First-Order Closure Theories for Series-Parallel Reaction in Simulated Homogeneous Turbulence

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Simple first-order closure models for covariances of concentration fluctuations, for use in modeling turbulent flow reactors, were tested by direct numerical simulations. Concentration covariances and other statistical functions were evaluated for a series-parallel reaction scheme in decaying, homogeneous turbulent flow. The simulations involve solving the unsteady Navier-Stokes and mass conservation equations by a pseudo-spectral method in a 64^3 *wavenumber domain, with initially segregated reactants, for an initial turbulence Reynolds number of 29.9. Simulation results show that covariances of concentration fluctuations normalized with respect to mean concentration values are almost constant and that the time dependence of concentration covariances can be estimated if the mean concentrations are known at any one time after the initial time. Predictions of the first-order closure models of Bourne and Toor, Brodkey and Lewalle, Li and Toor, and Dutta and Tarbell were compared to simulation results. While none of these closures are satisfactory for all the conditions tested, the Brodkey-Lewalle closure agrees best with the simulations.*

Introduction

Complex chemical reactions in turbulent flow are important in many manufacturing processes, and the complicated chemistry in such cases can usually be represented by a combination of series and parallel reactions. These series or parallel reaction steps often produce undesirable byproducts, and so the effective yield of desired product is reduced, giving rise to the problem of chemical selectivity. Some of the areas affected by this problem include chemical processing, air pollution, and combustion. Knowledge about chemical selectivity has been limited due to difficulties encountered in conducting turbulent reacting flow experiments under controlled conditions.

There have been many studies in support of a closure for the reaction term for the case of a single-step reaction. Some of these were summarized by Leonard et al. (1995). Studies for the case of complex chemistry are fewer. Chakrabarti and Hill (1990), Gao and O'Brien (1991) and Chakrabarti et al. (1995) have reported their findings on the subject of chemical selectivity for a series-parallel reaction using direct numerical simulations. The simulations involved solving the unsteady, three-dimensional Navier-Stokes equations and mass conservation equations in homogeneous turbulence for a series-parallel reaction. The differences in behavior of a single reaction system and a multiple reaction system have been discussed in Chakrabarti et al. (1995). Frankel et al. (1995) have used a linear eddy model (Kerstein, 1992) to study selectivity for a series-parallel reaction and have compared their model predictions to the DNS results of Chakrabarti (1991). The literature on closure schemes for a series-parallel reaction scheme is fairly limited but includes first-order closure models, mechanistic, and stochastic models. For example, Tsai and Fox (1995) use a pdf approach in their Generalized IEM (GIEM) model and Frankel et al. (1995) use a stochastic model.

In this article, direct numerical simulations (DNS) are used to evaluate covariances of concentration fluctuations for a series-parallel reaction. The behavior of the covariances is analyzed, and the first-order closure models of Bourne and Toor (1977), Brodkey and Lewalle (1985), Li and Toor (1986), and Dutta and Tarbell (1989) are examined.

Background

The present study deals with one of the simplest representations of complex chemistry, the single series-parallel reaction scheme

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$$\begin{aligned} A + B &\xrightarrow{k_1} R \\ R + B &\xrightarrow{k_2} S, \end{aligned} \tag{1}$$

where A and B are the reactants, the intermediate product R is the desired product, and S is the undesired product. The rates of depletion and formation of reactants and products may be expressed in terms of the instantaneous concentrations and the kinetic rate constants. For example, the rate of formation of R is

$$r_R = \frac{dC_R}{dt} = k_1 C_A C_B - k_2 C_B C_R. \tag{2}$$

The measure of selectivity X_S (Bourne et al., 1981; Chakrabarti et al., 1995) used for this reaction pair is often given by

$$X_S = \frac{2\bar{C}_S}{\left(2\bar{C}_S + \bar{C}_R\right)}. \tag{3}$$

If Reynolds' decomposition is applied to the concentration fields $C_i = \bar{C}_i + c_i$ where $\bar{C}_i$ is the average concentration and c_i is the fluctuating component of species i denoted by $c_i = a$, b, r for species A, B, R, then the averaged rate expression for the formation of species R, for example, is the averaged form of Eq. 2, that is

$$\overline{r_R} = k_1\left(\bar{C}_A \bar{C}_B + \overline{ab}\right) - k_2\left(\bar{C}_B \bar{C}_R + \overline{br}\right) \tag{4}$$

where $\overline{ab}$ and $\overline{br}$ are the covariances of the concentration fluctuations of species A, B, and R. (The overbar is time averaged or volume averaged value.) Equation 4 is used in conjunction with the mass conservation Eq. 13.

The first-order closure models provide relationships between second-order correlations such as $\overline{ab}$, $\overline{br}$ and the mean quantities $\bar{C}_A$, $\bar{C}_B$ or $\bar{C}_R$, and are thus essentially algebraic in nature. These models deal with the closure of the reaction term only, using the moment formulation described above. This article deals with first-order closure models only.

Toor (1969) was the first to propose a first-order closure method for reacting systems involving two species and finite rate chemistry. He suggested that the covariance of reactant concentrations $\overline{ab}$ is independent of the speed of the reaction, that is, the covariance depends only on the hydrodynamics and not on the reaction rate. The closed form of $\overline{ab}$, as suggested by Toor, is

$$\overline{ab} = \overline{(ab)}_0\left(\overline{a^2}/\overline{a_0^2}\right)_m \tag{5}$$

where the subscript m denotes values in the absence of reaction and the subscript 0 denotes initial values. This closure has been widely used and is the basis for many other models (see Givi and McMurtry, 1988; Leonard and Hill, 1989; Leonard et al., 1995).

Table 1. Summary of Some First-Order Closure Theories

Closures	$\overline{ab}$	$\overline{br}$
Toor (1969)	$(\overline{ab})_0(\overline{a^2}/\overline{a_0^2})_m$	—
Bourne and Toor (1977)	$(\overline{ab})_0(\overline{a^2}/\overline{a_0^2})_m$	≈ 0
Brodkey and Lewalle (1985)	$(\overline{a^2})_m$	$\overline{ab}(\bar{C}_R/\bar{C}_A)$
Li and Toor (1986)	—	$(\hat{C}_B - \bar{C}_S)(\hat{C}_R - \bar{C}_S) - C_B C_S$
Dutta and Tarbell (1989)	$-I_s(\bar{C}_A\overline{C_{B0}} + \bar{C}_B\overline{C_{A0}} - \bar{C}_A\bar{C}_B)$	$-I_s\bar{C}_R(\overline{C_{B0}} - \bar{C}_B)$

First-order closure schemes for the covariance $\overline{br}$, for a series-parallel reaction scheme, as proposed by Bourne and Toor (1977), Brodkey and Lewalle (1985), Li and Toor (1986), and Dutta and Tarbell (1989) are summarized in Table 1 and briefly stated below. Unless mentioned otherwise, the closure for $\overline{ab}$ is Toor's closure (Eq. 5).

The *Bourne-Toor* closure (Bourne and Toor, 1977) is based on the application of turbulent momentum and mass-transfer equations to determine velocity fluctuations and to relate them to concentration fluctuations and thus to local reaction rates. For a nonpremixed feed, they claim $\overline{ab} < 0$ and $\overline{br} \approx 0$, therefore, we take their closure for our case of nonpremixed feed to be

$$\overline{br} = 0. \tag{6}$$

The *Li-Toor* closure (Li and Toor, 1986) is based on a conserved scalar approach and is intended for the case where the reactants are segregated and the first reaction is almost diffusion controlled (that is, k_1 is very large compared to k_2). Time-averaged radial gradients and axial diffusion are neglected in the analysis. Their proposed closure is

$$\overline{br} = \left(\hat{C}_B - \bar{C}_S\right)\left(\hat{C}_R - \bar{C}_S\right) - \bar{C}_B \bar{C}_S, \tag{7}$$

where $\hat{C}_B$ and $\hat{C}_R$ are the time-averaged concentrations for B and R, for the case $k_2 = 0$.

The *Dutta-Tarbell* closure (Dutta and Tarbell, 1989) is based on fast and slow reaction asymptotics, and on some mechanistic models of turbulent mixing. 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 nonreacting species, by a decay law. It is assumed that the turbulent mixing process is unaffected by the presence of chemical reactions. The closure equations are

$$\overline{ab} = -I_s\left(\bar{C}_A \overline{C_{B0}} + \overline{C_{A0}}\bar{C}_B - \bar{C}_A \bar{C}_B\right) \tag{8}$$

$$\overline{br} = -I_s \bar{C}_R\left(\overline{C_{B0}} - \bar{C}_B\right), \tag{9}$$

where I_s is the time-dependent intensity of segregation for the nonreacting system, and $\overline{C_{A0}}$, $\overline{C_{B0}}$ are the initial mean concentrations of A and B, respectively.

The *Brodkey-Lewalle* closure (Brodkey and Lewalle, 1985) is based on an extension of Toor's hypothesis that mixing is independent of the speed of the reaction when reactants are fed in stoichiometric proportions. For the series-parallel reaction case, Brodkey and Lewalle extended Toor's hypothesis to the second reaction, assuming further that $\overline{ab}$ is unaffected by the second reaction. The proposed closure, relating mixing for the second reaction to that for the first, is

$$\overline{br}=\overline{ab}\left(\frac{\overline{C}_R}{\overline{C}_A}\right). \tag{10}$$

This model is claimed to be valid to within a few percents when $k_1 = k_2$, which is based on calculations made using a reaction cell model. The model is described in more detail in the Appendix.

Numerical Method

DNS is used in this article to study a series-parallel reaction system (Eq. 1), and the numerical method has been discussed in detail in Chakrabarti et al. (1995). The fluid is incompressible, and the scalar field is passive with respect to the velocity field. A decaying, homogeneous 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 reaction rates are second order, the rate constants are of the same order of magnitude for both reactions, and all physical properties are constant.

The physical situation is an initial value problem in homogeneous turbulence and is described in Chakrabarti et al. (1995). The problem is similar to that in which the observer follows the flow in a turbulent plug-flow reactor with the mean velocity. An initial turbulence level is specified, and then the velocity fluctuations decay in time as viscous dissipation reduces the velocity gradients. Initially, the reactants A and B are spatially segregated, are present in stoichiometric proportions with respect to the first reaction, and no products R or S are present.

The velocity field is governed by the Navier-Stokes equation, which is

$$\frac{\partial \boldsymbol{u}}{\partial t}+\boldsymbol{u}\cdot\nabla\boldsymbol{u}=-\frac{\nabla p}{\rho}+\nu\nabla^2\boldsymbol{u}, \tag{11}$$

where p is pressure, ν is kinematic viscosity, and ρ is density of the fluid. The incompressibility condition is

$$\nabla\cdot\boldsymbol{u}=0. \tag{12}$$

The concentration C_i of species $i = A, B, R, S$, is governed by the mass conservation equation

$$\frac{\partial C_i}{\partial t}+\boldsymbol{u}\cdot\nabla C_i=D_i\nabla^2 C_i+r_i, \tag{13}$$

where r_i is the rate expression for the creation of species i and D_i is the molecular diffusivity of species i. The governing equations are solved with a pseudo-spectral method using a code adapted from Kerr (1985). The initial energy spectrum for the velocity field has been chosen to be Gaussian, that is, of the form $\alpha k^4 e^{-\beta k^2}$, and is described in Chakrabarti et al. (1995). Decay of the velocity field proceeds as given by Leonard and Hill (1991).

Two types of scalar fields were used as initial conditions for concentration values—one is the slab case in which the initial scalar field corresponds to spatially segregated slabs of reactants parallel to the x plane, and the other is the blob or stirred case, where the scalar field is preconditioned to create realistic spatial structures for the concentrations of A and B but for which the reactants are still initially segregated. This is described in Chakrabarti et al. (1995) and more details are in Chakrabarti (1991).

The simulations were carried out in decaying isotropic turbulence on a grid of 64^3 Fourier modes. Initial conditions and parameters for the simulations along with the corresponding labels for the different cases are given in Table 2 (case labels are the same as those used in Chakrabarti et al., 1995). The calculations were done on a Cray X/MP and Cray Y/MP at the National Center for Supercomputer Applications, IL and on the Cray Y/MP at the Ohio Supercomputer Center.

Results and Discussion

The results of the analysis of DNS data for covariances of concentration fluctuations, and the results of testing and analyzing the first-order closures of Bourne and Toor, Brodkey and Lewalle, Li and Toor, and Dutta and Tarbell are presented in this section. Analysis of DNS data shows an interesting behavior of covariances that allows predictions of the time history of mean values. A detailed analysis of the Brodkey-Lewalle closure, including an expression for estimating the error in the closure, is presented in the Appendix.

Covariances of concentration fluctuations

The terms needed to "close" the equations for a series-parallel reaction are the covariances of the concentration fluctuations $\overline{ab}$ and $\overline{br}$. DNS data were used to evaluate volume averages of the concentration fluctuation terms $\overline{ab}$ and $\overline{br}$. A typical result for the time dependence of $\overline{ab}$ and $\overline{br}$ for conditions of Case A and a slab initial scalar field is shown in Figure 1.

The DNS data were analyzed to see if estimates of $\overline{ab}$ and $\overline{br}$ could be made in terms of known or measurable quantities. A feature in the behavior of such "normalized" variables as $\sqrt{\overline{a^2}}/\overline{C}_A$, $\sqrt{\overline{b^2}}/\overline{C}_B$, $\overline{ab}/\overline{C}_A\overline{C}_B$, $\overline{ab}/(\sqrt{\overline{a^2}}\sqrt{\overline{b^2}})$, $\overline{br}/\overline{C}_B\overline{C}_R$, and so on is that the change in their values over time is an order

Table 2. Initial Conditions for the Simulations

	Parameters						Dimensionless Groups			
Case	ν	D	k_1	k_2	u'	C_{A0}/C_{B0}	R_λ	Sc	Da_1	Da_2
A	0.025	0.036	5	1	0.96	1	29.93	0.7	5.16	1.03
L	0.025	0.036	5	2.5	0.96	1	29.93	0.7	5.16	2.58
M	0.025	0.036	5	5	0.96	1	29.93	0.7	5.16	5.16

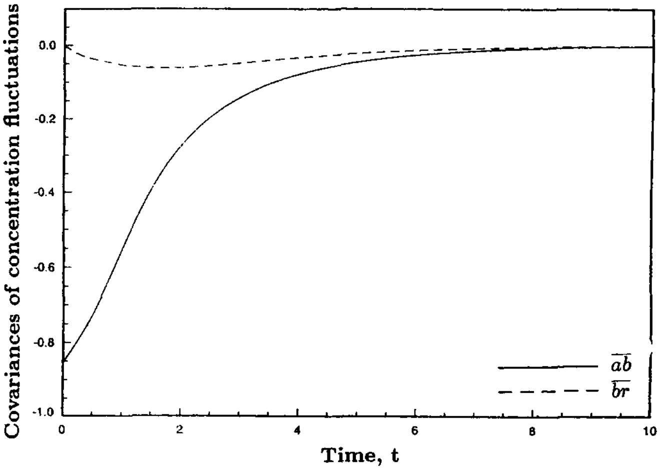


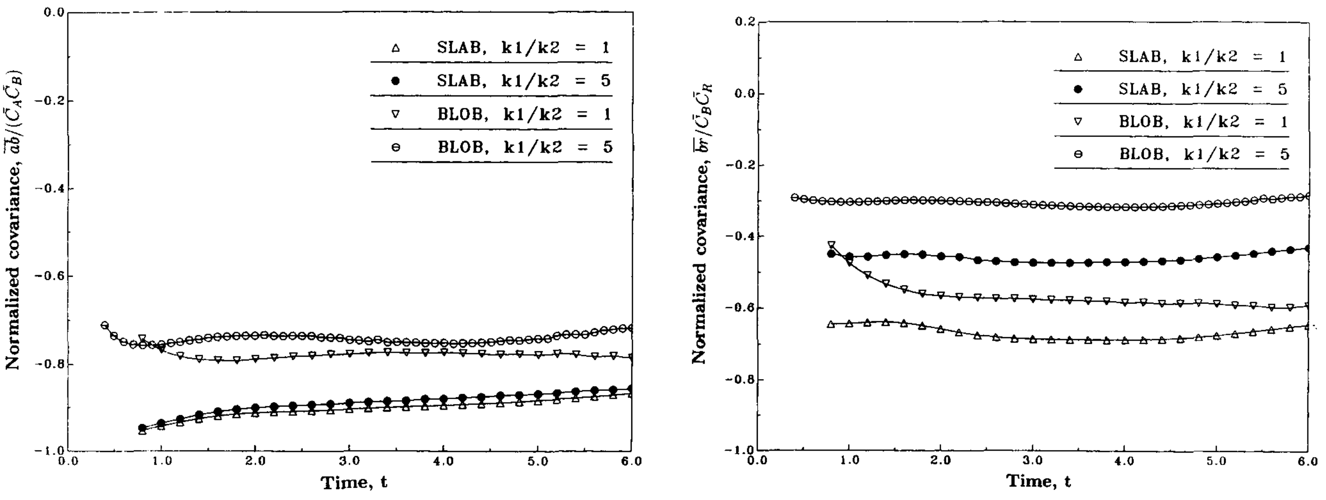
Figure 1. DNS results for $\overline{ab}$ and $\overline{br}$ for case A and a slab initial scalar field.

of magnitude less than the change observed in the primitive variables. Figure 2 shows the time evolution of some of these variables ($\overline{ab}/\overline{C}_A\overline{C}_B$, and $\overline{br}/\overline{C}_B\overline{C}_R$) for Case A and Case M, and for both slab and blob initial scalar fields. Plots of the correlation coefficient and intensity of segregation in Figures 4 and 5 of Chakrabarti et al. (1995) also show this feature clearly. Table 3 reports the normalized values of covariances for Cases A and M, and both initial scalar fields. It is seen that though the values of the normalized variables do depend on the scalar initial field, the dependence is not strong. This suggests that the variances, covariances, and triple moments may be expressed in terms of measurable mean concentrations; however, this observation is only based on the cases studied and no generality is expected.

Table 3. Approximate Normalized Values of Covariances

Normalized Covariances	Blob Initial Field		Slab Initial Field	
	$k_1/k_2=5$	$k_1/k_2=1$	$k_1/k_2=5$	$k_1/k_2=1$
$-\overline{ab}/\sqrt{\overline{a^2}}\sqrt{\overline{b^2}})$	0.6	0.5	0.6	0.58
$-\overline{ab}/\overline{C}_A\overline{C}_B)$	0.74	0.78	0.88	0.86
$-\overline{br}/\overline{C}_B\overline{C}_R)$	0.3	0.58	0.47	0.68
$(\overline{br}\overline{C}_A)/\overline{ab}\overline{C}_R)$	0.4	0.7	0.5	0.8

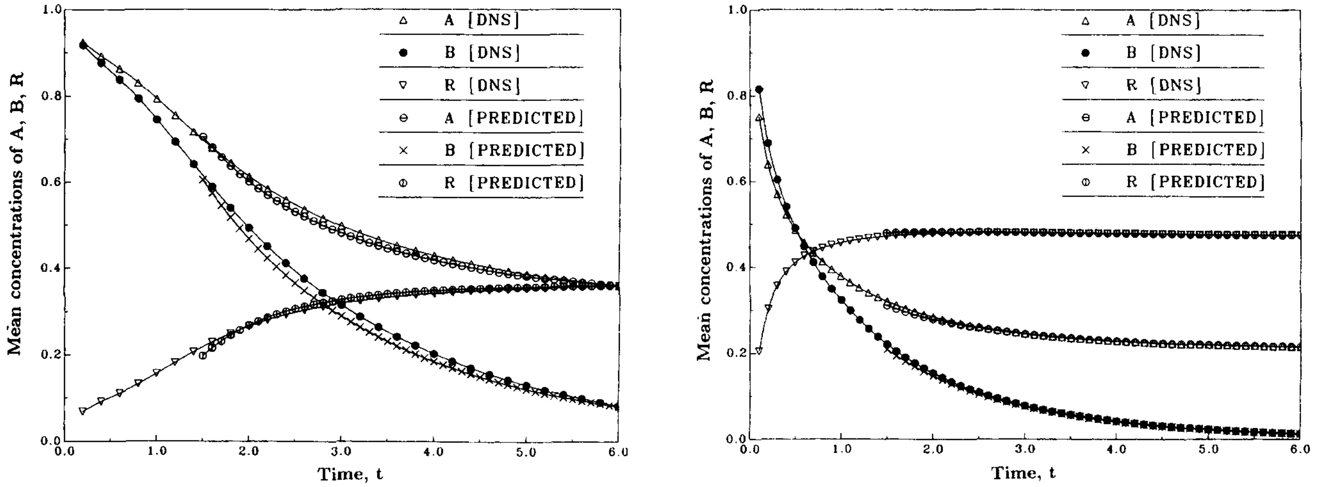
The time evolution of $\overline{ab}$ and $\overline{br}$ normalized with respect to the mean concentrations (that is, $\overline{ab}/\overline{C}_A\overline{C}_B$ and $\overline{br}/\overline{C}_B\overline{C}_R$ is shown in Figures 2a and 2b for $k_1/k_2=1$ and 5, and for both scalar field initial conditions. Figure 2a for case M and a blob initial scalar field shows that $\overline{ab}/\overline{C}_A\overline{C}_B$ decays from -0.9 to -0.7, and the decay is smooth. It is thus possible to get an estimate of the value of $\overline{ab}$ at any time, if $\overline{C}_A$ and $\overline{C}_B$ are known at some instant of time. Again, Figure 2b shows that the time behavior of $\overline{br}/\overline{C}_B\overline{C}_R$ shows very little variation—the ratio is bounded between -0.3 and -0.4 for the case of a blob initial scalar field, and $k_1/k_2=5$. These examples lead to the conjecture that some covariances normalized with respect to mean concentrations and/or r.m.s. values are almost constant in that they do not vary as much as the primitive (not normalized) variables, and this may be useful for some computational or theoretical models. The time evolution of $\sqrt{\overline{a^2}}/\overline{C}_A$ (≈ 0.9), $\sqrt{\overline{b^2}}/\overline{C}_B$ (≈ 1.5), and $\overline{ab}/(\sqrt{\overline{a^2}}\sqrt{\overline{b^2}})$ also supports the above conjecture. So, if for a given set of conditions, $\overline{C}_A$ and $\overline{C}_B$ are known at any instant of time, one can estimate $\overline{ab}$ over time. However, the value of estimating $\overline{ab}$ for a series-parallel reaction is limited since DNS results (Chakrabarti, 1991) show that it may be possible to use values of $\overline{ab}$ obtained from a pure mixing experiment (Toor's hypothesis). But, since there are no acceptable and simple closures for $\overline{br}$, as the next section will illustrate, any reasonable estimate on the behavior of $\overline{br}$ could be useful. So, as Figure 2b suggests, if $\overline{C}_B$ and $\overline{C}_R$ are known at any time, it is possible to provide a rough estimate of the value of $\overline{br}$, for a set of conditions (based on the value of $\overline{br}/\overline{C}_B\overline{C}_R$). Mean values of the concentration of B and R at any time, after the initial time, can be obtained experimentally. In fact, if $\overline{C}_A$ and $\overline{C}_B$



(a) **(b)**

Figure 2. Time evolution of normalized covariances for $k_1/k_2=1$, 5 for slab and blob initial scalar fields.

(a) $\overline{ab}/(\overline{C}_A\overline{C}_B)$; (b) $\overline{br}/(\overline{C}_B\overline{C}_R)$.



(a) **(b)**

Figure 3. Comparison of mean concentrations from simulations and predictions.

(a) $k_1/k_2 = 5$ and a slab initial scalar field; (b) $k_1/k_2 = 5$ and a blob initial scalar field.

can be measured experimentally, $\overline{C}_R$ and $\overline{C}_S$ can be obtained using a conserved scalar approach.

Time histories of the mean concentrations of A, B, and R were predicted using the observed relatively constant normalized values of $\overline{ab}$ and $\overline{br}$, and values of $\overline{C}_A$ and $\overline{C}_B$ at a single time. Figures 3a and 3b show that the predictions match DNS results reasonably well for $k_1/k_2 = 5$ and for both initial scalar fields, using known mean concentrations at $t = 6$. For $k_1/k_2 = 1$, the agreement is similar but not as good. Predictions made using measured concentration values at time $t = 3.0$ show similar behavior. It was also found that the triple moment, $\overline{ab^2}/\overline{C}_A\overline{C}_B\overline{C}_B$ remained constant at about -0.6, suggesting that higher-order moments may also have the same property as covariances.

Comparisons of DNS results with closure theories

In this section we compare predictions from the first-order closure theories of Bourne and Toor, Brodkey and Lewalle, Li and Toor, and Dutta and Tarbell, with results from DNS data. These closure models were tested in two ways. First, data from DNS were used to evaluate the covariance $\overline{br}$ for each of the closure models, and then the covariances predicted by the models 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 then compared to the actual values from the simulations. Also, the selectivity X_S was calculated and compared to DNS values. We first make some general remarks based on the comparisons and then discuss each model in turn.

The first test compares $\overline{br}$ of the closure models with the simulations. Equations 6, 7, 9 and 10 were used to evaluate $\overline{br}$ for the various closure models. For the Li-Toor closure evaluated using Eq. 7, DNS values of $\overline{C}_B$ and $\overline{C}_S$, and $\hat{C}_B$ and $\hat{C}_R$ were used, where the latter quantities were evaluated for a single reaction. For the Dutta-Tarbell closure, I_s and $\overline{C}_B$ evaluated from DNS results were used in Eq. 9. In Eq. 10 for the expression of the Brodkey-Lewalle closure, DNS values of $\overline{C}_A$, $\overline{C}_R$ and $\overline{ab}$ were used.

Figures 4a and 4b show comparisons of DNS results with the various closure theories for $\overline{br}$ for slab and blob initial scalar fields, respectively. For both initial scalar fields, the Brodkey-Lewalle closure and the Dutta-Tarbell closure show the same trend as DNS for the evolution of $\overline{br}$ and approach zero asymptotically, but the Li-Toor closure has an unphysical trend and $\overline{br}$ becomes more negative with time. For a slab initial scalar field, the Brodkey-Lewalle closure underpredicts the values of $\overline{br}$ (that is, the values predicted are more negative than the DNS values), and the Dutta-Tarbell closure and the Bourne-Toor closure overpredict the values of $\overline{br}$, compared to the DNS values. For a blob initial scalar field, both the Brodkey-Lewalle and Dutta-Tarbell closures underpredict the value of $\overline{br}$, whereas the Bourne-Toor closure overpredicts the value of $\overline{br}$. Frankel et al. (1995) have compared the Bourne-Toor closure and Brodkey-Lewalle closure with the predictions of their stochastic model and found results for $\overline{br}$ intermediate between Bourne-Toor and Brodkey-Lewalle for the DNS results presented here, although it should be noted that Frankel et al.'s study was for stationary turbulence and not for decaying turbulence presented here.

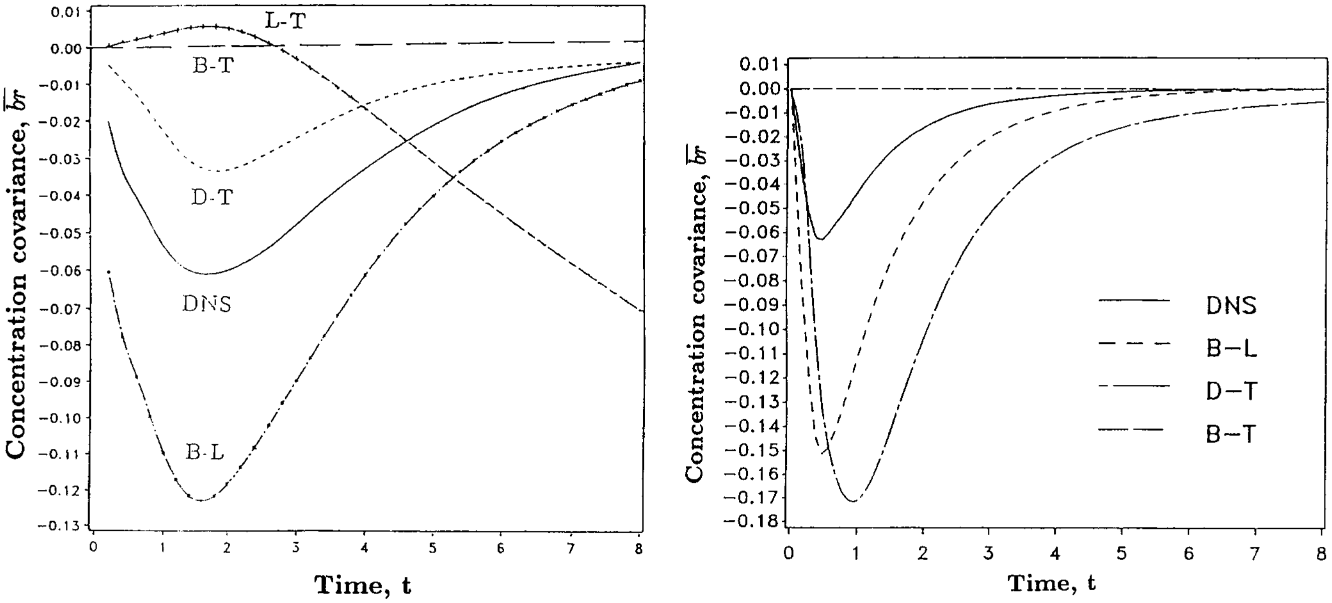
In the second test of closure models, predictions of integrated quantities are compared with DNS results. The Reynolds' averaged rate expressions for A, B, R and S are

$$\frac{d\overline{C}_A}{dt} = -k_1\left(\overline{C}_A\overline{C}_B + \overline{ab}\right) \tag{14}$$

$$\frac{d\overline{C}_B}{dt} = -k_1\left(\overline{C}_A\overline{C}_B + \overline{ab}\right) - k_2\left(\overline{C}_B\overline{C}_R + \overline{br}\right) \tag{15}$$

$$\frac{d\overline{C}_R}{dt} = k_1\left(\overline{C}_A\overline{C}_B + \overline{ab}\right) - k_2\left(\overline{C}_R\overline{C}_B + \overline{br}\right) \tag{16}$$

$$\frac{d\overline{C}_S}{dt} = k_2\left(\overline{C}_R\overline{C}_B + \overline{br}\right). \tag{17}$$



(a) (b)

Figure 4. Comparison of $\overline{br}$ values for DNS and closure theories for case A.

(a) Slab initial scalar field; (b) blob initial scalar field.

Equations 14, 15, 16 and 17 were used to predict the time behavior of $\overline{C}_A$, $\overline{C}_B$, $\overline{C}_R$ and $\overline{C}_S$ using $\overline{br}$ from the closure models. Figures 5, 6, 7 and 8 show the model predictions for the time evolution of the mean quantities for the Bourne-Toor, Li-Toor, Dutta-Tarbell and Brodkey-Lewalle closure models, compared with DNS results, respectively. Figure 5 shows that the Bourne-Toor closure underpredicts $\overline{C}_R$ and overpredicts $\overline{C}_S$. Figure 6 shows that the predictions of the Li-Toor model for the various mean concentrations do not match at all with DNS results; it shows that $\overline{C}_R$ continues to increase with time and $\overline{C}_S$ starts to decrease after a certain time. This unphysical prediction is a direct consequence of the strange behavior of $\overline{br}$ (becoming more negative with time) as predicted by the Li-Toor model. The Dutta-Tarbell closure underpredicts $\overline{C}_R$ and overpredicts $\overline{C}_S$, as shown in Figure 7. Figure 8 shows that the Brodkey-Lewalle closure overpredicts the mean value of R and underpredicts the mean value of S.

The selectivity X_S is also evaluated using mean concentrations predicted from the models. Figure 9 compares these values of X_S with the DNS results for the slab initial scalar field. It is seen that the Bourne-Toor model and the Dutta-Tarbell model overpredict the value of X_S, the Brodkey-Lewalle closure underpredicts the value of X_S, and the Li-Toor closure has an unphysical trend.

Although the Bourne-Toor closure assumes that $\overline{br}=0$ (Eq. 6), the expression for X_S defined in terms of time-integrals of Eq. 14 to Eq. 17 shows that the ratio of $\overline{br}/\overline{C}_B\overline{C}_R$ is more

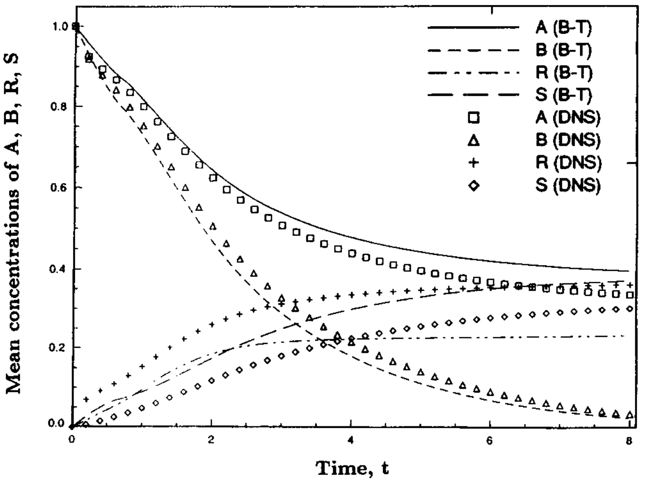


Figure 5. Predictions of the Bourne-Toor model with DNS for case A and a slab initial scalar field.

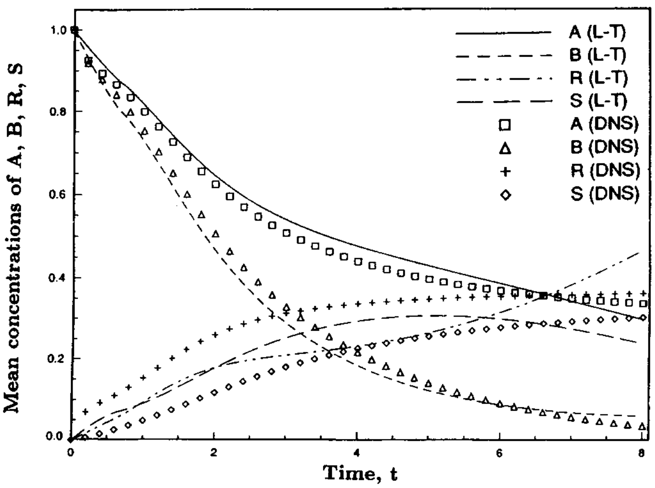


Figure 6. Predictions of the Li-Toor model with DNS for case A and a slab initial scalar field.

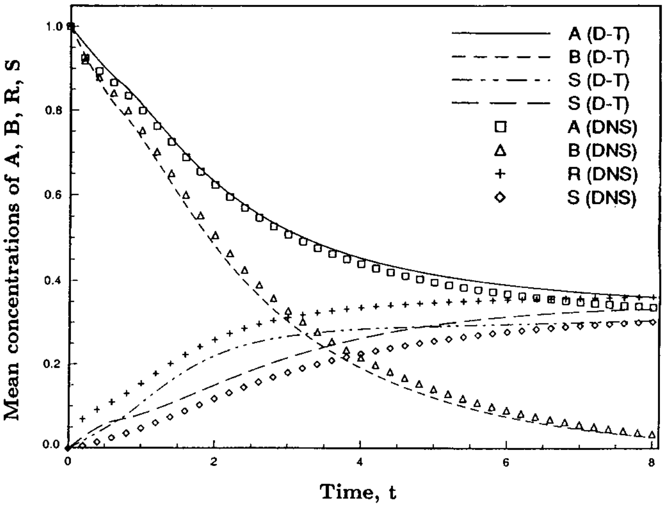


Figure 7. Predictions of the Dutta-Tarbell model with DNS for case A and a slab initial scalar field.

important than the value of $\overline{br}$ alone. The closure may be rewritten as $\overline{br}/\overline{C}_B\overline{C}_R = 0$. DNS results of Chakrabarti (1991) show that the values of $\overline{br}$ are small compared to $\overline{C}^2_{A0}$ (≈ 1), in accordance with Bourne and Toor, but that the value of $\overline{br}/\overline{C}_B\overline{C}_R$ is clearly nonzero (lying between -0.2 and -0.7), and so the expression $|\overline{br}| \ll \overline{C}_B\overline{C}_R$ is not true. Also, Figure 5 shows that the Bourne-Toor closure model underpredicts $\overline{C}_R$, overpredicts $\overline{C}_S$, and consequently overpredicts the value of X_S to such an extent that more S is formed compared to R, in contradiction to DNS results. However, the error in X_S is only 30% (for a slab scalar initial field). Since the model is very simple, the model may be useful in some cases.

As shown in Figure 4, the Li-Toor prediction of $\overline{br}$ has the wrong trend and, consequently, the predictions for the various mean concentrations (Figure 6) and X_S (Figure 9) are unphysical and do not compare well with DNS data. This may be because the Li-Toor closure is intended for very high k_1/k_2 ratios, which were not done in this study. For cases where reaction rate constants k_1 and k_2 are of the same order of magnitude, the closure does not give satisfactory results.

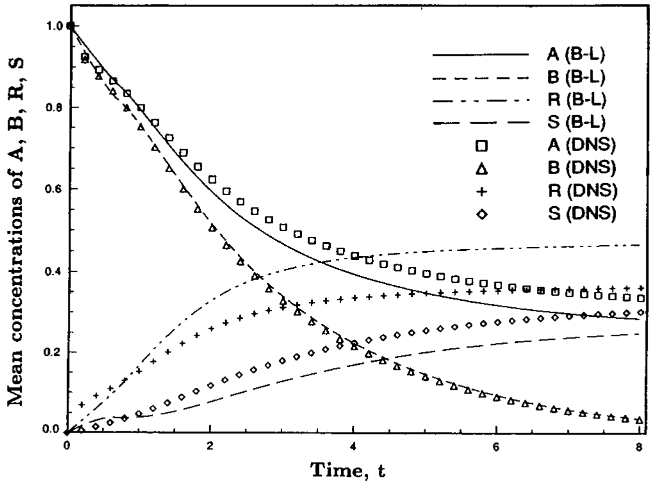


Figure 8. Predictions of the Brodkey-Lewalle model with DNS for case A and a slab initial scalar field.

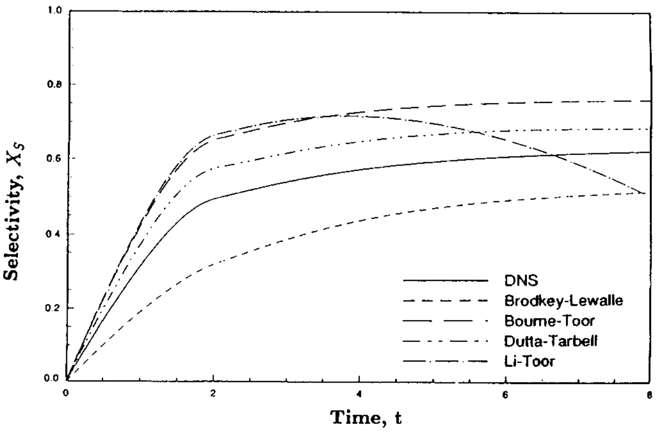


Figure 9. Comparison of X_S values for simulations and closure theories for case A and a slab initial scalar field.

Data from the DNS were used to evaluate $\overline{C}_B$, $\overline{C}_R$, and the intensity of segregation I_s of a nonreacting scalar $(\overline{a^2}/a_0^2)_m$ to test the Dutta-Tarbell closure using Eq. 9. This closure provides the best agreement with DNS results for the slab initial scalar field among the theories examined here, but the agreement is poorer for a blob initial scalar field. As shown in Figure 7 for a slab initial scalar field, this model overpredicts the mean concentrations of S and underpredicts the mean concentrations of R compared to the DNS results, overpredicting X_S as shown in Figure 9. For the blob case on the other hand, this closure overpredicts the magnitude of $\overline{br}$ by an order of magnitude, and the agreement worsens as time progresses.

Brodkey and Lewalle's claim that the second reaction does not affect the value of $\overline{ab}$ (that is, the value of $\overline{ab}$ for the case of a single reaction is the same as the value of $\overline{ab}$ for the case of two reactions) and their suggestion of using Toor's closure for $\overline{ab}$ (Eq. 5) were assessed using DNS. By comparing DNS values of $\overline{ab}$ for the case of no reaction and for the cases of a single reaction and a series-parallel reaction, Chakrabarti (1991) found that the value of $\overline{ab}$ for the case of no reaction is closer to the value of $\overline{ab}$ for a series-parallel reaction, than it is to the value of $\overline{ab}$ for a single reaction. This suggests that $\overline{ab}$ for the case of no reaction may be used in place of $\overline{ab}$ for the case of two reactions without introducing much additional error. In terms of the performance of the closure, for both initial scalar fields this closure is more consistent in its agreement with the simulations. Figure 9 shows that the model underpredicts the mean concentration of S and overpredicts the mean concentration of R, and consequently underpredicts the value of X_S, as shown in Figure 9. The closure underpredicts $\overline{br}$ for both initial scalar fields, but the underprediction is within a factor of 2 to 3, and the behavior of $\overline{br}$ follows the DNS pattern very closely.

The basis of the Brodkey-Lewalle closure is the extension of Toor's hypothesis to two reactions: the claim is that the evolution of dynamical quantities such as $\overline{ab}$, $\overline{br}$, and so on should not depend on the rate of the reaction. That is, in the evolution of the covariance terms, the reaction term is negli-

Table 4. Evaluation of Individual Terms in Evolution Equation for $\overline{ab}$

Rate Constants	Term (2)		Term (3)		Term (4)	
k_1/k_2	Max	Min	Max	Min	Max	Min
1	0.106	3.6×10^{-4}	0.07	3.47×10^{-4}	0.03	1.29×10^{-5}
5	0.11	5.5×10^{-4}	0.194	2.63×10^{-3}	0.123	2.08×10^{-3}

gible compared to the diffusion term. DNS results were used to compute the individual terms in the evolution equations to test the validity of that claim. For example, as Table 4 shows, term (2) in Eq. A1 (of the Appendix) is almost invariant to k_1/k_2, but term (3) and hence term (4) (the sum of terms (2) and (3)) do depend on k_1/k_2. So, the contribution of the kinetic term in the evolution equations does depend on the ratio of the rate constants. However, 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 term (4) is 0.03 for one set of conditions (case M). This observation that the dissipation term dominates the reaction rate term is in agreement with that of Leonard and Hill (1989) for a single-step reaction.

It is possible to arrive at an expression for the error term in the Brodkey-Lewalle closure from a combination of terms that appear in the evolution equations (Eq. A5 and Eq. A6 in the Appendix). Note that $X_4 - X_3 = \bar{C}_A\overline{br} - \bar{C}_R\overline{ab}$, which gives the following expression for $\overline{br}$

$$\overline{br} = \overline{ab}\bar{C}_R/\bar{C}_A + (X_4 - X_3)/\bar{C}_A. \tag{18}$$

Comparison of Eq. 18 with Eq. 10 shows that the last term is the error term in the Brodkey-Lewalle closure which we denote as

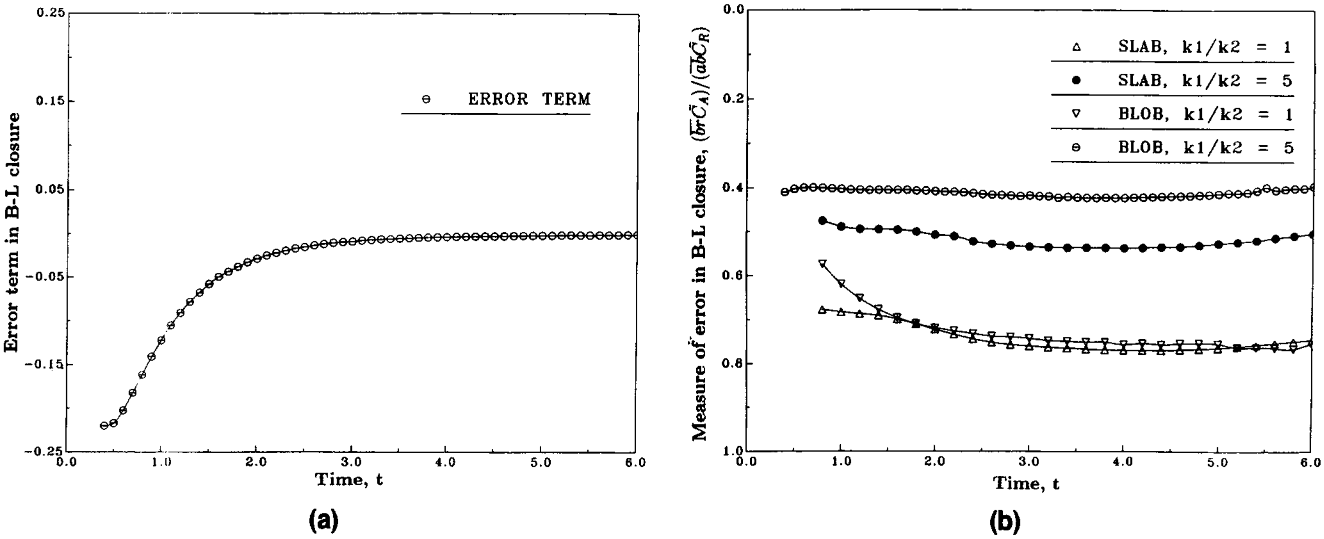
$$E_{BL} = (X_4 - X_3)/\bar{C}_A. \tag{19}$$

If $X_4 - X_3 = 0$, then the Brodkey-Lewalle closure is exact. Since $X_4 < X_3$ in the DNS results, the Brodkey-Lewalle closure underpredicts the value of $\overline{br}$, as has been observed by comparison with DNS results. Figure 10a shows the time evolution of the error term for conditions of Case A and a blob initial scalar field. A means of estimating this error term would be useful and is discussed in the Appendix. Another measure of the error in the Brodkey-Lewalle closure is the ratio of $(\overline{br}/\overline{ab})(\bar{C}_A/\bar{C}_R)$—the closer the ratio is to 1.0, the better the performance of the closure. Figure 10b shows the time behavior of this ratio for conditions of Case A and Case M, and for both slab and blob initial scalar fields. Again, we notice that this ratio is almost constant for a set of conditions and that the performance of this closure is best when the rate constants are equal. An analysis of the Brodkey-Lewalle closure is presented in the Appendix.

It is tempting to propose other closures simply by inspection of the above results. Noting that the DNS results for $\overline{br}$ are intermediate between the results of Dutta and Tarbell and of Brodkey and Lewalle, one is tempted to use the geometric mean of the predictions of those theories to estimate $\overline{br}$, despite the lack of any physical reason. Figure 11a shows good agreement between the DNS results and this preposterous closure for the case of a slab initial scalar field, but the agreement is poor for the blob scalar field case as shown in Figure 11b, showing that even arbitrary closures can work well for some conditions and fail for other conditions.

Conclusions

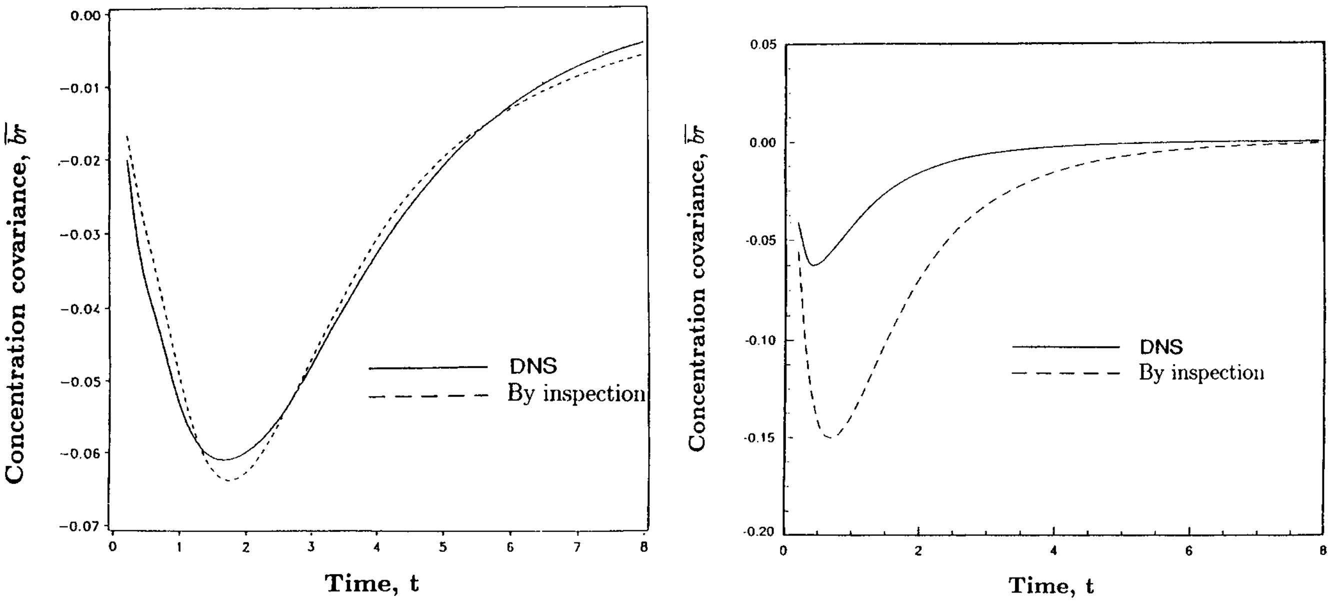
In this article, DNS results were analyzed to provide information on the behavior of covariances of concentration fluctuations for use in models. It was found that covariances of concentration fluctuations normalized with respect to the mean concentration values are almost constant over time. These estimates of covariances can be very useful in closing the equations for reactor modeling. It is thus possible to estimate the time behavior of covariances such as $\overline{br}$ if the mean



(a) (b)

Figure 10. Evolution of error term in Brodkey-Lewalle closure.

(a) Error in $\overline{br}$ (E_{BL}) for case A and a blob initial scalar field; (b) time evolution of $(\overline{br}\bar{C}_A)/\overline{ab}\bar{C}_R)$ for case A and M and for slab and blob initial scalar fields.



(a) (b)

Figure 11. Comparison of closure by inspection with DNS results for case A.

(a) Slab initial scalar field; (b) a blob initial scalar field.

concentrations of B and R are known at any time. These covariances then give good estimates of the time behavior of mean concentrations.

Simple first-order closure theories for the covariance of the concentration fluctuation terms were tested and compared with results from the simulations. The Bourne-Toor closure overpredicts the value of $\overline{br}$ with time, but provides the correct asymptotic value. The Brodkey and Lewalle closure underpredicts the value of the concentration covariance $\overline{br}$ by a factor of about 2 for a slab initial scalar field and by a factor of 3 for a blob initial scalar field, but the qualitative behavior of $\overline{br}$ closely follows the DNS pattern and approaches zero asymptotically. The Li-Toor prediction of $\overline{br}$ agrees neither quantitatively nor qualitatively with the DNS results for the conditions of the simulations. Dutta and Tarbell's closure works well for the slab initial scalar field: it overpredicts the value of $\overline{br}$ by only a factor of between 1 and 2. However, for a blob initial scalar field, the closure overpredicts $\overline{br}$ by an order of magnitude. Among the first-order closure theories available in the literature and discussed here, the Brodkey-Lewalle closure gave the best overall agreement with the simulations. It was thus concluded that none of the first-order closures considered here are satisfactory. The fact that first-order closures such as these do not work as well for two-step as for single-step reactions suggests that more study is needed, as also pointed out by Frankel et al. (1995). Future studies should consider unequal volumes of initial reactants, unequal diffusivities of the species.

Acknowledgments

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Notation

Da_1 = Damköhler number for the first reaction $= k_1\sqrt{C_{A0}C_{B0}}\,\Lambda_f/u'$
Da_2 = Damköhler number for the second reaction $= k_2\sqrt{C_{A0}C_{B0}}\,\Lambda_f/u'$
R_λ = turbulence Reynolds number $= u'\lambda/\nu$
Sc = Schmidt number
$\overline{a^2},\overline{b^2},\overline{r^2}$ = variances of concentration fluctuations of species A, B, and R, respectively
k = wave number
k_1, k_2 = kinetic rate constants for the first and second reaction, respectively
k_0 = peak wave number
u' = turbulence intensity
ν = velocity

Subscripts

0 = initial values

Literature Cited

Bourne, J. R., F. Kozicki, and P. Rys, "Mixing and Fast Chemical Reaction: I. Test Reactions to Determine Segregation," *Chem. Eng. Sci.*, **36**, 1643 (1981).

Bourne, J. R., and H. L. Toor, "Simple Criteria for Mixing Effects in Complex Reactions," *AIChE J.*, **23**, 602 (1977).

Brodkey, R. S., and J. Lewalle, "Reactor Selectivity Based on First Order Closures of the Turbulent Concentration Equations," *AIChE J.*, **31**, 111 (1985).

Chakrabarti, M., R. M. Kerr, and J. C. Hill, "Direct Numerical Simulation of Chemical Selectivity in Homogeneous Turbulence," *AIChE J.*, **41**, 2356 (1995).

Chakrabarti, M., "Numerical Studies of Chemical Selectivity and Heat Transfer in Decaying Homogeneous Turbulence," PhD Diss., Iowa State Univ. (1991).

Chakrabarti, M., and J. C. Hill, "Direct Numerical Simulation of a

Parallel Consecutive Reaction Pair in Homogeneous Turbulence," *Proc. Twelfth Symp. on Turbulence*, Rolla, MO (1990).

Dutta, A., and J. M. Tarbell, "Closure Models for Turbulent Reacting Flows," *AIChE J.*, **35**, 2013 (1989).

Frankel, S. H., P. A. McMurtry, and P. Givi, "Linear-Eddy Modeling of Reactant Conversion and Selectivity in Turbulent Flows," *AIChE J.*, **41**, 258 (1995).

Gao, F., and E. E. O'Brien, "Direct Numerical Simulations of Reacting Flows in Homogeneous Turbulence," *AIChE J.*, **37**, 1459 (1991).

Givi, P., and P. A. McMurtry, "Non-Premixed Reaction in Homogeneous Turbulence: Direct Numerical Simulations," *AIChE J.*, **34**, 1039 (1988).

Kerr, R. M., "Higher-Order Derivative Correlations and the Alignment of Small-Scale Structures in Isotropic Numerical Turbulence," *J. Fluid Mech.*, **153**, 31 (1985).

Kerstein, A. R., "Linear-Eddy Modeling of Turbulent Transport: 7. Finite-Rate Chemistry and Multistream Mixing," *J. Fluid Mech.*, **240**, 289 (1992).

Leonard, A. D., and J. C. Hill, "Direct Numerical Simulation and Simple Closure Theory for a Chemical Reaction in Homogeneous Turbulence," *Turbulent Reactive Flows*, Lecture Notes in Engineering, R. Borghi and S. N. B. Murthy, eds., Vol. 40, Springer-Verlag, New York, p. 515 (1989).

Leonard, A. D., and J. C. Hill, "Scalar Dissipation and Mixing in Turbulent Reacting Flows," *Phys. Fluids A*, **3**, 1286 (1991).

Leonard, A. D., R. C. Hamlen, R. M. Kerr, and J. C. Hill, "Evaluation of Closure Models for Turbulent Reacting Flows," *Ind. Eng. Chem. Res.*, **34**, 3640 (1995).

Li, K. T., and H. L. Toor, "Turbulent Reactive Mixing with a Series-Parallel Reaction: Effect of Mixing on Yield," *AIChE J.*, **32**, 1312 (1986).

Toor, H. L., "Turbulent Mixing of Two Species with and without Chemical Reactions," *Ind. Eng. Chem. Fundam.*, **8**, 655 (1969).

Tsai, K., and R. O. Fox, "Modeling Multiple Reactive Scalar Mixing with the Generalized IEM Model," *Phys. of Fluids*, **7**, 2820 (1995).

Appendix: Analysis of the Brodkey-Lewalle Closure

Toor's hypothesis for $\overline{ab}$ may be extended to include other dynamical quantities such as $\overline{a^2}$, $\overline{br}$, and so on, and it may be claimed that the evolution of such quantities 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, that is, the reaction term is negligible compared to the diffusion term. DNS results presented in this article support this idea.

A generalization of the extension of Toor's hypothesis to a series-parallel reaction is that in an evolution equation for covariance of concentration fluctuations, it is the contribution of the sum of the reaction terms (rather than the individual reaction terms) that is negligible, compared to the contribution of the dissipation term.

For example, in the evolution equation for $\overline{ab}$ given by

$$\frac{d(\overline{ab})}{dt} = -\underbrace{2D\overline{\frac{\partial a}{\partial x_j}\frac{\partial b}{\partial x_j}}}_{(1)} \underbrace{-k_1\left[\overline{C}_B\overline{ab}+\overline{C}_A\overline{b^2}+\overline{ab^2}+\overline{C}_A\overline{ab}+\overline{C}_B\overline{a^2}+\overline{a^2b}\right]}_{(2)} \underbrace{-k_2[\overline{C}_B\overline{ar}+\overline{C}_R\overline{ab}+\overline{abr}]}_{(3)} \quad \text{(A1)}$$

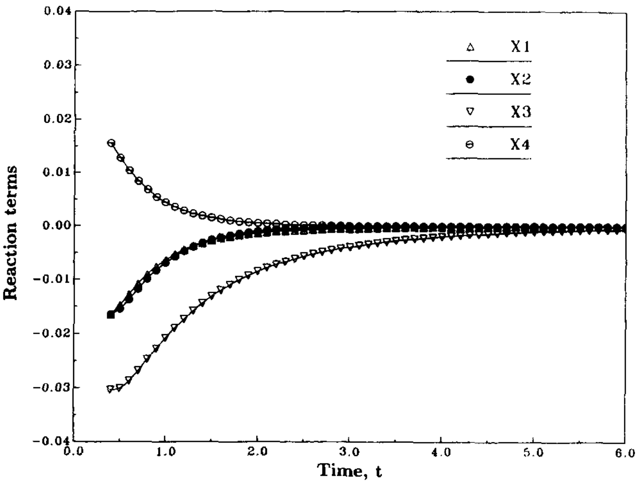

Figure 12. Time evolution of components of the evolution equations (X_1, X_2, X_3, X_4) for case A and a blob initial scalar field.

the total kinetic term is the sum of terms (2) and (3), and so the present authors' proposed extension of Toor's hypothesis yields

$$-k_1\left[\overline{C}_A\overline{b^2}+\overline{C}_B\overline{ab}+\overline{ab^2}+\overline{C}_A\overline{ab}+\overline{C}_B\overline{a^2b}\right] - k_2[\overline{C}_B\overline{ar}+\overline{C}_R\overline{ab}+\overline{abr}] = 0. \quad \text{(A2)}$$

We can define combinations of terms that appear in the evolution equations for $\overline{ab}$, $\overline{br}$, $\overline{ar}$, $\overline{b^2}$, $\overline{a^2}$ as follows

$$X_1 = \left[\overline{C}_A\overline{ab}+\overline{C}_B\overline{a^2}+\overline{a^2b}\right] \quad \text{(A3)}$$

$$X_2 = \left[\overline{C}_B\overline{ab}+\overline{C}_A\overline{b^2}+\overline{ab^2}\right] \quad \text{(A4)}$$

$$X_3 = [\overline{C}_B\overline{ar}+\overline{C}_R\overline{ab}+\overline{abr}] \quad \text{(A5)}$$

$$X_4 = [\overline{C}_A\overline{br}+\overline{C}_B\overline{ar}+\overline{abr}] \quad \text{(A6)}$$

$$X_5 = \left[\overline{C}_R\overline{br}+\overline{C}_B\overline{r^2}+\overline{br^2}\right] \quad \text{(A7)}$$

$$X_6 = \left[\overline{C}_B\overline{br}+\overline{C}_R\overline{b^2}+\overline{b^2r}\right]. \quad \text{(A8)}$$

Equation A2, then can be written as $k_1[X_1+X_2]+k_2[X_3]=0$. Also, the term k_1X_1 is the reaction rate term in the evolution equation for $\overline{a^2}$, and k_1X_2 is one of the reaction rate terms in the evolution equation for $\overline{b^2}$. The terms X_1, X_2, X_3, and X_4 evaluated using DNS for one set of conditions (Case A) are shown in Figure 12. All of them approach zero asymptotically, and X_4 approaches zero later in time than X_1, X_2 and X_3. Then considering the reaction terms in the evolution equations of $\overline{ab}$, $\overline{br}$, $\overline{ar}$, $\overline{b^2}$, and $\overline{a^2}$, the resulting equations are

$$k_1[X_1+X_2]+k_2[X_3] = k_1[X_4-X_2]+k_2[X_5+X_6] = k_1[X_1+X_4]-k_2[X_3] = k_1[X_2]+k_2[X_6] = k_1[X_1] = 0. \quad \text{(A9)}$$

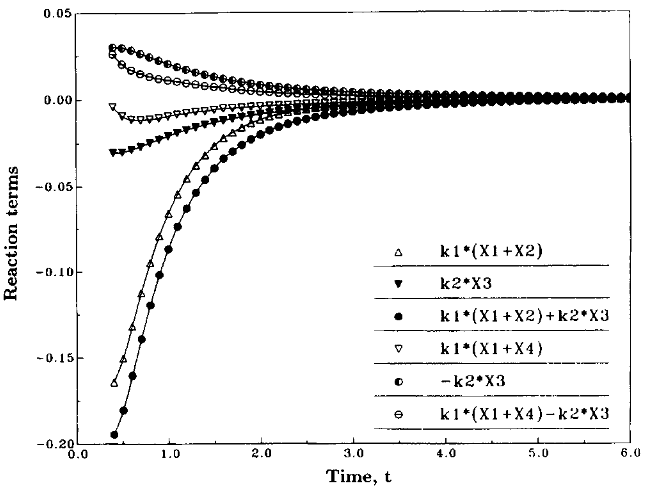

Figure 13. Contribution of individual and total reaction terms in evolution equations for $\overline{ab}[k_1(X_1+X_2)$, k_2X_3, $k_1(X_1+X_2)+k_2X_3]$ and $\overline{ar}[k_1(X_1+X_4)$, $-k_2X_3$, $k_1(X_1+X_4)-k_2X_3]$ for case A and a blob initial scalar field.

The reaction terms in the evolution equation for $\overline{ab}$ and $\overline{ar}$, evaluated using DNS for conditions of Case A and a blob initial scalar field, are shown in Figure 13. The individual contributions of the reaction terms are contrasted to the total contribution of the reaction terms, and as Figure 13 shows the total reaction term contribution is closer to zero than the individual reaction terms. This supports the current authors' extension of Toor's hypothesis. However, Eq. A9 is not a closed system, and further assumptions are necessary to arrive at a closure.

Brodkey and Lewalle'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, that is, terms (2) and (3) in Eq. A1 are both negligible. Therefore, the terms in Eq. A9 are individually zero, $k_1[X_1+X_2]=0$, $k_2[X_3]=0$. Following that rationale, the kinetic terms in the evolution equations for $\overline{ab}$, $\overline{br}$, $\overline{ar}$, $\overline{b^2}$, and $\overline{a^2}$ yield

$$k_1[X_1+X_2]=k_2[X_3]=k_1[X_4-X_2]=k_2[X_5+X_6]$$
$$=k_1[X_1+X_4]=k_1[X_2]=k_2[X_6]=k_1[X_1]=0. \quad \text{(A10)}$$

Some of these terms ($k_1[X_1+X_2]$, k_2X_3, $k_1[X_1+X_4]$) evaluated to see if the expressions are close to zero, as expected by the rationale of the Brodkey-Lewalle closure, are shown in Figure 13. It is seen that the terms go to zero asymptotically but not at short times. Algebraic manipulation of a linearly independent subset of Eq. A10 is used to arrive at the expression for the Brodkey-Lewalle closure (Eq. 10).

The analysis of the evolution equations further shows that when k_1 and k_2 are equal, the authors' generalized extension of Toor's hypothesis leads to the exact analytical form suggested by Brodkey and Lewalle (1985). As observed by Chakrabarti (1991), the agreement of the Brodkey-Lewalle closure with the DNS results is best when the rate constants are equal and the deviation increases as the ratio of the rate constants increases. So, any departures of predictions of the Brodkey-Lewalle closure from the DNS results, observed in the particular case of equal rate constants, should be attributable to the failure of the extension of Toor's hypothesis to multiple reactions or to the failure of Toor's hypothesis itself. This could be because Toor's hypothesis is for reactants which are present in stoichiometric amounts, but it is not possible to maintain stoichiometric quantities of reactants for both reactions in a series-parallel reaction.

A way of estimating the error term in the Brodkey-Lewalle closure is now attempted in the light of the current authors' extension of Toor's hypothesis. From Eq. A9, E_{BL} may be expressed as

$$E_{BL}\overline{C}_A=(X_4-X_3)=X_1[k_1/k_2-2]+X_2[k_1/k_2-1]. \quad \text{(A11)}$$

Some observations on the behavior of the error term may be noted as follows: If $k_1=k_2$, the second term in the expression for error disappears and the error becomes $E_{BL}=-X_1/\overline{C}_A$. Similarly if $k_1=2k_2$, the first term vanishes and $E_{BL}=X_2/\overline{C}_A$. As the ratio of k_1/k_2 increases from 2, the prediction gets worse because X_1 and X_2 have the same sign. For k_1/k_2 ratios of 1, 2 and 5, the prediction is worst when $k_1/k_2=5$, since the error term is the largest in that case, and the prediction is best when $k_1/k_2=1$, as noted earlier. If it is possible to find a good approximation to X_1 and X_2 based on constant values of central moments normalized with respect to mean concentrations, as per the earlier mentioned observation on normalized variances and demonstrated for the case of variances and in the preliminary results for triple moments, then E_{BL} may be estimated, and consequently a closure for $\overline{br}$ may be arrived at.

Finally, an attempt was made to develop a simple closure based on the generalized extension to Toor's hypothesis and some simplifying assumptions. If we assume (i) $\overline{a^2}=\overline{b^2}=\overline{a^2_m}$, and (ii) triple moments are negligible ($\overline{abr}=0$, $\overline{b^2r}=0$), algebraic manipulation of Eq. A9 yields the following ad-hoc closure

$$\overline{br}=\frac{k_1\overline{C}_R(\overline{ab}-\overline{a^2})+k_2\overline{C}_R\overline{a^2}}{k_1(\overline{C}_A+\overline{C}_B)-k_2\overline{C}_B}. \quad \text{(A12)}$$

When $k_1=k_2$, this closure reduces to the Brodkey-Lewalle closure. The closure works well for both initial scalar fields when DNS values of $\overline{a^2}$ are used, even though the assumption $\overline{a^2}=\overline{b^2}$ is incorrect. When values of $\overline{a^2}$ for the nonreacting case is used, the agreement between this closure and DNS values is reasonably good for the slab case, but deteriorates when a blob initial scalar field is used. This closure serves as another example of ad-hoc first-order closure theory which can work reasonably well under some conditions, but will fail under other conditions.

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