}{\partial x_1} \right)^2 \left( \frac{\partial u_1}{\partial x_1} \right)^{0.5} \left( \frac{\partial \theta}{\partial x_1} \right)^2 \]

and the scalar derivative skewness, \( S_\theta \), defined as

\[ S_\theta = \left( \frac{\partial \theta}{\partial x_1} \right)^3 \left( \frac{\partial \theta}{\partial x_1} \right)^2 \]

were calculated from their spectral representations given by Kerr (equations (22) and (23), Kerr (1985)).

Comparisons of DNS results with predictions of the DIA were made for the conditions of the experiments of Sirivat and Warhaft. Exact comparisons with experiments were not possible due to difficulties associated with matching the numerical initial conditions to the experimental conditions. However, DNS results of the asymptotic and qualitative evolutionary behavior of the various quantities were compared with experimental results and direct comparisons of DNS and DIA results were also made.
4.1 Isotropic turbulent scalar

For the case of isotropic scalar turbulence, the evolution of turbulence Reynolds number, kinetic energy and scalar variance were studied along with the evolution of dissipation, skewness, integral and Taylor microscales for both velocity and scalar fields. The effect of different initial spectra and different initial length scales on those quantities was also examined. In the figures, the curves for scalars 1, 2 and 3 refer to three different scalar spectra, corresponding to initial length scale ratios of 1, 0.5, and 1.5 respectively.

Figure 4.1 shows the time evolution of Reynolds number for runs B1 and B4, corresponding to two different initial energy spectra. Figure 4.2 shows the time evolution of the velocity and scalar derivative skewness obtained from direct numerical simulations for runs B1, B3 and B3. The results show that the velocity derivative skewness approaches -0.48 asymptotically for both initially exponential and initially Gaussian spectra and this agrees with the results of Kerr (1985). The asymptotic value of the scalar derivative skewness was about -0.2 for both initial spectra and for different initial length scales. Table 4.1 shows the asymptotic values of skewnesses for the different initial conditions. It is seen that the longtime or asymptotic behavior of the velocity derivative and scalar derivative skewness is independent of the initial spectra used, and the scalar derivative skewness is also independent of the initial length scales.

Since there is no imposed scalar gradient, the scalar variance decays with time. Figure 4.3 shows the time evolution of the scalar variance for different initial length scale ratios. The integral length scales for the velocity and scalar fields decrease a little initially and then increase with time, as is seen in Figure 4.4. The increase is more pronounced for runs B1, B2 and B3 than for the DIA as shown in Figure 4.4. Figure 4.5 shows that the evolution of the Taylor microscales shows a similar behavior. Figure 4.6 shows the evolution of the ratio of integral length scales for different initial length scale ratios. Figure 4.6 shows
Table 4.1: Asymptotic values of derivative skewnesses for isotropic scalar and velocity fields

<table>
<thead>
<tr>
<th>Initial spectra</th>
<th>Skewness</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>velocity, $S_u$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exponential</td>
<td>-0.484</td>
<td>-0.23</td>
<td>-0.21</td>
<td>-0.24</td>
</tr>
<tr>
<td>Gaussian</td>
<td>-0.483</td>
<td>-0.22</td>
<td>-0.21</td>
<td>-0.23</td>
</tr>
<tr>
<td>scalar, $S_\phi$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

results from a DNS calculation and DIA results are compared with it. The figures show that the length scale ratio changes initially, but soon becomes almost a constant. Table 4.2 shows the initial and asymptotic values of the integral length scale ratios for different initial spectra and different initial length scale ratios and that shows that the eventual state of the system is independent of the initial spectra but depends on the initial length scale ratio. Figure 4.7 shows the time behavior of scalar dissipation for the different initial length scale ratios and indicates that all three systems seem to be tending towards a similar state almost independent of the initial length scale ratio.

4.2 The “toaster” experiment

The conditions for the toaster experiment are shown in Table 3.3 in the previous chapter. The scalar field was set to zero initially and then allowed to develop from the imposed scalar gradient.

The decay of the kinetic energy for simulation runs C1, C2 and C3 is shown in Fig-
Table 4.2: Asymptotic values of integral length scale ratio for isotropic velocity and scalar fields

<table>
<thead>
<tr>
<th>Spectra</th>
<th>Initial</th>
<th>Final</th>
<th>Initial</th>
<th>Final</th>
<th>Initial</th>
<th>Final</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exponential (DNS)</td>
<td>0.98</td>
<td>0.91</td>
<td>0.52</td>
<td>0.77</td>
<td>1.4</td>
<td>1.04</td>
</tr>
<tr>
<td>Gaussian (DNS)</td>
<td>1.00</td>
<td>0.95</td>
<td>0.50</td>
<td>0.78</td>
<td>1.50</td>
<td>1.19</td>
</tr>
<tr>
<td>Gaussian (DIA)</td>
<td>1.00</td>
<td>0.76</td>
<td>0.50</td>
<td>0.59</td>
<td>1.50</td>
<td>0.99</td>
</tr>
</tbody>
</table>

The scalar variance was found to increase almost linearly with time for all the three runs, C1, C2 and C3, though the initial turbulence Reynolds number was different for the three cases, as is evident from Figure 4.9. Figure 4.10 shows that the value of the scalar transport correlation coefficient $\rho_{\|\theta}$ was initially $-1$, and it approached $-0.67$, $-0.69$ and $-0.73$ asymptotically for runs C1, C2, and C3 respectively. These results are in very good agreement with the value $\rho_{\|\theta} = -0.68$ reported by Sirivat and Warhaft. This agreement shows that the temperature fluctuations are highly correlated with the velocity fluctuations to start with, but the asymptotic time behavior is independent of the details of the velocity field. Figure 4.11 shows the evolution of the velocity and scalar integral length scales for run C2, and Figure 4.12, their ratio ($\Lambda_\theta / \Lambda_c$). The ratio increased from 0.67 to 0.86 for runs C1 and C2 and to 0.84 for run C3. This also is in very good agreement with the asymptotic value of 0.85 obtained in laboratory experiments and shows that the system evolves to an equilibrium state which is rather insensitive to the initial conditions (initial $R_\lambda$ in this case). Figure 4.13 shows the time evolution of the eddy diffusivity ratio $\epsilon_H/\alpha$ for runs C1,
C2 and C3. The diffusivity ratio, \( \epsilon_H/\alpha \), approached 13.7 asymptotically for run C1, 12.7 for run C2 and 10.1 for run C3. These results agree well with the experimental result of 18 reported by Sirivat and Warhaft. (Refer to Table 2.1 for a comparison with results available in literature.)

Some comparisons of results obtained from the DNS and from the DIA using one and two spherical harmonics, have been made for the “toaster” experiment for the conditions of run C4. The evolution of the ratio of the integral length scales, is compared in Figure 4.14 and the correlation coefficient \( \rho_{\epsilon\theta} \) in Figure 4.15. The asymptotic value of \( \rho_{\epsilon\theta} \) for the DNS calculation is \(-0.74\), that for the DIA calculation with one spherical harmonic is \(-0.84\), and that with two spherical harmonics is \(-0.81\). The evolution of the eddy diffusivity ratio is shown in Figure 4.16. It is observed that the predictions of the DIA calculation with two spherical harmonics is closer to the DNS results than the predictions with a single spherical harmonic.

### 4.3 The “mandoline” experiment

In this case, the velocity field and scalar field were initially perfectly uncorrelated, that is, \( \rho_{\epsilon\theta} = 0 \) initially. An exponential or Gaussian spectrum was used for the scalar field and the peak wave-number for the scalar spectra was changed so as to change the initial scalar length scale corresponding to different mandoline configurations.

The evolution of turbulent Reynolds number for run D4 is shown in Figure 4.17 and the evolution of kinetic energy for runs D3 and D4 is shown in Figure 4.18. Real space derivative skewnesses were calculated for two different initial Reynolds number, 83 and 65. The velocity derivative skewness, \( S_u \), approaches \(-0.49\), the mixed derivative skewness, \( S_{u\theta} \), approaches \(-0.26\), and the scalar derivative skewness, \( S_\theta \), approaches \(-0.31\) asymptotically for both values of initial \( R_\lambda \). The evolution of \( S_u \) for runs D3 and D4 is shown in Figure 4.19.
and the evolution of $S_\theta$ is shown in Figure 4.20. The value of the velocity derivative skewness agrees with the results reported by Kerr (1985). The scalar variance was found to increase almost linearly with time for the runs D3, D4, D5 and D6 as is shown in Figure 4.21. The initial velocity field for runs D4, D5 and D6 were the same, but the initial scalar fields were different having different initial length scales. Run D3 and D4 had the same initial scalar field, but the initial turbulence Reynolds number was higher for D3. Figure 4.22 shows that the scalar transport correlation coefficient $\rho_{\nu\theta}$ was 0 initially and approached $-0.73$ for runs D3, D4 and D5 and $-0.74$ for run D6. These results agree well with Sirivat and Warhaft's reported value of about $-0.7$. The results also show that the temperature and velocity fluctuations are highly uncorrelated initially but that the correlation builds up and the asymptotic time behavior is independent of the details of the velocity field. Figure 4.23 shows that the integral length scale ratio $(A_\theta/A_\nu)$ approached a value of 0.82 asymptotically for all the runs. When the configuration of the "mandoline" was changed, that is, the initial length scale ratio was changed, the ratio still approaches a value between 0.81 and 0.82 asymptotically, which compares reasonably well with the experimental asymptotic length scale ratio of 0.9. This confirms the experimental findings that the asymptotic state of the system is independent of initial length scale ratios. The eddy diffusivity ratio $\epsilon_H/\alpha (= \overline{\nu^\theta \text{Pr}/\beta \nu})$ increased to about 15 and then decreased to a value of about 9.3 for all of the runs as shown in Figure 4.24.

The DNS results for run D7 were compared with the DIA calculations using one or two spherical harmonics. The evolution of kinetic energy is compared in Figure 4.25, and the evolution of the velocity derivative skewness is compared in Figure 4.26. The kinetic energy values and velocity derivative skewness values for the DIA calculations with one harmonic and two harmonics are identical, since the velocity fields are identical for the two cases. Figure 4.27 compares the evolution of length scale ratios for the DIA and DNS calculations. The DIA calculation with two harmonics overpredicts the length scale ratio but reaches an
asymptote, whereas the DIA calculation with a single harmonic increases and then drops off. The evolution of the scalar transport correlation coefficient, is shown in Figure 4.28; the DIA calculation with two harmonics is closer to the DNS predictions than for a single harmonic. The same behavior is observed in the evolution of the eddy diffusivity ratio, shown in Figure 4.29. Figure 4.30 compares the time evolution of $\rho_{u\theta}$ for the mandoline and the toaster cases as predicted by DNS. Figure 4.31 compares the DIA and DNS predictions of the time evolution of $\rho_{u\theta}$ for mandoline and the toaster cases. The figures shows that the system evolves to a similar asymptotic state independent of the initial conditions. Also, the predictions of the DIA with two harmonics agree better with the DNS calculations than the single harmonic.
Figure 4.1: Evolution of Reynolds number for decaying isotropic turbulent scalar field for DNS runs B1 and B4
Figure 4.2: Evolution of velocity and scalar derivative skewness for decaying isotropic turbulent scalar field for DNS runs B1, B2 and B3 - scalars 1, 2 and 3 refer to initial length scale ratios of 1, 0.5 and 1.5 respectively.
Figure 4.3: Evolution of scalar variance for isotropic turbulent scalar for DNS runs B1, B2 and B3 (a) linear scale (b) log-log scale
Figure 4.3: Evolution of scalar variance for isotropic turbulent scalar for DNS runs B1, B2 and B3 (a) linear scale (b) log-log scale
Figure 4.4: Evolution of integral velocity and scalar length scales for decaying isotropic turbulent scalar field - DNS and DIA with initial Gaussian spectra
Figure 4.5: Evolution of Taylor velocity and scalar length scales for decaying isotropic turbulent scalar field – DNS and DIA with initial Gaussian spectra.
Figure 4.6: Evolution of length scale ratios for decaying isotropic turbulent scalar field – DNS and DIA with initial Gaussian spectra
Figure 4.7: Evolution of velocity and scalar dissipation for decaying isotropic turbulent scalar field for DNS runs B1, B2, B3
Figure 4.8: Evolution of kinetic energy for the toaster for DNS runs C1, C2 and C3
Figure 4.9: Evolution of scalar variance for the toaster for DNS runs C1, C2 and C3 (a) linear scale (b) log-log scale
Figure 4.9: Evolution of scalar variance for the toaster for DNS runs C1, C2 and C3 (a) linear scale (b) log-log scale
Figure 4.10: Evolution of the scalar transport correlation coefficient $\rho_{s}\theta$ for the toaster for DNS runs C1, C2 and C3.
Figure 4.11: Evolution of the integral velocity and scalar length scales for the toaster for DNS run C2.
Figure 4.12: Evolution of the integral length scale ratios for the toaster for runs C1, C2 and C3.
Figure 4.13: Evolution of the eddy diffusivity ratio $\epsilon_H/\alpha$ for the toaster for DNS runs C1, C2 and C3
Figure 4.14: Comparison of evolution of the length scale ratios for the toaster for conditions of DNS run C4
Figure 4.15: Comparison of the evolution of the scalar transport correlation coefficient $\rho_{u\theta}$ for the toaster for conditions of DNS run C4
Figure 4.16: Comparison of the evolution of the eddy diffusivity ratio $\epsilon_H/\alpha$ for the toaster for conditions of DNS run C4.
Figure 4.17: Evolution of turbulent Reynolds number for the mandoline for DNS run D4
Figure 4.18: Evolution of kinetic energy for the mandoline for DNS runs D3 and D4
Figure 4.19: Evolution of velocity derivative skewness for the mandoline for DNS runs D3 and D4
Figure 4.20: Evolution of scalar derivative skewness for the mandoline for DNS runs D3 and D4.
Figure 4.21: Evolution of scalar variance for the mandoline for DNS runs D3, D4, D5 and D6 (a) linear scale (b) log-log scale
Figure 4.21: Evolution of scalar variance for the mandoline for DNS runs D3, D4, D5 and D6 (a) linear scale (b) log-log scale
Figure 4.22: Evolution of scalar transport correlation coefficient $\rho_{u\theta}$ for the manifold for DNS runs D3, D4, D5 and D6.
Figure 4.23: Evolution of ratio of integral length scales for the mandoline for different mandoline configurations, DNS runs D4, D5 and D6
Figure 4.24: Evolution of eddy diffusivity ratio for the mandoline for different mandoline configurations for DNS runs D3, D4, D5 and D6
Figure 4.25: Comparison of evolution of kinetic energy for the mandoline for conditions of DNS run D7
Figure 4.26: Comparison of evolution of the velocity derivative skewness for the mandoline for conditions of DNS run D7
Figure 4.27: Comparison of evolution of the length scale ratios for the mandoline for conditions of DNS run D7
Figure 4.28: Comparison of the evolution of the scalar transport correlation coefficient for the mandoline for conditions of D7
Figure 4.29: Comparison of the evolution of the eddy diffusivity ratio $\epsilon_H/\epsilon$ for the mandoline for conditions of DNS run D7
Figure 4.30: Comparison of the evolution of the correlation coefficient $\rho_{\omega \theta}$ for the toaster and mandoline
Figure 4.31: Comparison of the evolution of the correlation coefficient $\rho_{\Theta\Theta}$ for the toaster and mandoline, DIA and DNS
5. CONCLUSIONS

The transport of a passive scalar in a homogeneous turbulent flow field has been studied for cases with and without a mean scalar gradient. The system evolves to an asymptotic state, almost independent of the initial conditions, when a scalar gradient is present in agreement with the experimental findings of Sirivat and Warhaft (1983). In the case of a decaying isotropic turbulent scalar, the system evolved from its initial state, but the extent of the evolution was not as pronounced as in the case when a scalar gradient is present. For example, in the presence of a scalar gradient, the ratio of integral length scales approaches the same value for different initial scalar spectral shapes, but for the case without a scalar gradient, the integral scale ratios approaches different values for different scalar spectra. Also, the correlation coefficient for the toaster and mandoline approach each other asymptotically. These observations agree with the laboratory experimental results of Sirivat and Warhaft. In general, very good agreement of the asymptotic behavior of quantities between numerical and physical experiments was obtained. But it was difficult, however, to compare the evolution of the fields for the laboratory experiments and numerical simulations, since the initial fields strongly affect their own behavior over time, and it was difficult to match the numerical initial conditions to the experimental velocity, scalar, and scalar transport fields immediately downstream of the turbulence generating grid. The DIA and DNS results also show fairly good agreement, at least for the correlation coefficient. DIA calculations with two spherical harmonics seem to agree better with DNS results than for calculations with a single spherical harmonic. This suggests that for the strength of the
scalar gradient and the resulting anisotropy of the scalar field requires additional spherical harmonics in the DIA equations.
6. REFERENCES


SUMMARY

In this dissertation, chemical selectivity in turbulent flow with complex chemistry, and the transport of a passive scalar in turbulent flow with a uniform mean scalar gradient, is examined. Direct numerical simulations of moderate Reynolds number flow were used in both studies. The first part deals with turbulent reacting flows and the second part addresses the problem of turbulent heat transfer.

In Part I, the effect of various physical parameters on the product distribution of a series-parallel reaction pair was determined. It was found that the degree of homogenization of reactants and products is crucial in determining the product distribution. Simulations showed that any mechanism sustaining segregation of reactants depresses the formation of intermediate $R$, whereas any mechanism causing homogenization favors the formation of $R$. Simple first-order closure theories for the covariance of concentration fluctuations were also examined. The mean values of reactants and products, as predicted by the various models, were compared with the values obtained from the direct numerical simulations. The performance of the first-order closures was, in general, not satisfactory, but the closures work reasonably well for very specific conditions.

In Part II, the transport of a passive scalar by a uniform mean scalar gradient was studied. The results of direct numerical simulations were compared with results from the direct interaction approximation theory (Kraichnan, 1964) and also with laboratory experiments of Sirivat and Warhaft (1983). Also, the long time behavior of various statistical quantities is independent of the initial conditions when there is a uniform scalar gradient.
imposed on the flow.
REFERENCES


ACKNOWLEDGEMENTS

I would like to thank my major professor, Dr. James C. Hill, for his kind letters which influenced my decision to come to Iowa State and for his support, guidance and advice during my studies here. I really appreciate the understanding he has shown at all times. I would also like to thank the members of my program of study committee, Dr. William H. Abraham, Dr. John M. Eggebrecht, Dr. Richard H. Pletcher, and Dr. Lennox N. Wilson. I am particularly grateful to the Department of Chemical Engineering for providing me with financial assistance for my graduate studies and Dr. Richard C. Seagrave for his kind and friendly behavior. I would like to thank Dr. Andy D. Leonard for his help with the simulation code and Robert C. Sanderson for his help with the second part of this work. I would also like to thank Anindya Roy, Dana Haugli and Günther Peters for their helpful advice and unfailing friendship.

I would like to thank the National Center for Supercomputing Applications, Urbana-Champaign, Illinois for providing us with the computational facilities needed for this work. Thanks are due to Prof. Robert S. Brodkey for providing us with the opportunity to carry out some preliminary runs at the Ohio Supercomputer Center, Columbus, Ohio to test feasibility of a future collaborative work. The computational resources provided by IBM, Palo Alto Scientific Center, California is gratefully acknowledged and thanks are due to Dr. L.J. Shieh of the IBM Palo Alto Research Center for his help. I would like to acknowledge the support of Hitachi Data Systems for computer time on their EX V80 computer in Santa Clara, California and for the assistance provided by Dr. James Hoekstra from the
ISU Computation Center funded by grant from Hitachi Data Systems under the direction of Prof. Glenn Luecke of ISU.

I would like to thank my parents, Prof. Nirmal B. Chakrabarti and Mrs. Jharna Chakrabarti, for their constant encouragement all through my educational career and for their help and support all my life. I would like to thank my sister Dr. Chaitali Chakrabarti for being my role model. I would also like to thank all my friends for their support during my stay here. I would especially like to thank Sreela Datta for her patience and understanding and for her help with the figures in the thesis. And finally I would like to thank my husband, Dr. Shuvra Das, for his care and concern and for all the help and support he has given me over the years and for his help with drawing, cutting and pasting whenever required.
APPENDIX A: BACKGROUND ON TURBULENCE

Turbulence prevails in almost all flow situations that occur naturally, or in industries. This chapter provides an introduction to the field of turbulence. A qualitative description of turbulence and brief explanations of commonly encountered terms and concepts will be given. A summary of the different approaches to the turbulence problem will then be presented.

The physics of turbulence

Characteristics of turbulence

Turbulent flows are characterized by inherent disorder, enhanced mixing, and the presence of vorticity. These characteristics distinguish turbulence from wave motion and two-dimensional flows (Hinze, 1975; Lesieur, 1987; Panton, 1984; Shapiro, 1961; Stewart, 1969; Lumley and Tennekes, 1972).

Disorder: A turbulent flow is unpredictable in detail, i.e., the characteristics are irreproducible in its entire detail even if all the experimental conditions are reproduced in the greatest detail. But averages over suitably large intervals of space or time seem to be well-defined and stable.

Mixing: Turbulent flow is able to mix transported quantities (like heat, momentum, dyes etc.) much more quickly than if only molecular diffusion were involved.
Vorticity: Vorticity is distributed continuously but irregularly in all three dimensions in a turbulent flow.

A physical model of turbulence

Voke and Collins (1983) have described the turbulent flow of a viscous fluid as one of the most complex and beautiful macroscopic phenomena found in nature. The flow is essentially four-dimensional, involving the time-dependent interchange of energy and momentum between vortices of different sizes and lifetimes, oriented with respect to each other in three-dimensional space.

In turbulent flow the motion is made of an array of eddies of widely different sizes. The largest eddy sizes are on the order of the dimensions of the expanse of turbulent motion and the smallest are on the order of the dimension across which molecular viscosity can effectively transport momentum and thus shear out velocity gradients. The large eddies contain most of the energy, perform most of the turbulent transport, and interact most with the overall mean rate of strain of the flow. The small eddies are more isotropic, random, and dissipate most energy. Thus many of the important practical properties of the flow are determined by the large eddies, while the smaller ones play a more passive role of removing kinetic energy from the large scales and dissipating it. This wide range of eddy sizes is generated by neighboring-size eddies successively becoming eddies of the next order smaller in size by a mechanism of vortex stretching. The process occurs in a cascading fashion with eddies breaking down into smaller eddies and the energy of the over-all flow (i.e., the mean flow kinetic energy) being transferred to smaller and smaller scales, the smallest scale being reached when the eddies lose energy by the direct action of viscous stresses (Frost and Bitte, 1977).

The following descriptions of vortex stretching and the energy cascade have been adapted from Frost and Bitte (1977), Voke and Collins (1983), Corrsin (1961), Stewart
Vortex stretching: A fluid element under the influence of a linear strain will be stretched in the direction of the strain and its cross-section in a plane perpendicular to the strain will become smaller. In the case of a vortex element, the vortex or eddy in the direction of the strain becomes smaller in cross-section while that normal to the rate of strain becomes larger. The vorticity component in the direction of stretching, increases rapidly and that in the direction of compression, decreases slowly. Thus eddies are stretched at a rapid rate into smaller eddies, while their growth to larger sizes occurs at a much slower rate.

With negligible viscosity, it follows from the principle of conservation of angular momentum that the product of the vorticity and the square of radius must remain constant — or, the circulation of the vortex elements must remain constant in the absence of viscous forces during the stretching process. Thus the kinetic energy of rotation increases at the expense of the kinetic energy of the velocity component that does the stretching. Therefore an extension in one direction decreases the length scales and increases the velocity components in the other two directions, which stretches other elements of fluid with vorticity components in these directions. Thus an increasing strain rate field is generated, which is experienced by another vortex causing it to stretch. As it stretches, a new strain field is created, stretching in turn other vortices, and so on. This process continues with the length scale of the augmented motion getting smaller at each stage. Thus, qualitatively, initial stretching in one direction results in progressively more stretching in all three directions. Figure 6.1, adapted from Frost and Bitte (1977), illustrates these concepts. Consequently the orienting effect of the mean rate of strain is weakened with each stretching or breaking down of eddies. The small-scale eddies in turbulence thus tend toward a universal structure that is homogenous and isotropic despite the fact that the mean flow and large-scale disturbances in any real turbulent flow are non-homogenous and anisotropic (Frost and Bitte,
Energy cascade: A typical turbulent flow has a characteristic spectral dynamic behavior. The largest "eddy" of all is the gross mean flow whose energy arises from imposed shear, pressure gradients, buoyancy or other body forces, constrained by boundary conditions. The mean flow loses energy through vortex formation or other mechanisms to eddies of the next smaller size — these are the largest true turbulent eddies. They in turn lose energy to smaller structures through vortex-stretching, or tilting. The energy transfer between eddies occurs as the smaller eddies are exposed to the strain-rate field of the larger eddies. The straining increases the vorticity of the smaller eddies with a consequent increase in their energy at the expense of the energy of the larger eddies — thus a flux of energy from larger to smaller eddies takes place. The energy increase of smaller eddies during vortex stretching comes from work performed by the strain rate. The energy cascade may continue through many orders of magnitude in a high Reynolds number flow. The transfer is overwhelmingly in the direction from lower wave numbers to higher wave numbers. Thus eddies that benefit most during energy transfer from the eddies higher in scale are also immediately neighboring eddies. Molecular viscosity comes to play an increasingly important role at the higher wave numbers, until eventually a scale is reached where all the energy extracted from larger eddies is dissipated by friction, with none left to pass on down the cascade to smaller scales. At this point the energy spectrum starts to fall increasingly rapidly towards zero. The cascade of energy of the turbulent motion thus takes place predominantly from neighboring eddies to neighboring eddies continuing to smaller and smaller scales (larger and larger velocity gradients) until viscosity finally dissipates the energy received by the smaller eddies (Frost and Bitte, 1977, Voke and Collins, 1983).

Length scales: Production of turbulent energy from the mean flow takes place at low wave numbers, so that large eddies contain most of the energy. Dissipation takes place predominantly at high wave numbers, where small eddies are destroyed. These two scales
are characterized by two length parameters: (i) the integral length scale of the velocity correlations, \( \Lambda_f \), which is determined primarily by the geometry that encloses the flow or produces the turbulence, and which limits the size of possible eddies and is defined as

\[
\Lambda_f = \frac{\pi}{2u^*} \int_0^\infty \frac{E(k,t)}{k} dk,
\]

where \( E(k,t) \) is the 3-d energy spectrum, and \( u^* \) is the turbulence intensity, (ii) the Kolmogorov length scale, \( \eta \), which characterizes the size of the eddies at which inertia balances dissipation. The Kolmogorov length scale simply adjusts itself in each flow so that the amount of energy passing down the cascade may be dissipated. It is defined as

\[
\eta = \left( \frac{\nu^3}{\varepsilon} \right)^{1/4}
\]

where \( \nu \) is the kinematic viscosity, and \( \varepsilon \) is the rate of dissipation of energy (per unit mass). Another length scale commonly used is the (iii) Taylor microscale

\[
\lambda_g = \left( \frac{\varepsilon}{15\nu u'^2} \right)^{-1/2},
\]

which is representative of the average size of a dissipating structure.

**Approaches to the turbulence problem**

Chapman and Tobak (1986), in their rather personal perspective of the scientific study of turbulence, claim that there have been three distinct movements (with some overlap) since Reynolds' (1883) observations of transition in pipe flow and that each movement can be characterized by a definite point of view (Chapman and Tobak, 1986).

1. The statistical movement is the earliest movement; it started with the work of Reynolds in 1883 and is theoretical in character;

2. The structural movement started around the late 1950s and is predominantly observational;
3. The deterministic movement is the most recent; it started with the work of Lorenz (1963) and is based upon the philosophy of "order within chaos".

A brief description of these movements follows.

**Statistical movement:** The statistical view of turbulence emphasizes on observations of the flow in terms of means and averages. The governing equations may be averaged but the non-linearities give rise to Reynolds-stress terms consisting of averages of products of perturbation quantities. The extension required to complete the modeling has to involve the next higher moment, requiring in turn an even higher moment, and so forth, leading to the closure problem. The unknown terms at some level in the hierarchy has to be modeled. An example of a particularly successful result of theoretical analysis within the statistical framework is Kolmogorov's "five-thirds law" formulated for the statistical regime consisting of "locally isotropic turbulence". However the success of the theory is limited because it ignores the regime of scales where most of the energy resides in most turbulent flows.

The approaches used in the statistical movement are:

(a) **Phenomenological theories:** These included, among others, Boussinesq's eddy viscosity theory, Prandtl's mixing-Length theory, Taylor's vorticity transport theory, von Karman's similarity hypothesis, etc. These theories, based on one mechanistic assumption or the other, were adequate for the prediction of the mean velocity profile – necessary for solving many practical problems – but could not be of much help in understanding the true mechanism of turbulent flow. Besides, the eddy-viscosity and mixing length ideas have serious shortcomings too. For example, the conditions justifying the mixing-length idea rest on the assumptions of kinetic theory – small units travelling relatively long distances between interactions – and these conditions are not completely fulfilled by the properties of turbulent eddies.
(b) **Statistical approach**: Statistical methods attempt to predict the behavior of quantities such as moments or probability distributions. The moment approach attempts to explain the dynamics of the flow in terms of the averaged flow characteristics. A method is classified as a probability method if equations for the probability distributions of velocity and scalar fields are solved. The probability methods are better suited for reacting turbulent flows. A review of statistical methods for reacting turbulent flows is given by Hill (1976).

Some of the conventional approaches used in solving turbulence problems are: (i) eddy viscosity (or eddy diffusivity) model, (ii) algebraic stress model, (iii) differential stress model (Launer, 1985). Other approaches include (i) truncation of higher moments, (ii) direct interaction approximation or DIA (Kraichnan, 1959), (iii) Lagrangian history DIA (Kraichnan, 1965), (iv) test field model (Kraichnan, 1971) (v) eddy-damped quasi normal Markovianized model or (EDQNM) (Orszag, 1970), (vi) probability distribution functions (PDF), (vii) renormalization group theory or RNG (Siggia, 1981), (viii) mapping closures etc.

The principal shortcoming of the statistical approach is the lack of imagery or structure. The theory did not originally incorporate knowledge about physical processes ("structures") that are understood better now.

**Structural movement**: This movement is dominated by observations. Observations include experimental observations, and observations of computer simulations.

(a) **Experimental observations**: There have been many observations regarding evidence of intermittency, instabilities in transitional flow and structures that occur in turbulent flows. Some outstanding examples are: Tollmien-Schlichting waves as evidence of initial instability in a transitional flow (Schubauer and Skramstad, 1948), Batchelor and Townsend’s (1949) observations regarding nonuniformities of vorticity in homogenous isotropic turbulent flows, Emmons (1951) turbulent spot revealing that structure in turbulence, structures in wall-bounded shear flows, observed by Kline and Runstadler (1959)

(b) **Numerical observations:** The use of computer simulations has a deterministic character since the computations are based on deterministic equations. Some of the numerical methods used in solving turbulence problems are: (i) finite-difference methods, (ii) finite-element methods, (iii) spectral methods, (iv) large eddy simulation and (v) random vortex methods. Observations of computer simulations of turbulent flow have contributed a lot to the structural movement. Examples include: Rogallo (1981) for homogenous, isotropic turbulence, Moin and Kim (1982) for turbulent channel flow, Leonard and Hill (1988, 1989, 1991) for turbulent flow with chemical reaction, Ferziger for incompressible turbulent flow, Eswaran and Pope for turbulent mixing of passive scalars and chemically reacting scalars in homogenous isotropic turbulent flows, Borghi for turbulent flow with chemical reaction.

The principal contribution of the structural movement has been the recognition of the presence and importance of structures in turbulence. Despite its promise, there are two main shortcomings of the structural movement. The first is that no theoretical ideas have emerged that could be translated into formal mathematical models; the other is the jungle of observational detail lacking the ordering hand of theory. A consistent, overall theory has been lacking which has the possibility of assimilating the random and deterministic elements into a single viewpoint allowing, e.g. deterministic chaos. The main criticism the structural movement faces, is precisely the opposite of that of the statistical movement: in place of theory without structure, it has been structure without theory.

**Deterministic movement:** The best descriptive title for this theory is "nonlinear dynamical systems". The recent developments which contributed to this deterministic movement are: (i) bifurcation theory, (ii) strange attractors (Ruelle and Takens, 1971), and (iii) fractals (Mandelbrot, 1982). These beliefs are supported by an ever increasing number of scientists who study turbulence from a purely deterministic point of view, by studying ei-
ther the behavior of dynamical systems, or the stability of flows in various situations. A framework for the description of fully-developed turbulent flows has not arisen, except for the notion that the fractal dimension of dissipative structures is assumed to represent the total (reduced) number of degrees of freedom in the system.
Figure 6.1: Schematic diagram of vortex stretching showing the compression and stretching of fluid elements (Frost and Bitte, 1977)
APPENDIX B: LITERATURE REVIEW ON MIXING AND REACTION

Mixing and chemical reaction

It is desirable to be able to design mixers and chemical reactors from a knowledge of basic hydrodynamic parameters, geometry, and molecular properties (Patterson, 1975). Physical parameters such as viscosity, density, diffusivity, and reaction rate constants are usually not affected by the mixing process. The hydrodynamic parameters and geometry determine the intensity of turbulence, which in turn determines the rate of mixing. The rate of mixing often determines the conversion within a reactor. Hence, it is important to understand mixing and the interaction of mixing, chemical reaction and turbulence.

Mixing

Villermaux (1982, 1988) describes the stages in the mixing process as: distribution of one fluid in the other and making the average composition uniform without decreasing local concentration variations, reduction of size of the regions of uniform composition and increase of contact areas between regions of different composition, and mixing by molecular diffusion. The mixing of two substances depends on the ability of both the components to diffuse into each other, as characterized by the diffusivity \( D \). The overall rate of diffusion can be increased by increasing the concentration gradient as well as by increasing the "exposed"
Dispersion is the mechanism by which the solute fluid is broken up into smaller droplets or parts, and it can only go so far in reducing the sample volume size in an effort to make a solution homogenous. After that it is only diffusion which can bring about homogeneity at the molecular levels. Dispersion, on this basis, can be said to be able to make a solution homogenous at larger scales of observation; while homogeneity at smaller scales of observation is the result of diffusion.

The case of no mixing at the molecular level is called macromixing (Patterson, 1975, 1985). Macromixing implies that fluid elements of a scale orders of magnitude larger than the molecular scale may be “mixed” with one another, but no diffusion takes place between them. Macromixing is thus a consequence of convective diffusion and reflects large scale fluid motions. The case of complete mixing to the molecular level is called micromixing. Micromixing implies that elements of fluid in proximity become completely mixed to molecular scale. Diffusive mixing is the controlling mechanism in fluid elements whose size is less than or equal to Kolmogorov’s velocity microscale, i.e. within the smallest eddies in the viscous subrange. According to Bourne, micromixing is a complex sequence of events involving the reduction of size of large, unmixed eddies, small-scale viscous convective engulfment and deformation and molecular diffusion in the deforming fluid elements (Baldyga and Bourne, 1984b; Baldyga and Rohani, 1987a,b).

Macromixing and micromixing are old chemical engineering models based on a simple mechanism of mixing, but modern ideas of mixing can sometimes be explained in terms of this framework. They really are not separate processes but only are idealizations.

**Turbulent mixing**

One of the main characteristics of turbulence is that it enhances mixing. The Reynolds number can be perceived as an indicator of the ratio of diffusion related quantities – it can
be interpreted as an index of the ratio of turbulence time scale to a molecular time scale that would prevail in the absence of turbulence in a problem with the same length scale. At high Reynolds number, the time scale for turbulent diffusion of a substance over a given length scale is much smaller than the time scale for molecular diffusion.

As mentioned earlier, the time rate of mixing can be enhanced by either increasing the surface area of the interface between the unmixed components, or the concentration gradient driving the diffusion process, or both. The easier and more effective way is to increase the area of the interface of the unmixed components. Some mechanisms in turbulent flow which enhance mixing are listed below (Patterson, 1985, Srivastava, 1988):

1. Shear: The process of distortion (stretching in one direction and contraction in the other) of fluid elements, by shear, makes the overall process of diffusion much faster and thus enhances the time rate of mixing.

2. Elongation and vortex stretching: In turbulent flow, energy is constantly being transferred from large eddies to small ones through the process of vortex stretching. Thus thinner and longer vortex tubes are constantly being formed and dissipated. If we have a blob of dye in a turbulent flow field, some of it is likely to be trapped in a vortex tube which gets elongated and thinned. The deformation of the vortex tube containing this dye will result in an increase in the interfacial surface area as well as a reduction in the distances which the molecules must travel before mixing with the surrounding fluid, and consequently, an increase in the time rate of mixing of the dye with the bulk solution via molecular diffusion.

The process of elongation continues to distort the fluid elements to dimensions of the order of the Kolmogorov microscale and smaller. As the vortex tube is dissipated by the viscous forces, it has a much lower Reynolds number than before, and thus the time scales for transport of the dye (over a given length scale) by molecular diffusion
is smaller than transport by fluid motion. In the dissipating eddy exists a shear field which distorts the dye element. Besides, the flow has a very low Reynolds number indicating that transport by diffusion continues to dominate.

In a turbulent flow field, both the mechanisms act simultaneously, resulting in an enhanced time rate of mixing of the dye with the bulk fluid. The fluid element gets entrained in eddies and goes through the same process of mixing through elongation, shear and molecular diffusion over and over again.

3. Bulk flow and velocity gradients in bulk flow: Apart from pure shear and stretching mechanisms, there is yet a third mechanism associated with turbulent flow which helps in enhancing the time rate of mixing of two components. The presence of spatial velocity gradients in a turbulent flow field causes particles initially close together to become dispersed and separated.

While turbulent diffusion is able to reduce the scale of segregation to a considerable degree, it is ultimately upto molecular diffusion to bring about fine scale mixing. The turbulence assists in this process by dispersing the original dye spot. It also transports these blobs throughout the mixing vessel, distributing them somewhat uniformly throughout the container. It is a combination of these steps that makes way for molecular diffusion to equalize the concentration differences on smaller length scales – length scales to which turbulence alone cannot be used to achieve uniformity in concentration. As shown in Figure 6 taken from Brodkey (1975), turbulence takes us from the first column to the third column. In this column, molecular diffusion takes us from the top row to the bottom row. All in all, the combination of turbulence with molecular diffusion provides us a much better mixing in a much smaller time than would have been possible with just molecular diffusion.
Turbulent mixing and fast chemical reactions

The rate at which a reaction between A and B proceeds depends on how rapidly encounters between A and B molecules occur. Reactions which occur with every encounter are said to be diffusion controlled. In chemically controlled reactions the rate depends on the probability that an encounter will lead to chemical reaction.

Many chemical reactions are sufficiently slow compared to mixing and their rates can be determined by chemical kinetics. Reagent streams can then first be well mixed (homogenization down to the molecular scale) before significant conversion takes place, and micromixing does not need detailed consideration. For a slow reaction, turbulent mixing may not be all that important while the reaction kinetics dictate the outcome of the process. That is, it will take a longer time for the reactants to react and form the products than the time needed to mix the reactants uniformly throughout the system and so, the major part of the reaction will occur in a system which has been uniformly mixed. Some reactions are, however, fast relative to mixing e.g. neutralization, precipitation and combustion, and are characterized by steep concentration gradients on the molecular scale, which ensure that the rate of reagent diffusion matches the high consumption rate due to reaction. Micromixing then needs to be well understood and its description must include molecular diffusion at least (Bourne, 1982, 1984; Baldyga and Bourne, 1984c,d; Angst et al, 1984). For fast chemical reactions, the turbulence and the resulting mixing play as important a role as the reaction kinetics. Here the rate at which the reactant molecules can come together is governing the overall speed and outcome of the reaction.

According to O'Brien (1975) the most useful single parameter for describing the role of turbulence on chemical reactions is a ratio of time scales, a time scale \( \tau_k \) characteristic of the kinetic scheme to a time scale \( \tau_m \) characteristic of turbulent mixing. In a single-step, irreversible reaction, the inverse of the reaction rate constant in conjunction with
characteristic concentrations can represent the chemical reaction time and the time for the
decay of fluctuations of a scalar field in the turbulence might represent the mixing time
adequately. Hill (1976) has defined three groups $N_T = \tau / \tau_m$, $N_D = \tau / \tau_D$ and $N_R = \tau / \tau_k$, where $\tau_m = L_0 / u_0$, $\tau_D = L_0^2 / D$, $\tau_k = \Gamma_0 / R_0$ and $L_0, u_0, \Gamma_0, R_0$ are characteristic turbulent
length scale, velocity, concentration and reaction rate respectively. $N_T$, $N_D$ and $N_R$ are
are measures of the relative ease of achieving mean uniformity by turbulent mixing, of
attaining detailed uniformity by molecular diffusion, and of reaching chemical equilibrium
respectively. O'Brien (1975) uses Toor's (1969) analysis and defines slow reactions as those
for which $\tau_k / \tau_m > 1$, moderately fast reactions as those for which $\tau_k / \tau_m \approx 0(1)$ and
very fast reactions as those for which $\tau_k / \tau_m < 1$. Hill (1976) recognizes the importance
of diffusion time for non-premixed reactants and so very slow reactions are defined as
those for which $\tau_k > \tau_D$ and $\tau_m$ and very fast reactions are defined as those for which
$\tau_k < \tau_m$ and $\tau_D$.

In the case of a slow reaction, it is expected that turbulence will induce chemical
homogeneity before any significant reaction occurs, and the fluctuations in concentration
do not affect the rate of reaction. In the case of moderate reaction rate, complex coupling
between the turbulence and the reaction is to be expected even under statistically homoge­
nous conditions. For the case of very rapid reactions, the behavior depends on the nature
of the reaction. For segregated reactants, the rate of the reaction will be diffusion limited
since molecules must first diffuse to the same point before the can react. It is the rate
of molecular diffusion, enhanced by turbulence which controls the rate of progress of the
reaction. The importance of this degree of mixing of two reactants has been discussed by
Danckwerts (1958, 1981). His recommendation is that the intensity of segregation must
be reduced rapidly so as to avoid local spots of concentrated reactant and the usually
associated undesirable side reactions.

Bourne (1982) describes mixing in a turbulent flow as follows:
1. The B-rich solution breaks up into large B-rich eddies, which exchange position with A-rich eddies to form a macroscopically uniform mixture. At a scale much smaller than the eddy size, no mixing occurs. These processes constitute distributive mixing.

2. The large eddies of (1) decay in size through the effect of turbulent shear and a finer grained dispersion is formed. This mixture remains highly segregated at the molecular scale, although some reaction starts at the boundaries of the eddies. The mixing in this phase is termed dispersive.

3. Diffusion within the finely dispersed structure of (2) operates over short distances and proceeds to randomize the substances at the molecular scale. The result of diffusive mixing is termed a homogenous mixture.

To some extent these three phases overlap, e.g. diffusion occurs already in (2). It is, however, simple to designate (1) and (2) as convective mixing (macromixing), being brought about by flow, turbulence and eddy diffusion, whereas mixing at the molecular scale (micromixing) and hence chemical reaction belong only to stage (3).

For the case of premixed feed, complete segregation (macromixed fluid) maximizes conversion for reactions whose order is greater than one and no segregation (micromixed fluid) maximizes conversion for reactions whose order is less than one. Levenspiel (1972) has provided design charts for both first- and second-order reactions for the macro- and micro-mixed cases, but only for stoichiometric feeds.

Both macromixing and micromixing, as well as any intermediate level of mixing, may occur within any possible residence time distribution. It is thus necessary to know more than the residence time distribution for a reactor in order to determine the conversion for any but a first-order, monomolecular reaction. Micromixing plays an important role in industrial processes when one of the controlling rates of the reaction is of the same order of magnitude as the rate of mixing. This may be the case of fast complex chemical reac-
tions, polymerizations, precipitations, or aerobic fermentations. In real situations, several simultaneous micromixing mechanisms are often in operation, as for instance in stirred tanks.

Corrsin (1958, 1961) found relationships, which indicated that the normalized mixing rate is most strongly affected by a group containing the turbulence energy dissipation rate and a scalar length scale, $\frac{\varepsilon}{L_s^2}$.

Studies that involve the effect of the degree of mixing on reaction rate and, therefore, reactor size for given conversion can be placed into two general categories (Patterson, 1975):

1. the "direct approach" whereby the reaction conversion is defined in terms of both the kinetic parameters (concentration, reaction rate constant, temperature and pressure) and the mixing parameters (concentration fluctuations, scale of turbulence and energy dissipation rates)

2. the "indirect approach" whereby a model, often unrelated to the real physical mechanism, is constructed to estimate how far the reaction conversion will deviate from an ideal situation such as a perfect mixer.

By far the bulk of literature concerning chemical reactors utilizes the indirect approach because of the difficulty in obtaining turbulence data, and even more, because of the complexity of the mass, momentum and energy balance relationships for these systems. The indirect approach includes residence time distribution techniques combined with the concepts of micromixing and macromixing, dispersion and diffusion models, coalescence models and the two-environment models.

In contrast to the indirect modeling attempts, the direct approach is an attempt to relate the reaction rate directly to the turbulence parameters of the system which are in turn related to the type of reactor, flow patterns, agitation, etc. The literature that contributes to the direct approach includes that by Vassilatos and Toor (1965), Toor (1969) and McKelvey
Multiple chemical reactions

Reactions in parallel

For reactions in parallel, the concentration level of reactants is the key to proper control of product distribution.

\[ A + B \rightarrow R, \quad r_R = \frac{dC_R}{dt} = k_1 C_A^{a_1} C_B^{b_1} \]

\[ A + B \rightarrow S, \quad r_S = \frac{dC_R}{dt} = k_2 C_A^{a_2} C_B^{b_2} \]

If the desired product is R and the undesired product is S, we want to minimize

\[ \frac{dC_S}{dC_R} \quad \text{or,} \quad \frac{k_2}{k_1} \frac{C_A^{a_2-a_1} C_B^{b_2-b_1}}{C_A^{a_1}}. \]

Thus certain combinations of high and low reactant concentrations are desirable depending on the kinetics of the competing reactions. The use of the proper contacting pattern is the critical factor in obtaining a favorable distribution of products for multiple reactions.

Reactions in series

For reactions in series, the mixing of fluid of different composition is the key to the formation of intermediate. The maximum possible amount of any and all intermediates is obtained if fluid of different compositions and at different stages of conversion are not allowed to mix.

For the reaction,

\[ A \rightarrow R \rightarrow S \]
where R is the desired product, plug flow and batch operations should both give a maximum
R yield because here there is no mixing of fluid streams of different compositions, but the
mixed reactor should not give as high a yield of R as possible because a fresh stream of
pure A is being mixed continually with an already reacted fluid in the reactor.

Series-parallel reactions

Multiple reactions which consist of steps in series and steps in parallel are called series-
parallel reactions.

A two-step reaction where the first substitution product is desired is

\[ \text{A} + \text{B} \rightarrow \text{R} \]

\[ \text{R} + \text{B} \rightarrow \text{S} \]

Series-parallel reactions can be analyzed in terms of their constituent series reactions and
parallel reactions in that optimum contacting for favorable product distribution is the
same as for the constituent reactions. For example, as far as A, R, and S are concerned,
the behavior is precisely the behavior of reactions in series. And with respect to B, the
behavior is precisely the behavior of parallel reactions of the same order.

The mode of mixing of A and B has a marked effect on product distribution (Leven-
spiel, 1972). The cases where A is added slowly to B, B is added slowly to A, and A and B
are mixed together rapidly, will be considered.

1. Case I : A is added slowly to B — A is poured a little at a time into a beaker
containing B, stirring thoroughly and making sure that all the A is used up and
that the reaction stops before the next bit is added. With each addition, a bit of R
is produced in the beaker. But this R finds itself in an excess of B, so it will react
further to form S. The result is that at no time during the slow addition will A and
R be present in any appreciable amount. The mixture becomes progressively richer in S and poorer in B. This continues until the beaker contains only S.

2. Case II: B is added slowly to A — B is poured a little at a time into a beaker containing A, stirring thoroughly. The first bit of B will be used up, reacting with A to form R. This R cannot react further for there is now no B present in the mixture. With the next addition of B, both A and R will compete with each other for other for the B added, and since A is in very large excess it will react with most of the B, producing even more R. This process will be repeated with progressive buildup of R and depletion of A until the concentration of R is high enough so that it can compete favorably with A for the B added. When this happens, the concentration of R reaches a maximum, then drops. Finally, after more B is added, than the required stoichiometric amount, the solution contains only S.

3. Case III: A and B are mixed together rapidly — Here A and B are rapidly mixed together, the reaction being slow enough so that it does not proceed to any appreciable extent before the mixture becomes uniform. During the first few reaction increments R finds itself competing with a large excess of A for B and hence is at a disadvantage. Carrying through this same line of reasoning, we find the same type of distribution curve as for the mixture in which B is added slowly to A.

When multiple reactions take place on mixing two reactant fluids and when these reactions proceed to an appreciable extent before homogeneity is attained, segregation is important and can affect product distribution. If the reactions are slow enough so that the contents of the vessel are uniform before reaction takes place, the maximum amount of R formed is governed by the $k_2/k_1$ ratio. This situation, is one in which we may assume microfluid behavior. If, the fluids are very viscous or if the reactions are fast enough, they will occur in the narrow zones between regions of high A concentration and high B concentration.
The zone of high reaction rate will contain a higher concentration of R than the surrounding fluid. But any nonhomogeneity in A and R will depress formation of R. Thus partial segregation of reactants will depress the formation of intermediate. For increased reaction rate, the zone of reaction narrows, and in the limit, for an infinitely fast reaction, becomes a boundary surface between the A rich and the B rich regions. Now R will only be formed at this plane. An infinitely fast reaction gives a maximum nonhomogeneity of A and R in the mixture, resulting in no R being formed.

This behavior of multiple reaction could provide a powerful tool in the study of partial segregation in homogenous systems. The important point is to achieve homogeneity in A and R throughout the reaction mixture before reaction has proceeded to any significant extent. This is done by making the reaction zone as large as possible by vigorous mixing or by dispersing B in A in as fine a form as possible, rather than A in B or by slowing the reaction (Levenspiel, 1972).

**Micromixing and selectivity**

Mixing plays a very important role in the case of competitive-consecutive reactions. For reactions of the type

\[ A + B \rightarrow R \]

\[ R + B \rightarrow S, \]

A and B react to form R and S. R, however, competes with A in reacting with B, to form S. Also, since it is necessary for the first reaction to occur and form R before the second reaction can occur, the reactions are consecutive. Thus, overall, these two reactions are called competitive-consecutive reactions. In such a reaction, the amounts of R and S formed, which can be predicted by using the rate constants of these two reactions, depend fundamentally on the ability of the molecules of A, B and R to diffuse in the solvent.
The steep concentration gradients in the reaction zones influence the product distributions of multiple reactions if different steps respond to concentration at various rates (Angst et al, 1984). Thus, consecutive-competitive reactions constitute one important class of mixing-sensitive reactions, where the yield of the intermediate R ranges from a maximum in the chemical regime (slow reaction) through intermediate values in the diffusion-reaction regime (fast reaction) to zero in the diffusional regime (instantaneous reaction). So for the case of fast reactions, we have a reduction in reaction rate relative to perfect mixing, thus calling for more reactor volume to maintain a given output, and a change in the product composition relative to perfect mixing (Bourne, 1982). This change can mean a loss of raw materials in manufacturing unwanted products, as well as an increased load on the separation stages after the reactor when purifying the desired product. Furthermore it implies difficulties when scaling up, since the agitation intensity and thus the product distribution often varies with scale. The influence of mixing on product distribution is in practice more important than its influence on reactor volume, because the penalty for manufacturing at low selectivity is greater.

In competitive-consecutive reactions, the product distribution is very much dependent on the mixing conditions (Srivastava, 1988) that is, on the intensity of mixing.

1. Case with no mechanical mixing: If a blob of B is introduced in a vessel full of A, the only regions where A and B molecules interact are the interfaces of the blob B, because that’s the only place from where molecules of B can diffuse into the bulk solution of A, meet them and react. So any R formed in the first step of this reaction sequence is very likely to diffuse equally in all directions (including in the direction of the blob of pure B), resulting in a fraction of the total R reacting with B through the second step of the consecutive-competitive reaction set to form S.

2. Case with extremely intense mixing: Here turbulence causes the blobs of pure B
to become very small. As the blobs are rapidly reduced in size, diffusion is able to spread B molecules into A in a much smaller time period, resulting in a relatively better (more uniform, as compared to the previous case) spatial distribution of A and B. Thus, any R formed by the reaction of A and B has much lesser B react with, than in the earlier, unmixed case. Therefore, as compared to the first case, more R will be formed and very little S. But when one reaction is much faster compared to the other, the presence of turbulence and its diffusive action complicates the situation even more by tilting the balance in favor of the faster reaction – particularly if the time scale of the reaction is comparable to the time scale of turbulent diffusion.

When a small volume of a concentrated solution of reagent B is added to a large, completely miscible volume of reagent A, turbulent stresses present in the A solution cause the dispersion of the B-feed stream, which is progressively sub-divided into smaller and smaller fluid elements. Comparitively little diffusion and hence also reaction accompany this dispersion. The smallest fluid elements thus formed have sizes comparable to the Kolmogorov velocity microscale and having attained this size, diffusion and chemical reaction proceed within the B-rich elements, whose thickness is now gradually reduced by the laminar velocity gradients. The deformation caused by such gradients was previously modeled as simple shear. Shear and extensional flows both accelerate molecular transport phenomena by shortening the distances for transport and by steepening the gradients of temperature, concentration, etc. The kinematics of both deformations can be related to $\varepsilon$ and $\nu$ and thus knowing these quantities the corresponding deformation rates can be estimated. At constant energy dissipation rate, extensional flow causes faster thinning of fluid elements than simple shear and thus faster mixing and less secondary product formation. Reagent B also diffuses within the reaction zone and thus a decrease in X with rising $\alpha$ at constant M might be expected. The model of diffusion and reaction in a shrinking lamina gives a product distribution for
the series-parallel reactions

\[ X = f(k_1/k_2, c_{A0}/c_{B0}, \alpha, M, \beta) \]

where \( M \) is the mixing modulus \( (k_2 c_{B0} \delta_0^2 / D) \),
\( \alpha \) is the volume ratio of reagent solutions,
\( \beta \) is the stretching parameter.

(Bourne and Rohani, 1983; Baldyga and Bourne, 1984a; Bolzern and Bourne, 1983). The effect of these dimensionless parameters have been stated by Bourne (1982) as follows:

1. \( k_1/k_2 \): An increase in this ratio of rate constants promotes the formation of \( R \) over \( S \). This trend is, however, greatest in the chemical regime, weaker in the mixed regime and vanishes in the diffusion controlled regime, where a reaction plane forms. For a given pair of competitive-consecutive reactions, \( k_1/k_2 \) can often only be varied slightly by changing the temperature over the range of normal operation.

2. \( N_{A0}/N_{B0} \): This is the initial stoichiometric ratio of \( A \) to \( B \). Using an initial stoichiometric ratio \( (N_{A0}/N_{B0}) > 0.5 \), \( B \) becomes the limiting reagent and \( R \) is not fully converted to \( S \) as the reactions run to completion (i.e., as \( N_B \to 0 \)). To form significant quantities of \( R \), the initial stoichiometric ratio \( (N_{A0}/N_{B0}) \) should be higher than 0.5 e.g. around 1. Ratios greatly in excess of 1 cause little \( S \) to be formed. Experimental results from a CSTR indicated that product distribution is not highly sensitive to stoichiometric ratio when this ratio is around 1.

3. \( \alpha \): In the chemical regime the volume ratio of the reactant solutions has no effect on product distribution; only the stoichiometric ratio is relevant. \( \alpha \) is, however, significant in the mixed regime. \( (V_A/V_B) = \alpha \) is the ratio of the volumes of reagent solutions which have to be mixed with each other. This ratio is irrelevant in the chemical regime, but is important in the diffusion-reaction formulation where the
volumetrically smaller feed stream is supposed to be dispersed in a turbulent and well-mixed environment. This assumption agrees much better with experimental results than assuming that the major feed stream is dispersed.

4. $M$: This is thus proportional to the ratio of the half-life times for diffusion and second order reaction. Low values of $M$ characterize the chemical regime, where no concentration gradients occur. At sufficiently high values of $M$, the reaction zone is narrow and the diffusion regime, with a reaction plane formed where A and B meet and react instantaneously, corresponds to high values of $M$. The mixed regime falls between these limits: concentration gradients extend over finite regions and the reaction is influenced by chemical (e.g. $k_1$, $k_2$) as well as by physical (e.g. stirrer speed, solution viscosity) factors.

5. $\beta$: This dimensionless constant ($\beta = \gamma \delta_0^2 / D$) is proportional to the ratio of the half-life times for diffusion ($\sim \delta_0^2 / D$) in the absence of reaction and for shrinkage ($\sim \gamma^{-1}$). Physically, $\beta$ is a shearing parameter, proportional to the time needed to mix the reaction zone by diffusion alone and inversely proportional to the time required to deform it. Stretching clearly reduces the formation of $S$ relative to the unstretched case (i.e. the effect of inhomogeneity on product distribution is smaller), all other conditions being equal.

Some significant points noted by Angst et al (1984) are:

1. The initial thickness of a fluid element 2 $\delta_0$ is on the order of the Kolmogorov microscale $\lambda_k = (\nu^3 / \varepsilon)^{1/4}$, so that $\delta_0$ is of order 10 $\mu$m in turbulent water.

2. The ratios of diffusivities can seldom be changed significantly.

3. In a given turbulent flow field, it is not so much the value of $k_2$, but rather of $k_2C_{B0}$ which decides the extent of any effect of mixing on product distribution.
4. The initial half-thickness of a fluid element $\delta_0$ depends upon the agitation intensity, expressed for example as the rate of energy dissipation $\varepsilon$, as well as upon the viscosity. There is no doubt that increasing viscosity leads to a marked increase in $\delta_0$ and exerts a strong influence on product distribution.

5. The factors determining $\delta_0$ are stirrer speed $N$, stirrer diameter $d$, stirrer power number $P_0$, the kinematic viscosity of the fluid $\nu$ and the location of the feed point.

6. Kolmogorov's concept of local isotropy states that the fine scale turbulence is independent of the macroscopic device generating the flow field and adding energy to it. Turbines and propellers produce very different macroscopic flow fields and yet the product distribution correlates well with only the power input. This agrees with Kolmogorov's local isotropy and with the notion that reaction is influenced only by the fine scale features.

7. All other conditions being equal, the product distribution from a semi-batch reactor is intermediate between those for batch and continuous, stirred tank reactors. When the operating mode is changed from semi-batch to continuous, a substantial increase in secondary product (S) formation was observed.

8. The instantaneous, point concentration depends on a parameter $\Delta P$ which characterizes the kinematics of fluid deformation. The general form is $\Delta P \sim \varepsilon^{1/2} \delta_0^2 / \nu^{1/2} D$ where the rate of deformation is proportional to $(\varepsilon / \nu)^{1/2}$ at scales on the order of the Kolmogorov length, irrespective of whether shear, longtime elongation or short-time deformation is considered. If furthermore $\delta_0 \sim \lambda_\varepsilon$, then $\Delta P \sim S_c$.

As an example of a quantitative matter, the size of the reaction zone can be considered. With rising stirrer speed, the selectivity $X$ decreases and thus mixing at the molecular scale is accelerated. In terms of diffusional theory this means that the reaction zone becomes
smaller. Also, a rise in viscosity increases the size of the reaction zone. In the turbulent regime the circulation and mixing times are independent of viscosity, but such times refer only to bulk motion and blending. Thus, it is again evident that micro-rather than macro-mixing is of primary importance when discussing chemical reactions. The observed dependencies on stirrer speed and hence power input and on viscosity suggest that the scale of the reaction zone (e.g. $2 \delta_0$) might be equal to the Kolmogorov microscale, $\lambda_k$.

Irrespective of whether the reaction zone is considered to be a sphere or a slab, the diffusion of the reagent B leads to a decrease of secondary product formation and $X$ is lowered. This seems plausible because any mechanism causing homogenization (mixing) reduces the concentration gradients, which are formed when the reaction is fast and thus reduces the further reaction of R to S (Angst et al, 1979, 1982a,b).

The way in which secondary product formation depends on the volume ratio of the reagent solutions is determined by whether B is immobile or diffuses. When B is immobile, $X$ increases with increasing $\alpha$ at constant $M$. When, however, B diffuses, an increase in $\alpha$ causes a small increase in $X$ at low values of $M$, but a significant decrease in $X$, at high values of $M$. When, furthermore, the slab is progressively sheared, the small increase in $X$ at low $M$ is no longer observed. Thus, when $\alpha$ is varied, the sign of the change of $X$ will depend upon the mobility of B.

Secondary product formation in the mixed regime can thus be reduced by one or a combination of the following measures: increasing agitator input, reducing solution viscosity, reducing reaction temperature, avoiding high volume ratios, using dilute reagent solutions, increasing the stoichiometric ratio etc (Bourne, 1984; Nabholz et al, 1978).
Models

Models aimed at describing reaction rate and product distribution in inhomogenous mixtures are still in a state of development and critical evaluation. Clearly a model should describe the physical situation using as few parameters as possible and be consistent with all available experiments. The problems of interest are: identification of relevant variables that influence product distributions, development of criteria in terms of the characteristic times of local motion, diffusion, and chemical reaction to indicate when mixing effects are important, correlation of selectivity modifications in terms of model parameters and sensitivity of model results to model parameters and flow, description (Chella and Ottino, 1984). Hill (1979) first proposed a classification of models of mixing and multiple chemical reactions in turbulent flows as (i) Mechanistic Models and (ii) Direct Turbulence Models. This classification has been adopted and widely used by other investigators like Mehta and Tarbell (1987), Dutta and Tarbell (1989) etc.

Mechanistic models are based on idealized mechanisms of turbulent micromixing. These models are attractive because of their simplicity and modest computational demands, but they do not necessarily describe correctly the underlying physical reality of the mixing-reaction process. All of these models have adjustable parameters which must be fit to experimental data.

Direct Turbulence Models are based on the Navier-Stokes equations and component continuity equations and thus have some physical basis. However, in order to arrive at a closed system of equations, the fundamental equations of direct turbulence modeling must be supplemented by closure models which relate higher order statistics to lower order statistics of the concentration distribution.
Mechanistic models

(1) Slab Diffusion Model: Mao and Toor, 1970, 1971

This model is based on the simultaneous interdiffusion and reaction between alternate slabs of reactants (Mao and Toor, 1970). The model divides the fluid into slabs of thickness $\delta$, which are alternately arranged with reactants A and B at constant initial values. Mixing is controlled by molecular diffusion between alternate slabs of thickness $\delta$, which depends upon fluid mechanics, and that in the case of chemical reactions a single constant Fickian diffusion coefficient can be used for all components. The slabs enter the reactor completely segregated and they proceed to intermix by molecular diffusion and undergo chemical reaction as they move through the reactor at the mean fluid velocity. The mixing parameter of this model is the double slab thickness $2\delta$. This model has been applied to single reactions and to series-parallel reactions.

(2) Interaction by Exchange with the Mean, (IEM) Model: David and Villermaux, 1975

This model considers mass transfer between segregated elements. For a two feedstream perfectly stirred reactor, the IEM model consists of two eddies, one associated with each feedstream, which act as well mixed batch reactors having a mass exchange with a mean environment whose concentration is assumed to be constant and to coincide with the mean concentration leaving the reactor. Micromixing is described by a first order exchange process between the mean environment and each eddy (the eddies do not interact directly) with concentration difference as the driving force. The exchange rate is characterized by a mass transfer coefficient, $h$, which is the micromixing parameter of the model. Though the IEM model was originally conceived for stirred reactors only, it can be applied to plug flow reactors also and the same turbulence analogy applies to plug flow reactors by using a plug flow residence time distribution.
(3) **The Three Environment Model**: Ritchie and Togby, 1979

In the 3E model, two entering environments (E.E.'s), one for each reactant feedstream in a two reactant system, are assumed to supply a single leaving environment (L.E.) at rates proportional to their respective masses (Tarbell and Mehta, 1986). While each E.E. acts as a totally segregated reactor (no age or species mixing), the L.E. behaves as a maximum mixedness reactor (complete age and species mixing). Micromixing is modeled by the first order transfer of material from the E.E.'s to the L.E. with a transfer coefficient \( R_c \) which is the model's micromixing parameter. The E.E.'s should be viewed as lumped representations of turbulent eddies of pure reactant which have only interacted with other pure reactant eddies and as such, they model the extremes of the turbulent concentration spectrum. The 3E model has only one reacting environment with reactant concentrations at the mean of the concentration spectrum.

(4) **The Four Environment Model**: Mehta and Tarbell, 1983

To overcome the limitation of only a single reacting environment in the 3E model, Mehta and Tarbell developed the 4E model by introducing a separate L.E. for each feed stream and allowing mutual interaction between the L.E.'s (Chang et al, 1986). The E.E.'s are segregated flow reactors, the L.E.'s are maximum mixedness reactors and the transfer of material from E.E. to L.E. is first order in the mass of the E.E. with a transfer coefficient \( R_c \). The reversible transfer between L.E.'s is first order in the mass of each L.E., also with a transfer coefficient \( R_c \). The two L.E.'s of the 4E model are a somewhat finer lumped representation of the intermediate region of the turbulent concentration spectrum than the single L.E. of the 3E mode. The reactant stoichiometry of each L.E. may now be rich in the reactant fed through its respective E.E., thus providing the structural feature of multiple reacting regions.

(5) **Diffusion-Reaction Model**: Belevi, Bourne and Rys, 1981
The model assumes that a blob of B-rich fluid is first surrounded by A-rich fluid. Then macromixing takes place, namely distribution and dispersion. The shape of the fluid elements formed by turbulent dispersion of the B-feed stream is assumed to be spherical. Deformations are brought about by velocity fluctuations in the inertial subrange and finer scale deformations take place partially due to viscous stresses. As a result of a burst of vorticity, a laminated structure is formed consisting of layers of the A and B solutions. Then thinning of the A and B layers in the radial direction takes place as a result of vortex stretching. The old vortex material, which because of the incorporation of A-fluid with the tongue of B-fluid has twice the volume of the original tongue, is again acted on by bursts of vorticity and the process continues (Bourne 1984; Baldyga et al, 1984). Figure 6.3 explains this model and the various steps taking place.

Being physically based, this model involves no arbitrary parameters and requires no fitting. This model has been compared to experiments and have verified that (i) in the chemical regime (reactants mix completely before reaction has occurred to any significant extent), for a given set of reaction conditions, the smallest amount of secondary product is formed, (ii) in the diffusional regime (reaction zone sinks to a plane where A and B cannot co-exist), the yield of the intermediate, R, is zero, (iii) in the mixed regime, product distribution depends partly on chemical (e.g. rate constant) and partly on diffusional (e.g. agitation, viscosity of solution) factors and so the quantity of S formed falls between the values for the chemical and diffusional regime, (iv) an increase in the stoichiometric ratio $N_{A0}/N_{B0}$ suppresses the formation of secondary product, (v) the product distribution in the mixed regime responds less to changes in $k_1/k_2$ than in the chemical regime.

(6) Engulfment-Deformation-Diffusion (EDD) model: Baldyga and Bourne, 1984

This is very similar to the diffusion-reaction model and is a finer revised form of that model. According to the engulfment-deformation-diffusion (EDD) model, the mechanisms involved
in micromixing are engulfment, deformation and diffusion. Vorticity causes one fluid to be engulfed by another and deformation causes kinetic energy to dissipated irreversibly to heat and accelerates diffusion. Diffusion then brings about mixing at the molecular level. This EDD model has been applied to interpret experiments showing an effect of mixing on product distribution of series-parallel reactions. The model requires the solution of coupled, non-linear, parabolic partial differential equations expressing unsteady diffusion and reaction within a deforming vortex. And since complete micromixing requires several vortex generations, the set of equations requires solving that many times.

(7) **Coalescence-redispersion Model:** Curl, 1963

This model visualizes mixing between fluid regions by coalescence at a frequency determined by the nature of turbulence when eddies coalesce (Tarbell and Mehta, 1986). The coalescence frequency is the parameter of this class of models. The CRD model was originally proposed by Curl to describe dispersed phase droplet mixing and concurrent chemical reaction. In his view, a chemical reactor population consists of a large number of equal size droplets each having uniform concentration and behaving as an ideal batch reactor. Mixing takes place by random and instantaneous pairwise coalescence, concentration homogenization, and redispersion into an identical pair of droplets. In the turbulence analog for a homogenous fluid, Curl’s droplets may be viewed as (isotropic) turbulent eddies and the coalescence rate as a measure of the turbulent micromixing. CRD is basically a deterministic population balance model and the governing equation is an integro-differential equation for the pdf. The micromixing parameter of the model, \( I \), is the average number of collisions experienced by an eddy during its passage through the mixer.

(8) **Mixing-Reaction Model:** Nabholz, Ott and Rys, 1978

A chemical reaction is subdivided into various individual processes: mixing of reactant species, molecular diffusion in which encounter complex is formed and dissociation of en-
counter complex, or bond-making and bond-breaking to lead to products (Nabholz et al., 1978). The concept of the model is based on the assumption that during the addition of one reactant solution to another, liquid elements, so-called eddies are formed. The mean size of these eddies, i.e. the extent of the segregation will depend on the intensity of the turbulence created. A fast mutual interchange among single eddies (eddy diffusion) is much faster than the molecular diffusion within the eddy; thus the concentration gradient between the interface of the eddies and the solution can be neglected. To obtain a simple mathematical description, some reactants within the eddy are considered fixed. In Version I, A is added to B, so eddies of solution A in solution B are created. The reactant A and the products R and S are assumed immobile. The moment the reaction occurs, the diffusing mobile molecules of B change their identity to R or S and consequently are considered as immobilized in the eddy. In Version II, B is added to A and the formation of eddies of solution B in solution A is assumed. B is considered immobile in the eddies into which mobile A penetrates. R is considered as a new mobile species which could diffuse to a further molecule of B to give S. Some examples include nitration of mesitylene, azo-coupling of 1-naphthol-6-sulfonic acid (A) with phenyldiazenium ion (B).


The model assumes that reactants are initially present in adjacent alternating sheets of fluid (Ou and Ranz, 1983a,b, Ranz, 1985). The reactants then diffuse from adjacent sheets of fluid undergoing a stretching motion, contact one another and react. This stretching motion causes deformation of the intermaterial surface and is designated mechanical mixing. Stretching influences reaction i) by convection, ii) by changing the area of the reaction zones and iii) by changing the diffusion rates. In this model, a mixing-reaction number ($\phi = KC_{B0}s^2/D_A$, $s$ is the striation thickness) is used and this represents the competition between mechanical mixing with molecular diffusion and chemical reaction in controlling
the conversion rate. The following three zones are observed.

(i) Fast reaction: \( \phi > 10^4 \): mixing rate is much slower than reaction rate, mixing controls the conversion rate.

(ii) Moderate reaction: \( 1 < \phi < 10^4 \): mixing rate and reaction rate are comparable.

(iii) Slow reaction: \( \phi < 1 \): mixing including diffusion is complete before significant reaction occurs - reaction controls.

They have shown that flow pattern influences mixing and hence the selectivity of chemical reactions. In principle, if \( s(t) \) is known for mixing flows in a reactor, complex chemical reaction systems can also be followed in that reactor.

(10) **Engulfment (E) model**: Baldyga and Bourne, 1989

The EDD model was simplified to the new engulfment (E) model by neglecting deformation and diffusion. The E model retains fluid engulfment as the rate determining step in micromixing and application to complex reactions has shown that product distribution does not depend on deformation and diffusion but is determined by engulfment. This model consists of a set of ordinary differential equations and it is at least an order of magnitude faster to compute than the equations for the EDD model. The effect of partial segregation on the product distribution for complex reactions was calculated for various operating modes as well as for different operating variables. This model is valid when \( Sc << 4000 \) and \( F << 1 \) where \( F = C_{A0}/C_{B0} \) (Bourne, 1989a, 1989b).

(11) **Linear Eddy Model**: Kerstein, 1991

This model simulates transport and mixing of diffusive scalars in turbulent flows based on a representation of the temporal evolution along a transverse line moving with the mean fluid velocity. The scalar field along this line evolves by molecular diffusion and by randomly occurring events called block inversions. Diffusion represents the molecular processes and the block inversion represents the effect of turbulent convection. Block inversion consists of
the random selection of an interval \((y_0 - l/2, y_0 + l/2)\) of the line and replacement of the scalar field \(\theta(y)\) within that interval by \(\theta(2y_0 - y)\). For fixed \(l\), the model requires the Peclet number as the single input parameter. The model has been used to compute spatial development of diffusive scalar fields downstream of several source configurations in homogenous turbulence. Incorporation of finite rate chemical reactions is a possibility (Kerstein, 1991).

(12) Turbulent-molecular-mixing model: Fox, 1991

This model for turbulent molecular mixing is derived based on the theory of diffusion in layer-like lamellar structures and is to be used in conjunction with the balance equations appearing in the probability density function (pdf) method for turbulent reacting flows. The model is formulated in terms of the Fokker-Planck (FP) equation, and all unknown parameters appearing in the FP closure correspond to fundamental physical quantities like molecular diffusivity. The FP closure model is derived for the joint pdf of the scalar concentration and the scalar gradient in lamellar structures and the closure predicts a Gaussian pdf for passive scalar mixing in the long time limit (Fox, 1991).

**Direct turbulence models**

**Bourne-Toor closure**: This closure is based on the application of turbulent momentum and mass transfer equations to determine velocity fluctuations and relating them to concentration fluctuations and thus to local reaction rates. (Bourne and Toor, 1977.) For a series-parallel reaction, the ratio of the rate of formation of R to the rate of formation of S is given by

\[
\frac{r_R}{r_S} = \frac{k_1(\bar{C}_AC_B + \bar{e}A\bar{c}B) - k_2(\bar{C}_B\bar{C}_R + \bar{c}_B\bar{c}_R)}{k_2(\bar{C}_B\bar{C}_R + \bar{c}_B\bar{c}_R)} = \frac{k_1(\bar{C}_AC_B + \bar{e}A\bar{c}B)}{k_2(\bar{C}_B\bar{C}_R + \bar{c}_B\bar{c}_R)} - 1.
\]

Consider two types of feed conditions:

(i) Premixed feed: If B is premixed with A, then an instantaneous excess of A will also cause
an instantaneous excess of B, since B and A originate together. When there is a deficiency of A, then there will be a deficiency of B. The intermediate is produced in the regions where the reactant concentrations are high; hence, the intermediate product is positively correlated with the reactants. Thus the closure:

\[ \overline{c_A c_B} > 0 \]

\[ \overline{c_B c_R} > 0 \]

Since both reaction rates are increased, the selectivity \( (r_R/r_S) \) is increased or decreased depending upon whether \( \frac{c_A c_B}{\overline{C_A C_B}} \) is greater than or less than \( \frac{c_B c_R}{\overline{C_B C_R}} \).

(ii) Separate feed: If A and B are fed separately, an excess of A requires an insufficiency of B and vice versa, since fluid elements originating in the A feed and B feed cannot both be at the same point at the same time. Thus, non-premixed feeds lead to a negative correlation. Using the local spatial average viewpoint, the fluctuations at a point occur as fluid elements with those profiles in them sweep by the point. Since they sweep by randomly, all parts of the fine scale profiles spend equal amounts of time at the point. Hence, \( \overline{c_A c_B} \) at a point is the spatial average of \( c_A c_B \) within the element, \( \overline{C_A} \) is the spatial average of A, and \( \overline{C_B} \) is the spatial average of B. But on the left, \( c_A > 0 \) and \( c_B < 0 \), so \( \overline{c_A c_B} < 0 \) ; on the right, \( c_A < 0 \) and \( c_B > 0 \), so again \( \overline{c_A c_B} < 0 \). The intermediate R is produced in the reaction zone regions, where A and B are mixed together at the molecular level by diffusion. Hence R must have its highest concentration in this region. On the right of the reaction zone, \( c_R < 0 \) and \( c_B > 0 \), so \( \overline{c_R c_B} < 0 \). On the left of the reaction zone, \( c_R < 0 \) and \( c_B < 0 \), so \( \overline{c_R c_B} > 0 \). Figure 6.4 clarifies the situation. In the reaction zone itself there will be a region where \( \overline{c_R c_B} \) is negative, but there may also be a region where \( \overline{c_R c_B} \) is positive as well. Because of the differences in sign throughout the volume of the element, the local spatial average will be relatively small. Thus the closures are:

\[ \overline{c_A c_B} < 0 \]
With segregation, the rate of product \((R)\) formation would fall, while the rate of by-product \((S)\) formation would remain relatively unchanged. Thus, imperfect mixing lowers the selectivity \(r_R/r_S\).

**Brodkey-Lewalle closure:** This is an extension of Toor’s hypothesis that mixing is independent of the speed of the reaction when reactants are fed in stoichiometric proportion (Brodkey and Lewalle, 1985). For the series-parallel reaction, Toor’s hypothesis has been extended to apply to the second reaction, and a second hypothesis (mixing closure) has been made to relate the mixing for the second reaction to that for the first. For the series-parallel reaction, the mixing for the first reaction involves \(c_A c_B\) and that for the second reaction involves \(c_R c_B\). The mixing closure hypothesis which allows solution of the equations is:

\[
\bar{c}_R c_B = \bar{c}_A c_B \left( \bar{C}_R / \bar{C}_A \right).
\]

This is valid to at least within few percent when \(k_1\) and \(k_2\) are equal.

The one-dimensional, Reynolds averaged form of the evolution equation for \(c_A c_B\) is

\[
U_x \frac{d}{dx} (c_A c_B) = D \frac{d^2}{dx^2} (c_A c_B) - 2D \frac{dc_A}{dx} \frac{dc_B}{dx} - k\{c_A c_B^2 + c_A^2 c_B + \bar{C}_A c_B^2 + \bar{C}_B c_A^2 + \bar{C}_A \bar{C}_B (c_A + c_B)\}.
\]

Toor’s hypothesis results from the consideration of the two extreme cases of \(k \rightarrow 0\) and \(k \rightarrow \infty\). In the first case \((k \rightarrow 0)\), \(c_A c_B\) decreases only by the action of diffusion and in the latter \((k \rightarrow \infty)\), the term in square brackets must vanish because it is not balanced by any other term. Thus in the two limits,

\[
k\{c_A c_B^2 + c_A^2 c_B + \bar{C}_A c_B^2 + \bar{C}_B c_A^2 + \bar{C}_A \bar{C}_B (c_A + c_B)\} = 0.
\]

Toor conjectured that the above equation holds at least approximately for all values of \(k\). The consequences of the hypothesis are: \(c_A c_B\) and consequently \(I_s\) are independent of
whether or not there is a reaction in the flow, and thus can be determined independently from pure mixing experiments, or equivalently from fast reaction experiments. This hypothesis has been accepted as a powerful working tool after being checked by experimental data and with results of numerical simulations.

For the series-parallel reactions, the mass balance equation and other moment equations involve a $\overline{c_\text{A}c_\text{B}}$ term along with a $\overline{c_\text{A}c_\text{B}}$ term. Toor's hypothesis applied to both reactions, can help to simplify the expressions, but an additional closure is still required. It is an extension of Toor's hypothesis to apply it independently to the second reaction and thus further assume that the consumption of B in the second reaction has no effect on $\overline{c_\text{A}c_\text{B}}$ that appears in the first equation. An identical argument can be presented for the second reaction too. The generalized form of the rate expression is considerably simplified if the covariances obey the proposed closure.

One of the most useful quantities used by Brodkey and Lewalle (1985) is the intensity of segregation, $I_s$. This parameter is reputed to be adequate for the overall description of the material interface smearing, with or without reaction, for substitution in the averaged mass balance equations for contaminants, for easy measurability of the statistics involved in the definition and for flexibility of use where there is mixing of streams. For the plug flow case (completely segregated in time) with no backmixing, the yield of R and selectivity is independent of $I_s$ as long as $I_s < 1$. If $I_s$ remains at 1, there is complete segregation and therefore no reaction. This independence of the final conversion on the history of mixing is restricted to the plug flow reactor. For other reactor configurations, the yield of R and selectivity is a function of the history of mixing. The time-dependent conversion to R and the selectivity along the reactor is a strong function of $I_s$.

However the strongest limitation is the implicit assumption of an initially well-dispersed system but one that is not well mixed by molecular diffusion effects. Thus, there is a large scale homogeneity such that no matter where in the system one selects, the contents of
that subarea will not vary from selection to selection. Another assumption made in this approach is that the consumption of B in the second reaction has no effect on $c_A c_B$ that appears in the first equation. Besides, Toor's hypothesis fails when applied to series-parallel reactions with very large $k_1 / k_2$ ratios. However, the mixing closure and the independence of $I$, on the reactions (Toor's extended hypothesis) appear to be good working tools.

Two extreme cases of the mixing characteristics provide well-known models for the reactor: the complete segregation reactor (CSR) and the maximum mixedness reactor (MMR). Brodkey has examined the class of real-life reactors that can be modeled by a small number of such CSR and MMR in series, in any order. The flexibility of the model is governed by two parameters for each of the basic modules: the maximum residence time ($T_M$ or $T_S$) in that unit, and the decay parameter of $I$, between two successive stations in the discretized version of the input and output. In the CSR,

$$I_s = I_o e^{-z t}$$

is adopted whereas for the MMR,

$$\left( \frac{dI_s}{dt} \right)_{\text{decay}} = -z I_s$$

The parameter $z$ is considered as a measure of the turbulent mixing strength. Observations of selectivity as a function of mixing intensity has been reported. Generally, $k_1 \neq k_2$ or $\beta < 1$, favoring one reaction at the expense of the other, reduces the range of values of $\frac{C_R}{C_S}$.

**Li-Toor closure:** Their closure uses a conserved scalar approach. The closure is valid when the reactants are segregated and the first-reaction is almost diffusion controlled ($k_1$ is very large). The closure states:

$$c_B c_R = (\hat{C}_B - \hat{C}_S)(\hat{C}_R - \hat{C}_S) - \hat{C}_B \hat{C}_S$$
where $C_B$ and $C_R$ are the time averaged concentrations for B and R when $k_2 = 0$.

Li and Toor consider a tubular reactor and neglect time-averaged radial gradients and axial diffusion for their analysis. They chose linear combinations of reactants that are invariant to the reaction, i.e., conserved scalars. For the series parallel reaction, from stoichiometry, the conserved scalars are

$$r_A + r_R + r_S = 0$$

$$r_A - r_B - r_S = 0$$

The details of the derivation is given in the appendix of Li-Toor's (1986) paper.

**Dutta-Tarbell closure:** This is a simple first order closure model for turbulent concentration equations, derived based on fast and slow reaction asymptotics and from mechanistic models of turbulent mixing (Dutta and Tarbell, 1989; Tarbell and Dutta, 1987; Tarbell, 1988). The three-environment model is the mechanistic model which forms the basis of the new closure model. The 3E model assumes that the reactor consists of three environments or eddies; two of the environments are associated with the separate feed streams of A and B. These are the ‘entering environments’ (EEs) and their initial volumes at the feed end of the reactor are proportional to the volumetric flowrates of their respective feed streams. These EEs feed a single perfectly mixed environment, the ‘leaving environment’ (LE), at rates proportional to their respective volumes. The three environments move in unison down the reactor at the mean velocity. Mehta and Tarbell have shown that the decay of the concentration variance of a nonreactive tracer in a plug flow (batch) mixer as predicted by the 3E model has the same form as prescribed by Corrsin's isotropic turbulent mixing theory. Thus the 3E model has a turbulence analogy and the closure model is an extension of the turbulence analogy ($R_s = 1/\tau_m$) where $\tau_m$ is the time constant for turbulent micromixing. The turbulence analogy, thus, provides a means of predicting the mixing parameter of the 3E model ($R_s$) from basic turbulent properties (since $\tau_m$ is known in terms
of \( L_s, \varepsilon, \nu, N_e \). It is implicit in Toor's hypothesis that the micromixing parameter \( \tau_m \) or \( R \), obtained in a nonreactive mixing experiment, can be used to describe micromixing in a reacting system having the same hydrodynamics. The basic hypothesis which underlies the closure model is that the leaving environment does not contribute to any ensemble average which involves fluctuating variables and this is a version of Toor's hypothesis. It is assumed that the turbulent mixing process is unaffected by the presence of chemical reactions. The three first order closure models required to describe a two feedstream reactor are:

1. \( \bar{c}_{AB} \) is the correlation between the concentration fluctuations of two feedstream components,
   \[
   \bar{c}_{AB} = -I_s(\overline{C_A C_B} + \overline{C_A C_B} - \overline{C_A C_B})
   \]
   This closure can be applied to reacting and non-reacting flows. \( I_s \) is the intensity of segregation.

2. \( \bar{c}_{RB} \) is the correlation between a feed and a non-feed component,
   \[
   \bar{c}_{RB} = -I_s \overline{C_R C_B}
   \]

3. \( \bar{c}_{RS} \) is the correlation between two non-feed components,
   \[
   \bar{c}_{RS} = I_s \overline{C_R C_S}
   \]
   This will not be required for modeling of the parallel-consecutive reaction scheme, but may be required for modeling of a more general reaction mechanism in which two non-feed components react.

The value of \( \tau_m \) was determined by Mehta and Tarbell to provide the best fit of the four-environment model to the data. The 4E model was the only mechanistic model tested which fit the data well, and the best fit value of \( \tau_m \) was close to estimates based on turbulence measurements. This closure model provides an excellent fit to the experimental R and S
profiles over the entire range of operating conditions. Thus, this model is capable of providing satisfactory fit to all of the data with a single value of the micro-mixing parameter.

Kosály’s comments: If the characteristic times of the first and second reaction are defined as \( T_1 = 1/k_1 C_{B0} \) and \( T_2 = 1/k_2 C_{B0} \), the Damköhler numbers of the two reactions may be defined as \( Da_1 = T_m/T_1 \), \( Da_2 = T_m/T_2 \) where \( T_m \) is the characteristic time of turbulent molecular mixing. Kosály claims that both the Bourne-Toor and the Brodkey-Lewalle schemes are valid if \( Da_2 << 1 \). The Brodkey-Lewalle closure is also valid if \( Da_1 >> 1 \) and \( Da_2 >> 1 \). In the \( Da_2 << 1 \) case, the Brodkey-Lewalle scheme recovers the Bourne-Toor scheme which is simpler. The closure of the \( \overline{c_B c_R} \) term suggested by Brodkey-Lewalle becomes valid if both reactions are mixing limited.
Figure 6.2: Mechanism of turbulent mixing, Brodkey (1975)
Figure 6.3: Bourne's diffusion-reaction model, Bourne (1984): A, B, C, show large scale deformations of a blob of B-rich fluid surrounded by A-rich fluid, D, E show fine scale deformations.
Figure 6.4: Fine scale concentration profiles for a series-parallel reaction as explained in Bourne and Toor's (1977) closure model
APPENDIX C: SPECTRAL METHODS

Introduction

Spectral methods have become the prevailing numerical tool for large-scale calculations in various areas of computational fluid dynamics like direct simulation of homogenous turbulence, computation of transition in shear flows, and global weather modeling. For many other applications, such as heat transfer, boundary layers, reacting flows, compressible flows, and magneto-hydrodynamics, spectral methods have proven to be a viable alternative to the traditional finite-difference and finite-element techniques (Hussaini and Zang, 1987). Hussaini and Zang (1987) have an extensive review on the application of spectral methods to fluid mechanics. Givi (1989) discusses spectral methods as applied to turbulent reacting flows. The spectral method is often used in simulations of homogenous three-dimensional "box" turbulence. This technique is usually limited to small or moderate grid Reynolds numbers. With the development of the FFT algorithm, the spectral technique came within reach of the digital computer and thus gained widespread popularity. Patterson and Orszag (1972) were one of the first to carry out direct numerical simulations of homogenous isotropic turbulent flow using spectral methods.
The spectral (Galerkin) method

Spectral methods involve representing the solution to a problem as a truncated series of known functions of the independent variables (Gottlieb and Orszag, 1977). Here the fundamental variables are approximated by a finite series of orthogonal global basis functions,

\[ f(x) = \sum_{k=1}^{N} a_k B_k(x). \]

Basis functions are generally chosen that meet the boundary conditions trivially. The choice of complex exponentials for basis functions requires the function \( f(x) \) to have periodic boundary conditions on an interval of length \( 2\pi \) to avoid the appearance of boundary conditions in the transformed dynamical equations. Spatial derivatives are evaluated easily and accurately with spectral methods if the function to be approximated is smooth enough and if the basis functions are chosen properly (Leonard and Hill, 1989). If the basis functions are complex exponentials, the expansion for the spatial derivative is

\[ \frac{df}{dx} = \sum_{k=1}^{N} ik a_k e^{ikx}, \]

which is evaluated locally in the transform space. The error in the approximation of the derivative goes to zero faster than any power of \( 1/N \) as \( N \) goes to infinity. This is referred to as infinite-order or spectral accuracy. Orszag (1971a,b) has shown that a spectral method with \( N \) degrees of freedom in each direction is at least as accurate as a finite-difference method with \( 2N \) degrees of freedom in each direction. Givi (1989) has demonstrated with an example that infinite-order accurate Galerkin approximations give considerably more accurate results than finite-difference approximations. The monograph by Gottlieb and Orszag gives a very thorough treatment of spectral methods.

In its most general form, the spectral method expresses the fluid velocities as the
expansion
\[ u(x, t) \approx \sum_{n=1}^{N} G_n(t) a_n(x) \]
provided that the boundary conditions can be satisfied. The expression for velocity can be substituted into the Navier-Stokes equations to yield an appropriate representation of the transformed Navier-Stokes equations (Orszag, 1971a). The form of \( a_n(x) \), the Galerkin basis function, depends on the boundary conditions and type of flow to be simulated. The transformed equations are then integrated over time.

The advantages of the Galerkin procedure over finite difference methods have been discussed by Orszag, (1971a, 1971b). A summary of his observations (almost verbatim) follows:

1. For flows within three-dimensional simple boundaries, the Galerkin methods require about an order of magnitude less computer time and storage to achieve reasonable accuracy than do finite-difference methods.

2. For given number of independent degrees of freedom (Galerkin basis functions or space-grid mesh points), infinite-order accurate Galerkin approximations are likely to give considerably more accurate results than finite-difference approximations. Here Galerkin approximations are said to be infinite order if the error after \( N \) terms decreases more rapidly than any power of \( 1/N \).

3. If very accurate (or moderately accurate long-time) simulations are required, the Galerkin approximations offer the advantage of giving infinite-order approximations to infinitely differentiable flows.

4. The Galerkin equations preserve certain important integral constraints of motion aside from time-differencing errors and viscous dissipation, i.e., they "semiconservel the integral constraints. And this is necessary for stable long-term integration of the
equations of motion.

5. With proper choice of the basis functions \( a_n(x) \), the Galerkin method allows full utilization of any symmetries and invariances of the flow to be simulated, while finite-difference methods are not so versatile.

6. Galerkin approximations to flows within rigid no-slip boundaries obtained using expansions in orthogonal polynomials account properly for the boundary conditions while finite-difference approximations may be susceptible to instabilities due to improper imposition of boundary conditions, or the simulations may suffer significant loss of accuracy at boundaries due to the necessity for one-sided differences at boundaries.

7. The Galerkin equations are easily interpretable as finite-mode model dynamical systems.

The Galerkin approximations of infinite-order accuracy can be conveniently formulated and efficiently implemented for problems within box geometries with rather general boundary conditions. Problems within cylindrical and spherical geometries are also conveniently handled and efficiently implemented using Chebyshev expansions and surface-harmonic expansions. Galerkin methods were not used for major flow-simulation studies because large cutoff Galerkin methods are grossly inefficient when used without transform methods.

**Pseudospectral method**

In the spectral collocation technique or the pseudospectral method, the fundamental unknowns are the solution values at selected collocation points and the series expansion is used solely for the purpose of approximating derivatives as opposed to the spectral Galerkin method where the fundamental unknowns are the expansion coefficients. In collocation
methods, N points $x_n$ are chosen in the range $[x_-, x_+]$, such that

$$x_- < x_1 < ... < x_N < x_+$$

These collocation points are effectively the grid points of the method. The distinguishing feature is that the continuum equation is satisfied exactly at only the grid points.

Orszag (1972) has shown that the widely applicable and efficient pseudospectral approximations are roughly as accurate as spectral approximations. The pseudospectral method is usually used for the full turbulence simulations of flows with suitable boundary conditions, rather than the full spectral or Galerkin spectral method. Nonlinear terms are evaluated by transforming variables to physical space in order to evaluate the product — hence avoiding the computation of convolutions in transform space — and then transforming the product back to transform space so that derivatives are evaluated there to take advantage of spectral accuracy. The main advantage of pseudospectral methods for incompressible flows is that the amount of machine computing time appears to be much less than for other methods to achieve comparable accuracy in a simulation, primarily because a Poisson equation does not need to be solved at each time step (Leonard and Hill, 1989). Pseudospectral methods are currently the best choice for the full simulation of incompressible, homogenous turbulent flows. According to Orszag (1972), the pseudospectral approximation possesses several operational advantages over the spectral approximation:

1. For complicated problems in several space dimensions, the fastest spectral method requires at least twice the number of fast Fourier transforms as the corresponding pseudospectral method.

2. Pseudospectral codes are considerably simpler than spectral codes.

3. The pseudospectral approximation applies to a much more general class of problems than spectral approximation. For example, periodic boundary conditions are not es-
ential to the pseudospectral method. However, other boundary conditions require different series expansions in order to ensure rapid convergence.

4. Even when FFTs are used, over 80% of the time required by a spectral calculation is spent doing transforms whose cost can become excessive for physically complex, non-linear problems. The philosophy of pseudospectral approximation is to calculate in either spectral or physical space, according to whichever representation is more natural.

However there are problems associated with this method too - aliasing errors are introduced since pseudospectral methods set residuals zero only at collocation points. The evaluation of nonlinear products produces aliasing errors, that is, the bilinear products of the variables in physical space generate wave numbers higher than those retained in the original orthogonal series expansion (Givi, 1989). The pseudospectral approximation may be susceptible to numerical instability due to the aliasing terms. However most realistic physical problems have some kind of damping associated with them that limit aliasing and, along with it, aliasing instability. Aliasing errors can be reduced by shifting the collocation points and by truncating the Fourier coefficients outside of a sphere, and a combination of the two eliminates aliasing errors arising from quadratic nonlinearities (Orszag, 1972).

Some problems in dealing with the results of the pseudospectral simulations have been discussed by Leonard and Hill (1989). A summary of their discussion follows.

1. Realistic boundary conditions – full turbulence simulations with spectral methods have so far been limited to flows with periodic or no-slip boundary conditions, because fast transform methods can be used with Fourier and Chebyshev expansions.

2. Flows with variable physical properties – if the coefficients of viscosity are functions of position through temperature dependence, the number of additional transforms to
physical space and back to Fourier space, to evaluate the nonlinear viscous terms, is significantly increased.

3. Compressible flows – the problem with spectral solutions for compressible flows is that the disturbances are felt instantaneously throughout the computational domain when variables are expanded in global basis functions, whereas a finite rate of propagation is required for the solution to match physical phenomena.

4. Resolution of discontinuities – the use of global basis functions limits the resolutions of discontinuities and steep gradients. Gibbs ringing contaminates the solution of sharp gradients if the resolution is inadequate.

5. Statistical sample size – each simulation is only one member of an ensemble of numerical experiments and though statistical averages should be made over an ensemble of experiments, since a sufficient number of experiments would be excessively expensive, a quasi-ergodic assumption is made.

6. Resolution and time-step limitations – time-stepping errors can be minimized by having a sufficiently small time step controlled by the CFL criterion or the Courant number. Though high Courant numbers decrease the computer time needed for the simulation by increasing the time step, they introduce significant time-stepping errors. For simulations to be well resolved, the highest wave numbers in the computational box must be large enough to represent the smallest length scales in the flow and the integral length scale of the velocity field must be sufficiently small so that the periodic boundary conditions do not affect the accuracy of the solution.
Recent developments

Some of the more recent variations to the spectral method have been discussed by in
the review article by Hussaini and Zang, (1987) and in the review on turbulent reacting
flows by Givi (1989).

The most attractive approach to very large problems is to combine a less accurate but
more readily inverted preconditioning with multigrid techniques. In a spectral multigrid
method one combines iterations on the desired grid with (much cheaper) iterations on
successively coarser grids.

Spectral multi-domain techniques are a recent variation to the spectral method. These
may be applied to geometries for which a single, global expansion is either impossible or
else inappropriate. In a multidomain technique the full domain is divided into subdomains
which are either patched together at interfaces or else overlap. The interface conditions are
a crucial part of the patched multidomain methods.

Another alternative to true spectral methods are the quasi-spectral methods. These
methods employ Fourier expansions in all directions, but as a result of nonperiodic boundary
conditions in at least one direction, infinite-order accuracy is not attained. Quasi-spectral
methods have been used by Riley and Metcalfe (1980) and Curry et al (1984) to study
mixing-layers and Benard convection respectively.

Another variation is the spectral element method which has been discussed by Givi
(1989). In these methods, developed by Patera (1984), the accuracy of the spectral method
is combined with the versatility of the finite element methods and the approach is more
flexible than either spectral methods or finite element methods alone. The computational
domain is broken into a series of finite elements and within these elements the variables are
approximated by high-order Lagrangian interpolant through Chebyshev collocation points.
By using an appropriate time differencing scheme, the differential equation governing the
transport of the variable is decomposed into a non-linear hyperbolic and a linear elliptic equation. The hyperbolic part is solved using a pseudo-spectral method and finite element techniques are used for the elliptic equations (Givi; 1989).
APPENDIX D: SOME DERIVATIONS

Definition of selectivity

For the series-parallel reaction

\[ A + B \xrightleftharpoons{\kappa_1} R \]

\[ R + B \xrightleftharpoons{\kappa_2} S, \]

let \( A, B, R \) and \( S \) denote the moles of \( A, B, R \) and \( S \) in the system. Let, the initial moles of \( A \) be \( A_0 \), the initial moles of \( B \) be \( B_0 \), the initial moles of \( R \) be \( 0 \), and the initial moles of \( S \) be \( 0 \).

Let \( B \) reacted by first reaction be \( b_1 \) moles and \( B \) reacted by second reaction be \( b_2 \) moles. Thus \( B \) reacted is \( b_1 + b_2 \) moles and \( A \) reacted is \( b_1 \) moles, \( R \) formed by the first reaction is \( b_1 \) moles and \( R \) consumed by the second reaction is \( b_2 \) moles, and \( S \) formed is \( b_2 \) moles.

Thus \( B \) remaining is \( B = B_0 - (b_1 + b_2) \) moles, \( A \) remaining is \( A = A_0 - b_1 \) moles, and \( R \) remaining is \( R = b_1 - b_2 \) moles and \( S \) remaining is \( S = b_2 \) moles.

Thus \( A \) reacted is \( A_0 - A = b_1 = b_1 - b_2 + b_2 = R + S \)

\( B \) reacted is \( B_0 - B = b_1 + b_2 = b_1 - b_2 + 2b_2 = R + 2S \)

Thus the material balance leads to \( A_0 - A = R + S \) and \( B_0 - B = R + 2S \)

The definition of selectivity, according to Bourne, is the fraction of \( B \) which is finally converted to secondary product, \( S \). Here, the total amount of \( B \) reacted (to form \( R \) or \( S \))
is \( B_0 - B \), that is, \( R + 2S \), from the material balance. To form \( b_2 \) moles of \( S \) by the second reaction, \( b_2 \) moles of \( R \) and \( b_2 \) moles of \( B \) are needed. And to form \( b_2 \) moles of \( R \) by the first reaction, \( b_2 \) moles of \( B \) are needed. Thus the total amount of \( B \) reacted to form \( S \) is \( b_2 \) to form \( R \) and \( b_2 \) to react with that \( R \) to form \( S \), that is, \( 2b_2 \) or \( 2S \). Thus the definition translates to

\[
X_S = \frac{\text{Amount of } B \text{ reacted to form } S}{\text{Total amount of } B \text{ reacted}} = \frac{2S}{R + 2S}
\]

**Definition of length scales for various initial spectra**

First the general form for the different initial spectra will be given and definitions for the integral length scale, Taylor microscale and Kolmogorov length scale for the velocity field and integral length scale and Taylor microscale for the scalar field will be provided. Then the exact equations for the initial spectra and the specific forms for the length scales for the various initial spectra will be derived. Since the analysis is the same for all the spectra, explicit details will be provided for the Gaussian spectrum and only some details will be shown for the exponential spectrum.

**Gaussian spectrum:**

\[
E(k,0) = ak^4e^{-bk^3}
\]  
\( (6.1) \)

**Exponential spectrum:**

\[
E(k,0) = ak^3e^{-bk}
\]  
\( (6.2) \)

**Von Karman spectrum:**

\[
E(k,0) = \frac{a(kb)^4}{(1 + (kb)^2)^{\frac{3}{2}}}
\]  
\( (6.3) \)

The initial velocity spectrum is denoted as \( E(k,0) \) and the initial scalar spectrum is denoted as \( E_\theta(k,0) \). In general, the subscript \( \theta \) refers to the scalar field.

The conditions needed to determine \( a \) and \( b \) are
For the velocity field:

\[
\frac{dE(k)}{dk} = 0 \text{ at } k = k_0 \quad (6.4)
\]

\[
\int_0^\infty E(k)dk = \frac{3}{2}u'^2 \quad (6.5)
\]

For the scalar field:

\[
\frac{dE_\theta(k)}{dk} = 0 \text{ at } k = k_0 \quad (6.6)
\]

\[
\int_0^\infty E_\theta(k)dk = \theta^2 \quad (6.7)
\]

**Integral length scale, \( \Lambda_f \):**

\[
\Lambda_f = \frac{\pi}{2u'^2} \int_0^\infty \frac{E(k)}{k} dk \quad (6.8)
\]

**Taylor microscale, \( \lambda_\theta \):**

\[
\lambda_\theta = \left( \frac{15\nu u'^2}{\epsilon} \right)^{\frac{1}{3}} \quad (6.9)
\]

where the dissipation \( \epsilon \) is given by

\[
\epsilon = 2\nu \int_0^\infty k^2 E(k)dk
\]

**Kolmogorov length scale, \( \eta \):**

\[
\eta = \left( \frac{\nu^3}{\epsilon} \right)^{\frac{1}{4}} \quad (6.10)
\]

**Scalar integral length scale, \( \Lambda_\theta \):**

\[
\Lambda_\theta = \frac{\pi}{2\theta^2} \int_0^\infty \frac{E_\theta(k)}{k} dk \quad (6.11)
\]

**Scalar microscale, \( \lambda_\theta \):**

\[
\lambda_\theta = \left( \frac{12D\theta^2}{\epsilon_\theta} \right)^{\frac{1}{3}} \quad (6.12)
\]

where the scalar dissipation rate \( \epsilon_\theta \) is given by

\[
\epsilon_\theta = 2D \int_0^\infty k^2 E_\theta(k)dk
\]
Gaussian spectrum

Velocity field: The first step is to determine $a$ and $b$ in (6.1) using equations (6.4) and (6.5). (6.1) is differentiated with respect to $k$ to give

$$\frac{dE_k}{dk} = 4ak^3e^{-bk^2} - 2kbak^4e^{-bk^2}. \quad (6.13)$$

At $k = k_0$, equation (6.4) holds and so equation (6.13) reduces to

$$4ak_0^3e^{-bko^2} - 2k_0bako^4e^{-bko^2} = 0 \quad (6.14)$$

which leads to

$$b = \frac{2}{k_0^2}. \quad (6.15)$$

Now $a$ has to be determined using (6.5).

$$\int_0^\infty E(k) = \int_0^\infty ak^4e^{-2(k/k_0)^2} dk \quad (6.16)$$

$$= ak_0^5 \int_0^\infty (k/k_0)^4e^{-2(k/k_0)^2} dk \quad (6.17)$$

Let $2(k/k_0)^2 = x$, or, $k = k_0\sqrt{x/2}$, or, $dk = k_0/(2\sqrt{2x})dx$, \quad (6.18)

so (6.17) reduces to

$$\int_0^\infty E(k) = ak_0^5 \int_0^\infty (x/2)^2e^{-xk_0}/(2\sqrt{2x}) dx \quad (6.19)$$

$$= \frac{ak_0^5}{8\sqrt{2}} \int_0^\infty x^{3/2}e^{-x}dx. \quad (6.20)$$

Now the relation for $\Gamma$ functions is:

$$\Gamma(n) = \int_0^\infty t^{n-1}e^{-t} \quad (6.21)$$

$$\Gamma(m + 1/2) = \frac{1.3.5...(2m - 1)\sqrt{\pi}}{2^m} \quad (6.22)$$
for \( m=1,2,3 \ldots \) Equations (6.21) and (6.22) are used to simplify (6.20).

\[
\int_0^\infty E(k) = \frac{ak_0^5}{8\sqrt{2}} \Gamma(5/2) 
\]

\[
= \frac{ak_0^5}{8\sqrt{2}} \Gamma(2 + 1/2) 
\]

\[
= \frac{ak_0^5 1.3\sqrt{\pi}}{8\sqrt{2} \frac{2^2}{2^2}} 
\]

\[
= \frac{ak_0^5 3\sqrt{\pi}}{32\sqrt{2}} . 
\]

Therefore,

\[
\frac{3ak_0^5 \sqrt{\pi}}{32\sqrt{2}} = \frac{3u^2}{2} 
\]

which leads to

\[
a = \frac{16u^2}{k_0^5} \sqrt{\frac{2}{\pi}} 
\]

So the actual form of (6.1) is

\[
E(k,0) = 16u^2 \sqrt{\frac{2}{\pi k_0^4}} e^{-2(k/k_0)^2} . 
\]

The next step is to determine the different length scales.

1. Integral length scale:

Using (6.8) and (6.29),

\[
\Lambda_f = \frac{\pi}{2u^2} \int_0^\infty 16u^2 \sqrt{\frac{2}{\pi k_0^4}} e^{-2(k/k_0)^2} \frac{dk}{k} 
\]

\[
= 16/k_0^5 \sqrt{\frac{2}{\pi}} \int_0^\infty k^3 e^{-2(k/k_0)^2} \frac{dk}{k} . 
\]

Using the substitution (6.18),

\[
\Lambda_f = 16/k_0^5 \sqrt{\frac{2}{\pi}} \int_0^\infty \left(\frac{x}{2}\right)^{3/2} k_0^3 e^{-x} k_0 dx/(2\sqrt{x}) 
\]

\[
= 16/k_0^5 \sqrt{\frac{2}{\pi}} k_0^5/8 \int_0^\infty x^{3/2} / \sqrt{xe^{-x}} dx 
\]

\[
= \frac{16\sqrt{\pi} k_0^4}{8\sqrt{2}k_0^5} \int_0^\infty xe^{-x} dx 
\]

\[
= \sqrt{2\pi} \Gamma(2)/k_0 . 
\]
Therefore,
\[ \Lambda_f = \frac{\sqrt{2\pi}}{k_0}. \] (6.36)

2. Taylor microscale

The dissipation \( \epsilon \) has to be evaluated first.

\[ \epsilon = 2\nu \int_0^\infty k^3 E(k) dk \] (6.37)
\[ = 32u'^2 (2/\pi)^{1/2} k^5 e^{-2(k/k_0)^2} dk/k_0^5 \] (6.38)
\[ = 32u'^2 (2/\pi)^{1/2} \nu k_0 \int_0^\infty (k/k_0)^6 e^{-2(k/k_0)^2} dk. \] (6.39)

Using the substitution (6.18),

\[ \epsilon = 32u'^2 (2/\pi)^{1/2} \nu k_0 \int_0^\infty (z/2)^3 e^{-z} k_0 dx/(2\sqrt{2}x) \] (6.40)
\[ = 32u'^2 (2/\pi)^{1/2} \nu k_0^2/(16\sqrt{2}) \int_0^\infty x^{5/2} e^{-x} dx \] (6.41)
\[ = 2/\sqrt{\pi} u'^2 \nu k_0^2 \Gamma(7/2) \] (6.42)
\[ = 2/\sqrt{\pi} u'^2 \nu k_0^2 \frac{1.35.\sqrt{\pi}}{2^3}. \] (6.43)

That reduces to

\[ \epsilon = 15/4 u'^2 \nu k_0^2. \] (6.44)

Substituting (6.44) in (6.9) gives

\[ \lambda_g = 2/k_0. \] (6.45)

3. Kolmogorov length scale

Substituting (6.44) in (6.10) gives

\[ \eta = (15)^{-1/4} \sqrt{\frac{2\nu}{u'k_0}}. \] (6.46)

**Scalar field:** The scalar spectrum has exactly the same form as (6.1) and is written as

\[ E_\theta = ak^4 e^{-5k^2} \] (6.47)
where $a$ and $b$ have to determined from (6.6) and (6.7). (6.47) differentiated with respect to $k$ gives
\[ \frac{dE_\theta}{dk} = 4ak^3e^{-bk^2} - 2kbak^4e^{-bk^2}. \] (6.48)

At $k = k_0$, equation (6.6) holds and so equation (6.48) reduces to
\[ 4ak_0^3e^{-bk_0^2} - 2k_0bak_0^4e^{-bk_0^2} = 0 \] (6.49)
which leads to
\[ b = \frac{2}{k_0^2}. \] (6.50)

Now $a$ has to be determined using (6.7).
\[ \int_0^t E_\theta(k) = \int_0^t ak^4e^{-2(k/k_0)^2}dk. \] (6.51)

This integral has already been evaluated in (6.17) through (6.26). Using the final result (6.26), (6.51) becomes
\[ \int_0^t E_\theta(k) = ak_0^5\sqrt{\pi} \frac{3\sqrt{2}}{32\sqrt{2}}. \] (6.52)
Therefore,
\[ \frac{3ak_0^5\sqrt{\pi}}{32\sqrt{2}} = \theta^2 \] (6.53)
which leads to
\[ a = \frac{32\sqrt{2}}{3\sqrt{\pi} k_0^5}. \] (6.54)

So the actual form of (6.47) is
\[ E_\theta(k, 0) = \frac{32}{3}\theta^2 \sqrt{\frac{2\pi}{k_0^5}} e^{-2(k/k_0)^2}. \] (6.55)

The next step is to determine the different scalar length scales.

1. Integral length scale:

Using (6.11) and (6.55),
\[ \Lambda_\theta = \frac{\pi}{2\theta^2} \int_0^t \frac{32}{3}\theta^2 \sqrt{\frac{2\pi}{k_0^5}} e^{-2(k/k_0)^2}dk/k \]
\[ = \frac{\pi 16}{3k_0^5} \int_0^t \frac{2\pi}{k_0^5} e^{-2(k/k_0)^2}dk. \] (6.56)
Using the substitution (6.18),

\[
\Lambda_\theta = \frac{\sqrt{2\pi}16}{3k_0^6} \int_0^\infty k_0^3(x/2)^{3/2}e^{-x}k_0dx/(2\sqrt{2}x) \tag{6.58}
\]

\[
= 2\sqrt{2\pi} \int_0^\infty xe^{-x}dx \tag{6.59}
\]

\[
= \frac{2\sqrt{2\pi}}{3k_0} \Gamma(2). \tag{6.60}
\]

Thus

\[
\Lambda_\theta = \frac{2\sqrt{2\pi}}{3k_0}. \tag{6.61}
\]

2. Taylor microscale:

\[
\frac{2}{\lambda_\theta^2} = \frac{1}{3\theta^2} \int_0^\infty k^2E_\theta(k)dk. \tag{6.62}
\]

Now,

\[
\int_0^\infty k^2E_\theta(k)dk = \frac{32}{3} \theta^2 \sqrt{\frac{k^0}{\pi k_0^5}} e^{-2(k/k_0)^2} \tag{6.63}
\]

Making the substitution (6.18)

\[
\int_0^\infty k^2E_\theta(k)dk = \frac{2\theta^2 k_0^2}{3\sqrt{\pi}} \int_0^\infty x^{5/2}e^{-x}dx \tag{6.64}
\]

\[
= \frac{2\theta^2 k_0^2}{3\sqrt{\pi}} \Gamma(7/2) \tag{6.65}
\]

\[
= \frac{2\theta^2 k_0^2}{3\sqrt{\pi}} \frac{53\cdot\sqrt{\pi}}{2^3} \tag{6.66}
\]

\[
= \frac{2\theta^2 k_0^2}{3\sqrt{\pi}} \frac{15\sqrt{\pi}}{8} \tag{6.67}
\]

\[
= \frac{5\theta^2 k_0^2}{4}. \tag{6.68}
\]

Therefore,

\[
\frac{2}{\lambda_\theta^2} = \frac{1}{3\theta^2} \frac{5\theta^2 k_0^2}{4} \tag{6.69}
\]
and,

\[ \lambda_0 = \frac{2}{k_0} \sqrt{\frac{6}{5}}. \]  (6.70)

### Exponential spectrum

**Velocity field** (6.4) and (6.5) are used to evaluate \( a \) and \( b \) in (6.2). (6.2) is differentiated with respect to \( k \) and at \( k = k_0 \),

\[ 3ak_0^2e^{-bk_0} - ak_0^3be^{-bk_0} = 0 \]  (6.71)

which leads to

\[ b = \frac{3}{k_0^2}. \]  (6.72)

Now,

\[ \int_0^\infty E(k)dk = \int_0^\infty ak^3e^{-3(k/k_0)}dk \]  (6.73)

\[ = ak_0^3\int_0^\infty (k/k_0)^3e^{-3(k/k_0)}dk. \]  (6.74)

Let \( 3k/k_0 = x \), or, \( dk = k_0dx/3 \),

\[ \int_0^\infty E(k)dk = \frac{ak_0^3}{3^3} \int_0^\infty x^3e^{-x}k_0dx/3 \]  (6.76)

\[ = \frac{ak_0^3}{81} \int_0^\infty x^3e^{-x}k_0dx \]  (6.77)

\[ = \frac{ak_0^3}{81} \Gamma(4) \]  (6.78)

\[ \frac{ak_0^3}{81} = \frac{3u^2}{2} \]  (6.79)

leading to

\[ a = \frac{81u^2}{4k_0^4}. \]  (6.80)
So the actual form of (6.2) is

\[ E(k) = \frac{81u^2}{4k_0^4} k^3 e^{-3(k/k_0)}. \]  \hspace{1cm} (6.81)

1. Integral length scale:

\[ \Lambda_f = \frac{\pi}{2} \int_0^{\infty} \frac{81u^2}{4k_0^4} k^3 e^{-3(k/k_0)} dk/k \]

Using the substitution (6.75)

\[ \Lambda_f = \frac{3\pi}{8k_0} \int_0^{\infty} x^2 e^{-x} dx \]

Thus

\[ \Lambda_f = \frac{3\pi}{4k_0}. \] \hspace{1cm} (6.86)

2. Taylor microscale

\[ \epsilon = \frac{2
\nu 81u^2}{4k_0^4} \int_0^{\infty} k^5 e^{-3(k/k_0)} dk. \]  \hspace{1cm} (6.87)

Using (6.75),

\[ \epsilon = \frac{\nu u^2 k_0^2}{18} \Gamma(6). \] \hspace{1cm} (6.88)

Thus,

\[ \epsilon = \frac{20}{3} \nu u^2 k_0^2. \] \hspace{1cm} (6.89)

Substituting (6.89) in (6.9) gives

\[ \lambda_g = \frac{3}{2k_0}. \] \hspace{1cm} (6.90)

3. Kolmogorov length scale Substituting (6.89) in (6.9) gives

\[ \eta = \left( \frac{3}{5} \right)^{1/4} \sqrt{\frac{\nu}{2u'k_0}}. \] \hspace{1cm} (6.91)
Scalar field: The same kind of analysis needs to be done and only the results are being presented.

\[ b = \frac{3}{k_0} , \quad (6.92) \]
\[ a = \frac{27 \theta^2}{2 k_0^2} , \quad (6.93) \]
\[ E_\theta(k) = \frac{27 \theta^2}{2 k_0^3} k^3 e^{-3(k/k_0)} , \quad (6.94) \]
\[ \lambda_\theta = \frac{\pi}{2k_0} , \quad (6.95) \]
\[ \lambda_\theta = \frac{3\sqrt{3}}{\sqrt{10}k_0} . \quad (6.96) \]

Von Karman spectrum

Only \( a \) and \( b \) can be determined analytically, the length scales cannot be obtained since the integral \( \int_0^\infty E(k)dk \) does not converge for this form of the spectrum.

\[ b = \frac{2\pi}{k_0} , \quad (6.97) \]
\[ a = \frac{8\sqrt{2} \mu^2}{\pi} \frac{1}{k_0} . \quad (6.98) \]

The table below summarizes the theoretical values for the different spectra.
Table 6.1: Theoretical values of length scales for different initial spectra

<table>
<thead>
<tr>
<th>Label</th>
<th>( E(k,0) )</th>
<th>( a )</th>
<th>( b )</th>
<th>( \Lambda_f )</th>
<th>( \lambda_g )</th>
<th>( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>( a k^4 e^{-bk^2} )</td>
<td>( \frac{16u^2}{k_0^6} \sqrt{\frac{2}{\pi}} )</td>
<td>( \frac{2b}{k_0^2} )</td>
<td>( \frac{\sqrt{2\pi}}{k_0} )</td>
<td>( \frac{2}{k_0} )</td>
<td>( (15)^{\frac{1}{4}} \sqrt{\frac{2\nu}{u'k_0}} )</td>
</tr>
<tr>
<td>Y</td>
<td>( a k^3 e^{-bk} )</td>
<td>( \frac{81u^2}{4k_0^4} )</td>
<td>( \frac{3}{k_0} )</td>
<td>( \frac{3\pi}{4k_0} )</td>
<td>( \frac{3}{2k_0} )</td>
<td>( (\frac{3}{8})^{\frac{1}{4}} \sqrt{\frac{\nu}{2u'k_0}} )</td>
</tr>
<tr>
<td>Z</td>
<td>( \frac{a(kb)^4}{(1 + (kb)^2)^3} )</td>
<td>( \frac{8\sqrt{2u^2}}{\pi k_0} )</td>
<td>( \frac{\sqrt{2\pi}}{k_0} )</td>
<td>( _ )</td>
<td>( _ )</td>
<td>( _ )</td>
</tr>
</tbody>
</table>
APPENDIX E: GENERALIZATION OF THE BRODKEY-LEWALLE CLOSURE

A careful study of the different closure models (for $\overline{c_Bc_R}$) shows that though none of the models predict $\overline{c_Bc_R}$ satisfactorily, the Brodkey-Lewalle closure model is the only one with a theoretical basis since it is based on an extension of Toor's hypothesis. So the Brodkey-Lewalle closure was studied in detail and a modification proposed.

Toor's hypothesis and its extension

According to Toor's hypothesis, the evolution of quantities like $\overline{c_Ac_B}$, $\overline{c_A^2}$, etc should not depend on the rate of the reaction. This suggests that the terms involving the kinetic rate constant do not contribute to the evolution of the covariance terms. The evolution equation for $\overline{c_Ac_B}$ for a single reaction is

$$
\frac{d(\overline{c_Ac_B})}{dt} = -2D \frac{\partial c_A}{\partial z_j} \frac{\partial c_B}{\partial z_j} - k_1[\overline{c_A^2c_B} + \overline{C_Ac_Ac_B} + \overline{c_Ac_B} + \overline{c_A^2c_B} + \overline{C_Bc_A^2} + \overline{c_Bc_A^2}] .
$$

(6.1)

Toor's conjecture was that for a single reaction, term(2) in equation (6.1) is zero, that is,

$$
k_1[\overline{c_Ac_B} + \overline{c_A^2c_B} + \overline{C_Ac_Ac_B} + \overline{c_Ac_B} + \overline{c_A^2c_B} + \overline{C_Bc_A^2} + \overline{c_Bc_A^2}] = 0
$$

(6.2)

approximately for all values of $k_1$. This hypothesis results from the consideration of the two extreme cases of $k_1 \to 0$ and $k_1 \to \infty$: If $k_1 \to \infty$, then the reaction term (2) in eqn
(6.1) becomes very large and since it is not balanced by any other term in the equation, the term has to be almost zero. On the other hand, if $f_{ci} \rightarrow 0$, then $c_A c_B$ decreases only by the action of diffusion. Thus, in the two limits (6.2) holds. As another example, for the case of a single reaction, the kinetic term in the evolution equation for $c_A$ is

$$- k_1 [C_A c_A c_B + C_B c_A^2 + c_A^2 c_B]$$

and the extension to Toor's hypothesis suggests that

$$- k_1 [C_A c_A c_B + C_B c_A^2 + c_A^2 c_B] = 0.$$  (6.4)

For the case with multiple reactions, such as the parallel-consecutive reaction scheme,

$$A + B \xrightarrow{k_1} R$$

$$R + B \xrightarrow{k_2} S,$$  (6.5)

the scenario is more complicated since two rate constants are involved. The evolution equation for $c_A c_B$ is

$$\frac{d(c_A c_B)}{dt} = - 2D \frac{\partial c_A}{\partial x_j} \frac{\partial c_B}{\partial x_j}$$

$$(1)$$

$$- k_1 [C_A c_A^3 + C_B c_A^2 c_B + C_A^2 c_B^2 + C_A c_A c_B + C_B c_A^2 + c_B c_A^2]$$

$$(2)$$

$$- k_2 [C_B c_A c_R + C_R c_A c_B + c_A c_R c_B]$$

$$(3)$$

and the evolution equation for $c_B c_R$ is

$$\frac{d(c_B c_R)}{dt} = - 2D \frac{\partial c_B}{\partial x_j} \frac{\partial c_R}{\partial x_j}$$

$$- k_1 [C_A c_A c_B + C_B c_A c_R - C_A c_A^2 - C_B c_A c_R - c_A c_R c_B]$$

$$- k_2 [C_B c_A^2 + C_R c_A c_B + C_B c_A c_R + C_B c_A c_R + C_R c_B^2 + c_R c_B^2].$$  (6.7)
Brodkey's interpretation of the extension of Toor's hypothesis to the second reaction is that the extension can be applied to the second reaction independently, i.e.,

$$k_1[\overline{C_A c_B} + \overline{C_B c_A} + \overline{C_A c_B} + \overline{C_B c_A} + \overline{e_A C_B(C_A + C_B)}] = 0 \quad \text{(6.8)}$$

$$k_2[\overline{C_B c_A c_R} + \overline{C_R c_A c_B} + \overline{e_A C_B c_R}] = 0 \quad \text{(6.9)}$$

Our interpretation of the extension to Toor's hypothesis is a little different from Brodkey's. We claim that (6.8) and (6.9) need not be zero independently, but that their sum will be zero, that is, the sum of the kinetic terms will be zero. So, our extension of Toor's hypothesis is

$$k_1[\overline{C_A c_B} + \overline{C_B c_A} + \overline{C_A c_B} + \overline{C_B c_A} + \overline{e_A C_B(C_A + C_B)}] + k_2[\overline{C_B c_A c_R} + \overline{C_R c_A c_B} + \overline{e_A C_B c_R}] = 0 \quad \text{(6.10)}$$

For the reaction scheme (6.5), the terms involving reaction in the evolution equations for $\overline{C_A c_B}$, $\overline{C_B c_R}$, $\overline{C_A c_R}$, $\overline{C_B c_A}$ are as follows:

For $\overline{C_A c_B}$,

$$- k_1[\overline{C_A c_B} + \overline{C_B c_A} + \overline{C_A c_B} + \overline{C_B c_A} + \overline{e_A C_B(C_A + C_B)}]$$

$$- k_2[\overline{C_B c_A c_R} + \overline{C_R c_A c_B} + \overline{e_A C_B c_R}] \quad \text{(6.11)}$$

For $\overline{C_B c_R}$,

$$- k_1[\overline{C_A c_B} + \overline{C_B c_A} - \overline{C_A c_B} - \overline{C_B c_A} + \overline{e_A C_B c_R} - \overline{c_A c_B^2}]$$

$$- k_2[\overline{C_B c_R} + \overline{C_R c_B c_R} + \overline{c_B c_R^2} + \overline{C_B c_B c_R} + \overline{C_R c_B^2} + \overline{c_R c_B^2}] \quad \text{(6.12)}$$

For $\overline{C_A c_R}$,

$$k_1[\overline{C_A c_B} + \overline{C_B c_A} + \overline{C_A c_B} + \overline{C_B c_A} + \overline{e_A C_B c_R} + \overline{c_A c_B c_R}]$$

$$- k_2[\overline{C_B c_A c_R} + \overline{C_R c_A c_B} + \overline{e_A C_B c_R}] \quad \text{(6.13)}$$
For $c_A^2$,
\[-k_1[C_A c_A c_B + C_B c_A^2 + c_A^3 c_B] \] (6.14)

For $c_B^2$
\[-k_1[C_A c_B^2 + C_B c_A c_B + c_A^3 c_B] - k_2[C_B c_B c_R + C_R c_B^2 + c_B^3 c_R] \] (6.15)

**Brodkey-Lewalle closure**

First, we will develop Brodkey-Lewalle's closure. According to Brodkey, Toor's hypothesis applied to (6.11) through (6.15) translates those equations to
\[\bar{C} c_A + \bar{C} c_B + \bar{C} c_C + \bar{C} c_A c_B + \bar{C} c_B c_C = 0 \] (6.16)
\[\bar{C} c_B + \bar{C} c_A c_B + \bar{C} c_b c_C = 0 \] (6.17)
\[\bar{C} c_A c_B + \bar{C} c_A c_B + \bar{C} c_A c_B = 0 \] (6.18)
\[\bar{C} c_b c_R + \bar{C} c_b c_R + \bar{C} c_b c_R = 0 \] (6.19)
\[\bar{C} c_A c_B + \bar{C} c_A c_B + \bar{C} c_A c_B + \bar{C} c_A c_B = 0 \] (6.20)
\[\bar{C} c_B c_R + \bar{C} c_B c_R + \bar{C} c_B c_R \] (Same as (6.17))
\[\bar{C} c_A c_B + \bar{C} c_A c_B + \bar{C} c_A c_B = 0 \] (6.21)
\[\bar{C} c_A c_B + \bar{C} c_A c_B + \bar{C} c_A c_B = 0 \] (6.22)
\[\bar{C} c_B c_R + \bar{C} c_B c_R + \bar{C} c_B c_R = 0 \] (6.23)

Now, (6.18) + (6.22) - (6.17) gives
\[\bar{C} c_A c_B = \bar{C} c_B c_R \] (6.24)
\[\bar{c} c_B c_R = \bar{c} c_B c_R \] (6.25)

(6.25) is the Brodkey-Lewalle closure.
Generalization of the Brodkey-Lewalle closure

Now we proceed to formulate the generalization of the Brodkey-Lewalle closure. According to our interpretation of the extension to Toor's hypothesis, the equations we get are

\[ k_1[CAc_B^2 + c_A^2c_B + CAc_B^2 + CBc_A^2 + c_Ac_Bc_A + c_Ac_Bc_B] + k_2[CBc_Ac_R + CRc_Ac_B + c_Ac_Bc_R] = 0 \quad (6.26) \]

\[ k_1[CAc_Bc_R + CBc_Ac_R - CAc_B^2 - CBc_Ac_R + c_Ac_Bc_R - c_Ac_B] \]
\[ + k_2[CBc_R^2 + CRc_Bc_R + c_Bc_R + CBc_Bc_R + CRc_B^2 + c_Rc_B^2] = 0 \quad (6.27) \]

\[ k_1[CAc_Bc_B + CBc_A^2 + c_Ac_B + CBc_Bc_R + CBc_Ac_B + c_Ac_Bc_B] \]
\[ - k_2[CBc_Ac_R + CRc_Ac_B + c_Ac_Bc_R] = 0 \quad (6.28) \]

\[ k_1[CAc_Ac_B + CBc_A^2 + c_Ac_B] = 0 \quad (6.29) \]

\[ k_1[CAc_B^2 + CBc_Ac_B + c_Ac_B] - k_2[CBc_Ac_R + CRc_B^2 + c_Bc_R] = 0 \quad (6.30) \]

We would like to develop a closure using these equations and some reasonable assumptions.

The case of equal rate constants

If \( k_1 = k_2 \), (6.26)-(6.30) are simplified.

(6.26) becomes

\[ c_Ac_B + c_Ac_B + CAc_B^2 + CBc_A^2 + c_Ac_Bc_A + c_Ac_Bc_B] \]
\[ + [CBc_Ac_R + CRc_Ac_B + c_Ac_Bc_R] = 0 \quad (6.31) \]

(6.27) becomes

\[ CAc_Bc_R + CBc_Ac_R - CAc_B^2 - CBc_Ac_R + c_Ac_Bc_R - c_Ac_B \]
\[ + [CBc_R^2 + CRc_Bc_R + c_Bc_R + CRc_B^2 + c_Rc_B^2] = 0 \quad (6.32) \]
(6.28) becomes

$$\left[ C_A^c A^c B^c + C_B^c B^c A^c + C_A A^c B^c R^c + C_B B^c A^c R^c + C_A C^c A^c B^c R^c + C_B C^c B^c A^c R^c \right]$$

$$- \left[ C_B B^c A^c R^c + C_B^c B^c A^c R^c + C_A C^c A^c B^c R^c \right] = 0$$

(6.33)

(6.29) remains the same

$$\left[ C_A^c A^c B^c + C_B^c B^c A^c + C_A^c A^c B^c \right] = 0$$

(6.34)

(6.30) becomes

$$\left[ C_A^c B^c A^c B^c + C_A^c C^c A^c B^c \right] - \left[ C_B^c B^c B^c R^c + C_B^c B^c A^c R^c + C_A^c C^c B^c R^c \right] = 0$$

(6.35)

(6.28) - (6.29) gives

$$C_A^c \overline{B^c R^c} = C_R^c \overline{A^c B^c}$$

(6.36)

$$\overline{B^c R^c} = \frac{C_R^c \overline{A^c B^c}}{C_A^c}$$

(6.37)

And (6.37) is the Brodkey-Lewalle closure!

**General case of unequal rate constants**

Some simplifying assumptions necessary were:

1. \( \overline{c^c_A} = \overline{c^c_B} \)
2. \( \overline{c_A A^c B^c R^c} = 0 \)
3. \( \overline{c^c_B B^c R^c} = 0 \)

The equations (6.26)-(6.30) become

$$k_1 \left[ \overline{c^c_A B^c} + \overline{c^c_A c^c B^c} + \overline{c^c_A c^c A^c} + \overline{c_B B^c A^c} + \overline{c_A A^c B^c} + \overline{c_A B^c B^c} \right]$$

$$+ k_2 \left[ \overline{c_B B^c A^c} + \overline{c_B c^c A^c B^c} \right] = 0$$

(6.38)
\begin{align*}
&k_1[C_A^2 \overline{C_B^2} + C_B \overline{C_A^2} - C_A \overline{C_R^2} - C_B \overline{C_A^2} - \overline{C_A^2}]
+ &k_2[C_B^2 \overline{C_B^2} + C_R^2 \overline{C_B^2} + \overline{C_B^2} + C_B \overline{C_B^2} + C_R \overline{C_A^2} + \overline{C_A^2}] = 0 \quad (6.39) \\
&k_1[C_A^2 \overline{C_B^2} + C_B^2 \overline{C_A^2} + \overline{C_A^2} + C_A \overline{C_B^2} + C_B \overline{C_A^2} + \overline{C_B^2}] = 0 \\
&- k_2[C_B \overline{C_A^2} + \overline{C_R^2} + \overline{C_A^2} + \overline{C_A^2}] = 0 \quad (6.40) \\
&- k_1[C_A^2 \overline{C_B^2} + C_B^2 \overline{C_A^2} + \overline{C_A^2}] = 0 \quad (6.41) \\
&- k_1[C_A^2 \overline{C_A^2} + C_B \overline{C_A^2} + \overline{C_A^2}] - k_2[C_B \overline{C_B^2} + \overline{C_A^2}] = 0 \quad (6.42)

\text{From (6.41),} \\
&\overline{c_A^2} = -[C_A \overline{C_A^2} + \overline{c_A^2} \overline{C_B}] \quad (6.43)

\text{Substituting (6.43) in (6.38),} \\
&k_1[C_A^2 \overline{C_B^2} + C_B^2 \overline{C_A^2} + \overline{c_A^2}] + k_2[C_B \overline{C_A^2} + C_B \overline{C_A^2}] = 0 \quad (6.44) \\
&\text{or,} \quad \overline{c_A^2} = -\frac{k_2}{k_1} \overline{C_B \overline{C_A^2}} - [C_A^2 \overline{C_A^2} + C_B \overline{C_B^2} + \frac{k_2}{k_1} \overline{C_B \overline{C_A^2}}] \quad (6.45)

\text{Substituting (6.43) in (6.40),} \\
&k_1 C_A \overline{C_B^2} - (k_1 \overline{C_B} - k_2 \overline{C_B}) \overline{C_A^2} - k_2 \overline{C_R \overline{C_A^2}} = 0 \quad (6.46)

\text{Substituting (6.45) in (6.42),} \\
&-k_2 \overline{C_B \overline{C_A^2}} - k_2 \overline{C_R \overline{C_A^2}} + k_2 \overline{C_B \overline{C_B^2}} + k_2 \overline{C_B \overline{C_B^2}} = 0 \quad (6.47) \\
&\text{or,} \quad -k_2 \overline{C_B \overline{C_A^2}} - k_2 \overline{C_B \overline{C_A^2}} = 0 \quad (6.48)

\text{Multiply (6.46) by } k_2 \\
&k_1 k_2 \overline{C_A \overline{C_B^2}} - (k_1 - k_2) k_2 \overline{C_B \overline{C_A^2}} = 0 \quad (6.49)

\text{Multiply (6.48) by } (k_1 - k_2) \\
&(k_1 - k_2) k_2 \overline{C_B \overline{C_B^2}} - (k_1 - k_2) k_2 \overline{C_B \overline{C_A^2}} - (k_1 - k_2) k_2 \overline{C_B \overline{C_A^2}} + (k_1 - k_2) k_2 \overline{C_R \overline{C_A^2}} = 0 \quad (6.50)
Adding (6.49) and (6.50)

\[ \epsilon_B c_R \left[ k_1 k_2 (C_A + C_B) - k^2_C C_B \right] - k_1 k_2 \overline{C_R} c_A c_B + k_1 k_2 \overline{C_A C_B} - k_1 \overline{k_2 C_A C_B} = 0 \] (6.51)

or, \[ \epsilon_B c_R = \frac{k_1 \overline{C_R} (c_A c_B - c_A^2)}{k_1 (C_A + C_B) - k_2 C_B} \] (6.52)

Thus (6.52) is the proposed Hill-Chakrabarti generalization of the Brodkey-Lewalle closure.

If \[ k_1 = k_2 \] :

\[ \epsilon_B c_R = \frac{k_1 \overline{C_R} (c_A c_B - c_A^2) + k_1 \overline{C_R c_A^2}}{k_1 (C_A + C_B) - k_1 C_B} \] (6.53)

That reduces to

\[ \epsilon_B c_R = \frac{\overline{C_R c_A c_B}}{C_A} \] (6.54)

which is the Brodkey-Lewalle closure !!!
APPENDIX F: REFERENCES TO APPENDIX MATERIAL


nous turbulence. Private communication.


t numerical simulations. AIChe J. 34(6):1039-1047.

lications. SIAM, Philadelphia.

Heeb, T.G., and R.S. Brodkey. 1990. Examination of turbulent mixing with multiple second­
order chemical reactions by the statistical analysis technique. AIChe J. 36(10):1457-1470.

Mech. 8:135-161.


Kline, S.J., and P.W. Runstadler. 1959. Some preliminary results of visual studies of the


