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A Coupled Two-Dimensional Diffusion and Chemistry Model for Turbulent and Inhomogeneously Mixed Reaction Systems

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A Coupled Two-Dimensional Diffusion and Chemistry Model for Turbulent and Inhomogeneously Mixed Reaction Systems

by

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TABLE OF CONTENTS

NOMENCLATURE

A_i	moment term defined by Equation 4.5
B_1	ratio of mean concentrations $\overline{C}_\alpha/\overline{C}_{\alpha I}$
B_2	ratio of reaction rates $\left(\frac{\partial \overline{C}_\alpha}{\partial t}\right)\Big/\left(\frac{\partial \overline{C}_\alpha}{\partial t}\right)_I$
C_i	concentration of ith chemical species
f	moment term defined by Equation 4.7
F	horizontal flux defined by Equation 6.3
g	acceleration due to gravity
k	reaction rate constant
M	value of $\frac{\overline{C_\alpha' C_\beta'}}{\overline{C}_\alpha \overline{C}_\beta}$ when $\overline{C_\alpha'^2 C_\beta'} = 0$
n_i	frequency distribution of ith species
N	$\sum_i n_i$
p	pressure
q	square root of twice the turbulent kinetic energy
r	correlation coefficient defined by Equation 3.15
S	wind shear
t	time
t_i	intermittency factor
T	absolute temperature
T_o	adiabatic temperature
u	velocity
x	axial coordinate

z	vertical distance
λ	micro-scale length
Λ_1	length scale
Λ_2	length scale
Λ_3	length scale
ν_o	kinematic viscosity
σ_z	standard deviation

Superscripts

—	mean component
'	fluctuating component

Subscripts

chem	reaction rate due to chemistry
I	reaction rate neglecting third-order correlations (Table 1)
s	steady state value (see e.g. Equation 3.12)
$\alpha,\beta,\gamma,\delta$	chemical species
o	initial value
1,2	species designation

1. INTRODUCTION

This section of the A.R.A.P. final report on Contract EPA 68-02-0014 covers the work on modeling of chemical reactions in turbulent and inhomogeneously mixed binary reaction systems performed during the period September 1972 through January 1973. The primary intent of the EPA-supported portion of this work has been the assessment of the combined effects of turbulent diffusion and inhomogeneous chemistry on the dispersion and chemical alteration of reactive pollutants and natural constituents of the lower atmosphere. Parallel programs aimed at similar assessments in the lower stratosphere, particularly as they pertain to the impact of proposed SST exhaust emissions on the natural environment, have been supported (under Contracts NAS1-11433 and NAS1-11873) by NASA/Langley and, by transfer of funds, by the DOT/CIAP program. Credit for the support of the basic technological developments common to these problems is therefore shared by EPA, NASA, and DOT. The applications of this technology reported here are restricted to the EPA orientation, however, and have been supported solely by that Agency.

At the time this work was undertaken in mid-1972, a general assessment of the potential importance of inhomogeneous mixing in chemical reaction rates, and the basic approach to modeling these effects via second-order closure of the chemical kinetic equations had been developed by an in-house program at A.R.A.P. These earlier developments were reported in two papers by Donaldson and Hilst, one entitled "Effect of Inhomogeneous Mixing on Atmospheric Photochemical Reactions," which was published in ENVIRONMENTAL SCIENCE AND TECHNOLOGY, Volume 6, September 1972, and a second entitled "Chemical Reactions in Inhomogeneous Mixtures: The Effect of the Scale of Turbulent Mixing," which appeared in the Proceedings of the 1972 Heat Transfer and Fluid Mechanics Institute, Stanford University Press, June 1972. Since the work reported here stems directly from these earlier considerations, reprints of these papers are appended to this report. The reader is urged to read these appendices (A and B) first, if he is not already familiar with their contents.

In addition to this preliminary work on chemical kinetics modeling, several years of effort at A.R.A.P. have been devoted to invariant modeling (second-order closure) of the structure of turbulence and turbulent diffusion in boundary layer shear flows under various conditions of hydrostatic stability and surface roughness. This facet of model development has also been sponsored by several agencies, including work under the EPA Contract EPA 68-02-0014, and is reported extensively in Volumes I and II of this final report. In the present report on coupled diffusion and chemistry models, familiarity with the material in Volumes I and II will be assumed.

2. THE PROBLEM

The objective of this program, and therefore the primary problem which we have addressed, has been to fabricate a useful coupled model which can simulate the combined effects of turbulent diffusion and chemical depletion on the concentration patterns of reactive chemical species emanating from common or separate sources. However, against the background of assessment and modular model development described in the previous section, it was evident at the initiation of the present program that two major problems had to be solved first.

1. More rigorous analyses were required in order to determine the magnitude of the effects of inhomogeneous mixing on chemical reaction rates, the conditions under which these effects could be realized, and an evaluation of the likelihood that these conditions actually occur in atmospheric pollutant situations. For example, if it could be shown that these effects were either always insignificant or constituted only a transient perturbation of the chemical kinetic rates, a coupled diffusion/chemistry model could be readily constructed using the conventional mean-value chemical kinetic equations.

2. Given that the results of the above analyses were not totally negative, i.e., negative in the sense that no important real-world situations could be found in which concentration fluctuations played a significant role, it was recognized that the second immediate problem was the development of a useful closure scheme for the third-order correlations inherent in the complete chemical kinetic equations. It was also recognized that under some circumstances the third-order correlations could be neglected. However, this assumption restricts strongly the range of joint frequency distributions of reactant concentrations

which can be considered, and denies any semblance of generality in the chemical sub-model. A more appropriate, although approximate, closure scheme was required.

With these considerations in mind, first efforts were devoted to these two problems. By mid-November 1972 both had been resolved, and attention was focussed on the assembly of the first coupled diffusion/chemistry model. The results of the earlier work on the analyses of the magnitude and significance of inhomogeneous mixing on chemical reactions and the development of a closure scheme at the level of third-order correlations of concentration fluctuations have been assembled as a technical paper which was presented at the 11th Aerospace Sciences Conference of the AIAA in Washington, D. C., January 10, 1973.* A slightly modified version of this paper is included as Section 3 and 4 of the present report. The major results discussed there are:

1. There are indeed real-world atmospheric pollution problems in which neglect of the fluctuations of concentrations of reacting species introduces significant errors. These effects associate primarily with multiple source situations, many of which are very common in the urban pollution arena.

2. An approximate closure scheme for the chemical sub-model which conforms to the principles of invariant modeling and which accounts for the effects of inhomogeneous mixing over a wide range of conditions (concentration variance-to-mean-squared ratios up to 100) has been developed. This sub-model predicts reaction rates to within a factor of two of the exact chemical kinetic solutions for situations where the mean-value chemical kinetic approximation incurs errors of a factor of 100. On the other hand, the chemical kinetic sub-model recovers the mean-value approximation when the concentration fluctuations are indeed insignificant in

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*G. R. Hilst, "Solutions of the Chemical Kinetic Equations for Initially Inhomogeneous Mixtures," AIAA Paper No. 73-101, January 1973, Washington, D. C.

chemical reaction rates. This second-order closure model may therefore be considered as a generalized (but still approximate) solution of the chemical kinetics equations.

3. AN EVALUATION OF THE EFFECTS OF INHOMOGENEOUS MIXING

The Basic Chemical Kinetic Equations for Inhomogeneous Mixtures

Following Donaldson and Hilst (Appendix A) we assume an isothermal, irreversible, two-body reaction between chemical species α and β to form γ and δ .

$$\alpha + \beta \rightarrow \gamma + \delta \tag{3.1}$$

Further, we assume that the reaction rate for any joint values of the concentrations of the reacting chemical species are correctly specified by

$$\frac{\partial C_\alpha}{\partial t} = - k_1 C_\alpha C_\beta \tag{3.2}$$

$$\frac{\partial C_\beta}{\partial t} = - k_2 C_\alpha C_\beta \tag{3.3}$$

and

$$\frac{\partial}{\partial t} (C_\gamma + C_\delta) = \frac{\partial}{\partial t} (C_\alpha + C_\beta) \tag{3.4}$$

where C_i denotes the concentration of the ith chemical species (expressed as a mass fraction), and k_1 and k_2 are the reaction rate constants.

Equations (3.2) and (3.3) specify the <u>local</u> instantaneous rate of change of the concentration of the reactants. In order to determine the average rate of change, we assume the local history of the joint values of C_α and C_β at a fixed location comprises a stationary time series and each may be dissected into its mean and fluctuating components

$$C_\alpha = \overline{C}_\alpha + C'_\alpha \tag{3.5}$$

and

$$C_\beta = \overline{C}_\beta + C'_\beta \tag{3.6}$$

and, by definition, $\overline{C'_\alpha} = \overline{C'_\beta} = 0$. Under these assumptions the chemical kinetic equations for the average rates of change of the concentrations of α and β at that location are readily shown to be

$$\frac{\partial \overline{C}_\alpha}{\partial t} = - k_1 \left(\overline{C}_\alpha \overline{C}_\beta + \overline{C'_\alpha C'_\beta}\right) \tag{3.7}$$

and

$$\frac{\partial \overline{C}_\beta}{\partial t} = - k_2 \left(\overline{C}_\alpha \overline{C}_\beta + \overline{C'_\alpha C'_\beta}\right) \tag{3.8}$$

In order to solve Equations (3.7) and (3.8) we need a prediction equation for $\overline{C'_\alpha C'_\beta}$. This is readily derived (Appendix A) as

$$\begin{aligned} \frac{\partial \overline{C'_\alpha C'_\beta}}{\partial t} = & -k_1 \left(\overline{C}_\alpha \overline{C'^2_\beta} + \overline{C}_\beta \overline{C'_\alpha C'_\beta} + \overline{C'_\alpha C'^2_\beta}\right) \\ & -k_2 \left(\overline{C}_\beta \overline{C'^2_\alpha} + \overline{C}_\alpha \overline{C'_\alpha C'_\beta} + \overline{C'^2_\alpha C'_\beta}\right) \end{aligned} \tag{3.9}$$

which introduces four new terms, $\overline{C'^2_\alpha}$, $\overline{C'^2_\beta}$, $\overline{C'_\alpha C'^2_\beta}$, and $\overline{C'^2_\alpha C'_\beta}$. The prediction equations for $\overline{C'^2_\alpha}$ and $\overline{C'^2_\beta}$ are

$$\frac{\partial \overline{C'^2_\alpha}}{\partial t} = - 2k_1 \left(\overline{C}_\beta \overline{C'^2_\alpha} + \overline{C}_\alpha \overline{C'_\alpha C'_\beta} + \overline{C'^2_\alpha C'_\beta}\right) \tag{3.10}$$

and

$$\frac{\partial \overline{C'^2_\beta}}{\partial t} = - 2k_2 \left(\overline{C}_\alpha \overline{C'^2_\beta} + \overline{C}_\beta \overline{C'_\alpha C'_\beta} + \overline{C'_\alpha C'^2_\beta}\right) \tag{3.11}$$

and they do not introduce any more new terms. In order to close Equations (3.7) through (3.11), and thereby achieve a chemical sub-model for reactions in inhomogeneous mixtures, we require prediction equations for the third-order correlations $\overline{C_\alpha'^2 C_\beta'}$ and $\overline{C_\alpha' C_\beta'^2}$.

Before proceeding to the closure problem, however, it is instructive to examine more closely the limits of the effects of concentration fluctuations on chemical reaction rates and the conditions under which these effects become significant. This examination may be made in two steps; 1. when are the fluctuations of concentration negligible (i.e., when are the reaction rates predicted satisfactorily by the mean values of concentration alone?) and 2. when may the third-order correlations be neglected? For the latter cases, Equations (3.7) through (3.11) comprise the closed set discussed by Donaldson and Hilst (Appendix A).

The Limits of Errors in Reaction Rate Predictions if Concentration Fluctuations are Neglected.

Since the neglect of concentration fluctuations in determining reaction rates is equivalent to the assumption that the local values of C_α and C_β are constant in time, $C_\alpha' = C_\beta' \equiv 0$ and the reaction rates predicted under this assumption are simply

$$\left(\frac{\partial \overline{C}_\alpha}{\partial t}\right)_s = -k_1 \overline{C}_\alpha \overline{C}_\beta \tag{3.12}$$

and

$$\left(\frac{\partial \overline{C}_\beta}{\partial t}\right)_s = -k_2 \overline{C}_\alpha \overline{C}_\beta \tag{3.13}$$

where the subscript s denotes the steady state assumption. Then the ratio of reaction rates predicted from the inclusion of concentration fluctuations to those predicted neglecting these terms are

$$\frac{\partial \overline{C}_\alpha/\partial t}{(\partial \overline{C}_\alpha/\partial t)_s} = 1 + \frac{\overline{C'_\alpha C'_\beta}}{\overline{C}_\alpha \overline{C}_\beta} \tag{3.14}$$

and an identical equation for the relative rates of depletion of the β species.

The limits on Equation (3.14) are readily determined from Equations (3.7) or (3.8) and elementary statistics. First, we note from Equation (3.7) that for irreversible reactions, $\partial \overline{C}_\alpha/\partial t \leq 0$ and therefore

$$\frac{\overline{C'_\alpha C'_\beta}}{\overline{C}_\alpha \overline{C}_\beta} \geq -1 \tag{C1}$$

Further, from elementary statistics we note that

$$-1 \leq \frac{\overline{C'_\alpha C'_\beta}}{(\overline{C'^2_\alpha}\,\overline{C'^2_\beta})^{\frac{1}{2}}} \leq +1 \tag{C2}$$

and therefore

$$-\left(\frac{\overline{C'^2_\alpha}}{\overline{C}^2_\alpha}\,\frac{\overline{C'^2_\beta}}{\overline{C}^2_\beta}\right)^{\frac{1}{2}} \leq \frac{\overline{C'_\alpha C'_\beta}}{\overline{C}_\alpha \overline{C}_\beta} \leq \left(\frac{\overline{C'^2_\alpha}}{\overline{C}^2_\alpha}\,\frac{\overline{C'^2_\beta}}{\overline{C}^2_\beta}\right)^{\frac{1}{2}} \tag{C3}$$

Substituting conditions (C1) and (C3) into Equation (3.14), we establish the limits

$$0 \leq 1 - \left(\frac{\overline{C_\alpha'^2}}{\overline{C}_\alpha^2} \frac{\overline{C_\beta'^2}}{\overline{C}_\beta^2} \right)^{\frac{1}{2}} \leq \frac{\partial \overline{C}_\alpha / \partial t}{(\partial \overline{C}_\alpha / \partial t)_s} \leq 1 + \left(\frac{\overline{C_\alpha'^2}}{\overline{C}_\alpha^2} \frac{\overline{C_\beta'^2}}{\overline{C}_\beta^2} \right)^{\frac{1}{2}} \tag{C4}$$

Conditions (C4) set the maximum errors in the prediction of reaction rates which the neglect of concentration fluctuations can produce. These limits are set by the individual variance-to-mean-squared ratios of C_α and C_β and are therefore functions of the marginal frequency distributions of C_α and C_β .

The limits established by conditions (C4) are shown graphically in Figure 1 and we note immediately that the limiting errors in reaction predictions occasioned by neglect of concentration fluctuations are small for $\left(\frac{\overline{C_\alpha'^2}}{\overline{C}_\alpha^2} \frac{\overline{C_\beta'^2}}{\overline{C}_\beta^2} \right)^{\frac{1}{2}} < 0.5$, but increase to highly significant values as this ratio exceeds 1.0. The potential for order-of-magnitude errors in the prediction of the reaction rate exists whenever the product of the variance-to-mean-squared ratios greatly exceeds 1.0.

The actual error depends, of course, on $\overline{C_\alpha' C_\beta'} / \overline{C}_\alpha \overline{C}_\beta$. This actual error may be examined by forming the ratio

$$r = \frac{\overline{C_\alpha' C_\beta'}}{\overline{C}_\alpha \overline{C}_\beta} \bigg/ \left(\frac{\overline{C_\alpha'^2}}{\overline{C}_\alpha^2} \frac{\overline{C_\beta'^2}}{\overline{C}_\beta^2} \right)^{\frac{1}{2}} = \frac{\overline{C_\alpha' C_\beta'}}{(\overline{C_\alpha'^2}\ \overline{C_\beta'^2})^{\frac{1}{2}}} , \tag{3.15}$$

where r is the ordinary correlation coefficient and in this usage expresses the ratio of the actual error in reaction rate predictions to the maximum possible error for any given joint

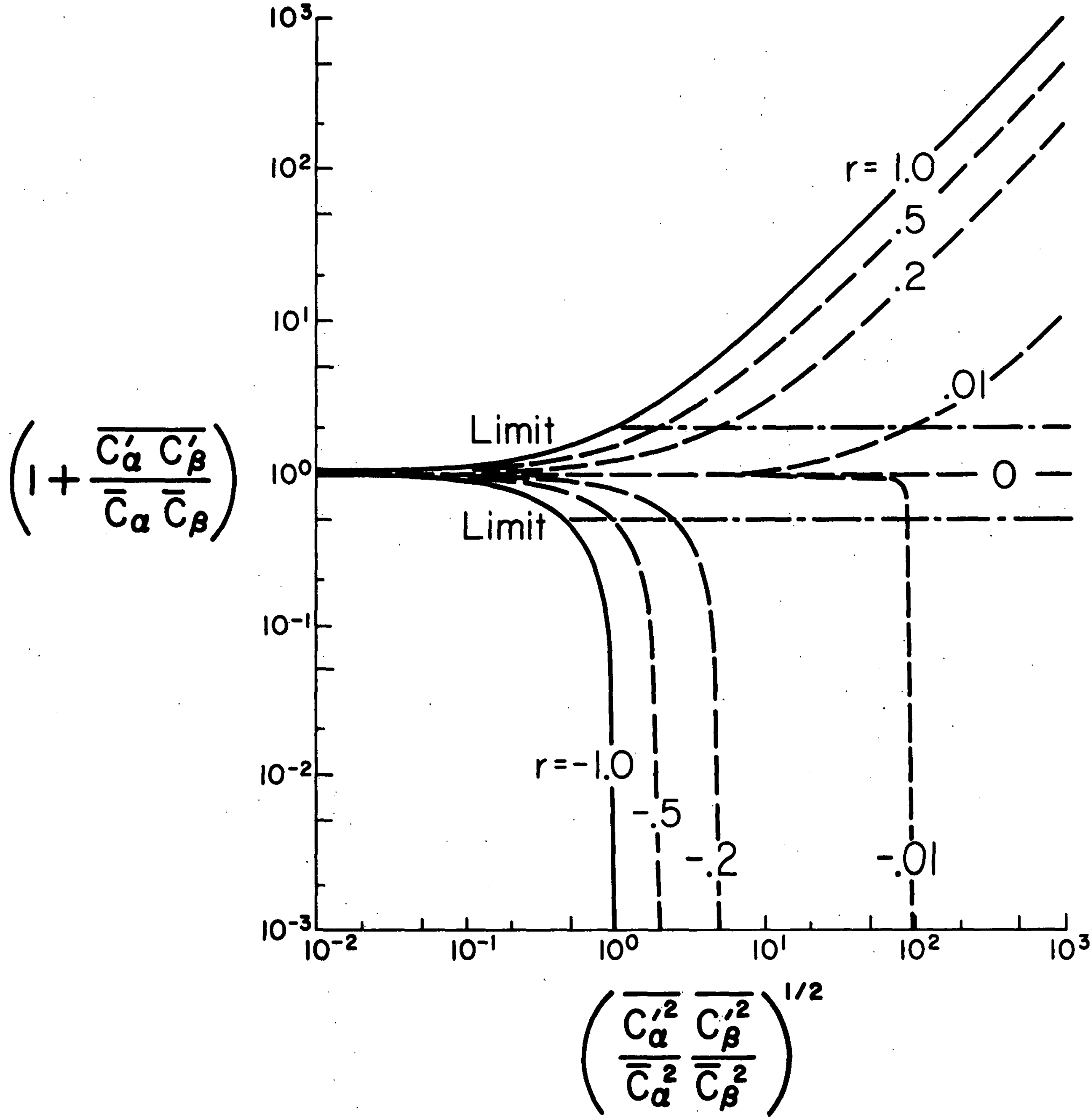

Figure 1. The limits of errors of prediction of chemical reaction rates incurred by the neglect of concentration fluctuations. (See text for explanation of terms.)

distribution of C_α and C_β. Selected values of r are also graphed in Figure 1. In the limit of $r = 0$ no error in reaction rate predictions is occasioned by the neglect of concentration fluctuations. This is, of course, the situation when C_α and C_β are randomly distributed and $\overline{C'_\alpha C'_\beta} = 0$. However, it is clear from Figure 1 that even modest values of r produce significant errors in the reaction rate prediction when $\left(\frac{\overline{C'^2_\alpha}}{\overline{C}^2_\alpha} \frac{\overline{C'^2_\beta}}{\overline{C}^2_\beta}\right)^{\frac{1}{2}} > 1$, particularly when $r < 0$.

We shall return to this analysis, and identify joint distributions of C_α and C_β for which the fluctuations of concentration must be included later. For the purpose of model development, we now turn attention to the importance of the third-order correlations in the chemical kinetics equations.

The Role of the Third-Order Correlation Terms

Returning to Equations (3.9) to (3.11), it is evident that the primary role of the third-order correlations is to be found in their control of the rate of change of $\overline{C'_\alpha C'_\beta}$, both directly and through the rates of change of the variances, $\overline{C'^2_\alpha}$ and $\overline{C'^2_\beta}$. The effects of the third-order correlations on the reaction rates will therefore appear primarily as a time-integrated effect on $\overline{C'_\alpha C'_\beta}$ and any cumulative error in the estimates of $\overline{C'^2_\alpha C'_\beta}$ and $\overline{C'_\alpha C'^2_\beta}$ will produce a cumulative error in $\overline{C'_\alpha C'_\beta}$.

We may deduce immediately from Equations (3.9) through (3.11) that if

$$\left.\begin{aligned} &\overline{C'^2_\alpha C'_\beta} \ll \overline{C}_\beta \overline{C'^2_\alpha} + \overline{C}_\alpha \overline{C'_\alpha C'_\beta} \\ \text{and} \quad &\overline{C'_\alpha C'^2_\beta} \ll \overline{C}_\alpha \overline{C'^2_\beta} + \overline{C}_\beta \overline{C'_\alpha C'_\beta} \end{aligned}\right\} \qquad \text{(C5)}$$

their effect on $\overline{C'_\alpha C'_\beta}$ is negligible and we may close the model equations by setting $\overline{C'^2_\alpha C'_\beta} = \overline{C'_\alpha C'^2_\beta} = 0$. To illustrate that conditions (C5) are met under any given circumstance, we must evaluate the joint distributions of C_α and C_β from which these moments are derived since there are now no limiting conditions on their marginal distributions. In other words, we must turn attention to the distribution functions from which the means and moments have been derived if we are to determine the importance of third- or higher-order correlations in chemical reaction rates. Ideally, we would examine simultaneous experimental measurements of $C_{\alpha i}$ and $C_{\beta i}$ to make this assessment; unfortunately, very few such data exist. However, so long as we assume that the basic chemical kinetic equations are correct (and our whole theory is based on this assumption) we can proceed by solving these basic equations for various initial distributions of $C_{\alpha i}$ and $C_{\beta i}$, determining in the process the time histories of all of the relevant moments of these distributions.

The Moment Generating Model

Under the assumption that only chemical reactions are operative in changing the concentrations of α and β , the chemical kinetic equations can be written as total derivatives and integrated directly as a function of reaction time.

$$\frac{dC_{\alpha i}}{dt} = -k_1 C_{\alpha i} C_{\beta i} \tag{3.16}$$

$$\frac{dC_{\beta i}}{dt} = -k_2 C_{\alpha i} C_{\beta i} \tag{3.17}$$

and

$$C_{\alpha i}(t) - C_{\alpha i}(0) = \frac{k_1}{k_2} \left(C_{\beta i}(t) - C_{\beta i}(0)\right) \tag{3.18}$$

while

$$C_{\beta i}(t) = \frac{C_{\beta i}(0) - \frac{k_2}{k_1} C_{\alpha i}(0)}{1 - \frac{k_2}{k_1} \frac{C_{\alpha i}(0)}{C_{\beta i}(0)} \exp\left\{- (C_{\beta i}(0) - \frac{k_2}{k_1} C_{\alpha i}(0))k_1 t\right\}} \tag{3.19}$$

Equations (3.18) and (3.19) specify the joint values of $C_{\alpha i}$ and $C_{\beta i}$ at time t, given their initial values and the reaction rate constants. They may be used to specify the frequency distribution of $(C_{\alpha i}, C_{\beta i})$ at any time t, given their initial frequency distribution, $n_i(0)$ since, in the absence of mixing, n_i is conserved as $C_{\alpha i}$ and $C_{\beta i}$ change value due to chemical reaction. Equations (3.18) and (3.19) provide the information necessary to calculate all of the relevant moments of $n_i(C_{\alpha i}, C_{\beta i})$ and their rates of change. We may introduce any arbitrary initial distribution $n_i(C_{\alpha i}, C_{\beta i})$, subject only to the constraints

$$\left.\begin{array}{l} 0 \leq C_{\alpha i} \leq 1 \\ 0 \leq C_{\beta i} \leq 1 \\ 0 \leq C_{\alpha i} + C_{\beta i} \leq 1 \end{array}\right\} \quad \text{and} \tag{C6}$$

In order to illustrate the general behavior of the distribution of C_α and C_β and the associated first-, second-, and third-order moments, we have chosen a simple distribution of points along the line $C_\alpha = 1 - C_\beta$ and weighted each point equally $(n_i = 1/N)$. The time history of $n_i(C_{\alpha i}, C_{\beta i})$ is shown in Figure 2 and the moments of these distributions are plotted in Figure 3. Note particularly the distortion of the originally linear distribution of (C_α, C_β) and the associated decrease (from zero) of the third-order moments. The relative

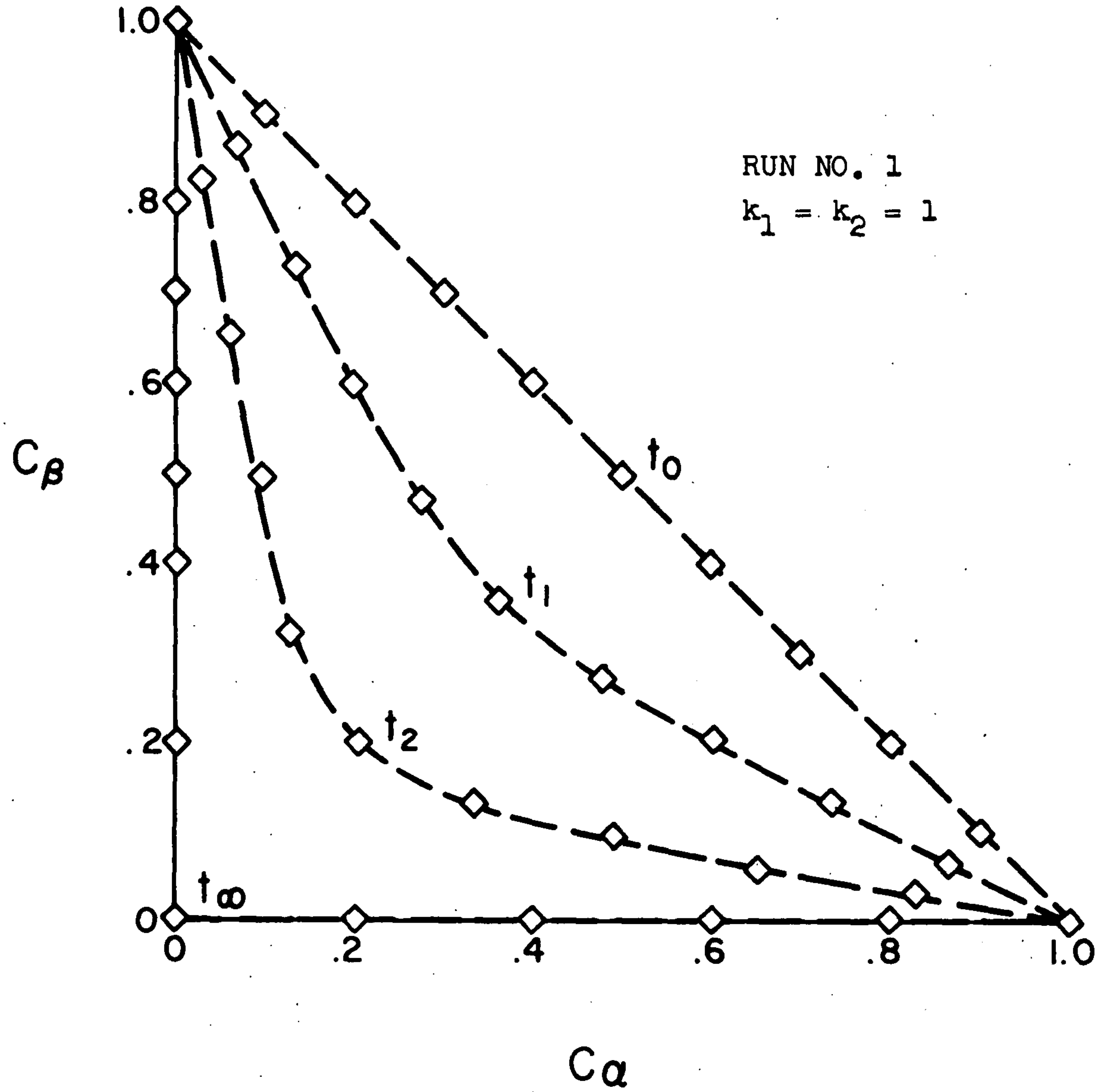

Figure 2. Example of the time history of the joint frequency distribution of $(C_{\alpha 1}, C_{\beta 1})$ given the initial distribution shown for t_0 and $k_1 = k_2 = 1$. Each point was weighted equally $(n_1 = 1)$ for calculation of the moments of these distributions (shown in Figure 3).

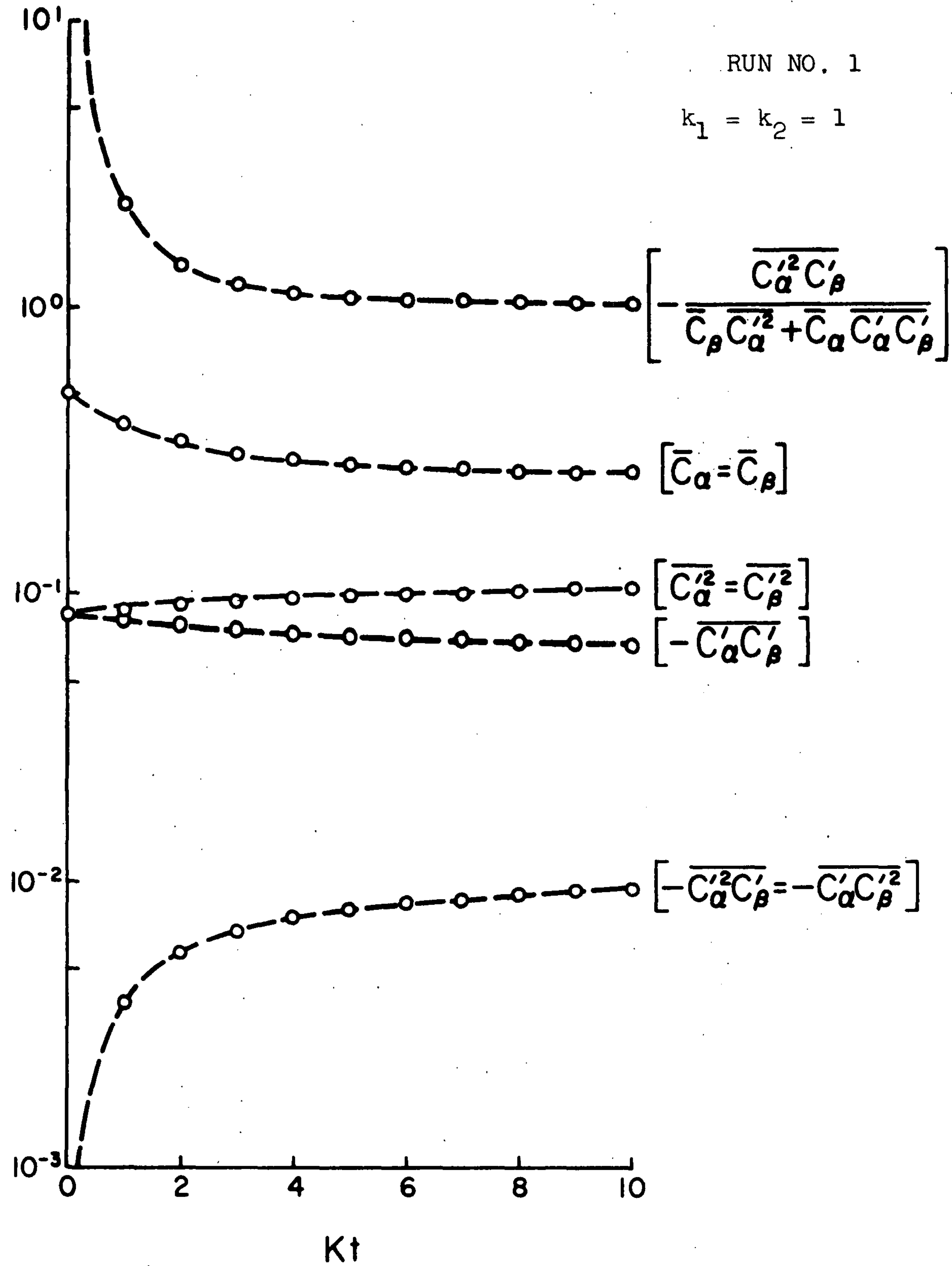

Figure 3. Time history of the first-, second-, and third-order moments of $n_1(C_{\alpha i}, C_{\beta i})$ for the distributions shown in Figure 2.

magnitudes of $\overline{c_\alpha'^2 c_\beta'}$ and $\overline{C}_\beta \overline{c_\alpha'^2} + \overline{C}_\alpha \overline{c_\alpha' c_\beta'}$ are also plotted in Figure 3 and, as can be seen there, $\overline{c_\alpha'^2 c_\beta'}$ and $\overline{c_\alpha' c_\beta'^2}$ completely dominate the initial change of $\overline{c_\alpha' c_\beta'}$. However, this latter effect is too short-lived to be significant in the prediction of the time history of mean concentrations. This fact is shown in Figure 4, where the predictions of $\overline{C}_\alpha$ and $\overline{C}_\beta$ as a function of time, first, neglecting the fluctuations completely, and then neglecting only the third-order moments, are compared with the exact solution. The latter assumption produces an error of approximately 10 per cent at kt = 10 while the total neglect of the fluctuations produces an error of 300 per cent at that time.

As a further example, and one which illustrates the importance of the third-order correlations, we have constructed the distribution functions which simulate the case of intermittent sources. For physical perspective, imagine a free-way, oriented across the wind and on which the automobile traffic ranges from a steady, bumper-to-bumper stream to only an occasional vehicle. We assume that each vehicle emits approximately the same amount of pollutants per unit time, but that the ratio of the α and β species emitted is slightly variable from one vehicle to another. Now we ask, "What is the average reaction rate for these exhaust materials immediately downwind from the roadway as a function of the intermittency of the traffic?"

We simulate this situation by the frequency distribution for (C_α, C_β) shown in Figure 5. The variability of C_α and C_β due to variable exhaust emissions is portrayed as a circularly symmetric distribution and we take $C_\alpha = C_\beta = 0$ when there is no traffic upwind of our observation line. (Small background concentrations have been assumed in another calculation but produce no significant effect.) We assume further that the pairs of nonzero values of (C_α, C_β) occur

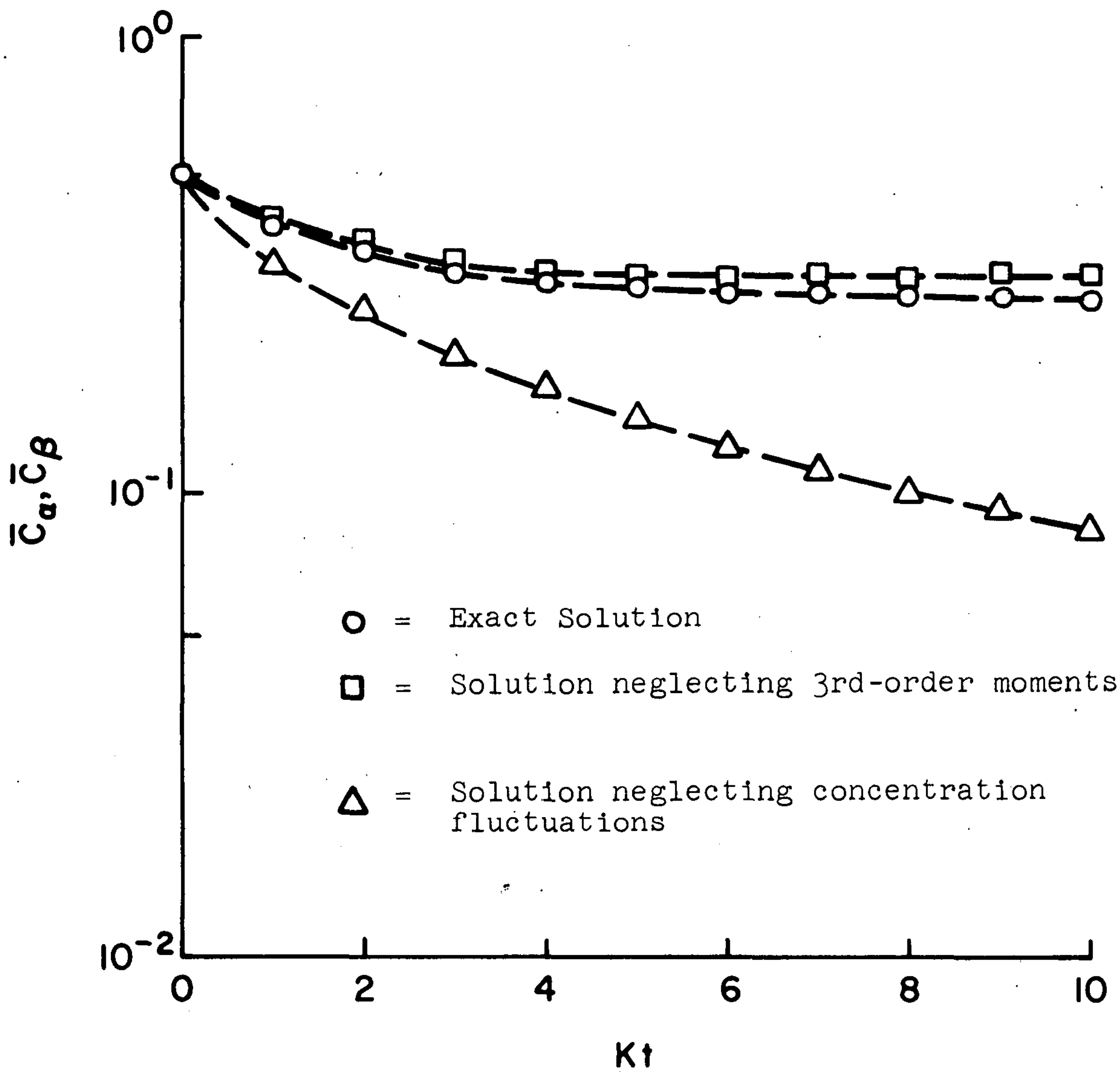

Figure 4. Comparison of the predictions of $\overline{C}_\alpha$ and $\overline{C}_\beta$, under assumptions listed, with exact values from the moment generating model using the distributions shown in Figure 3.

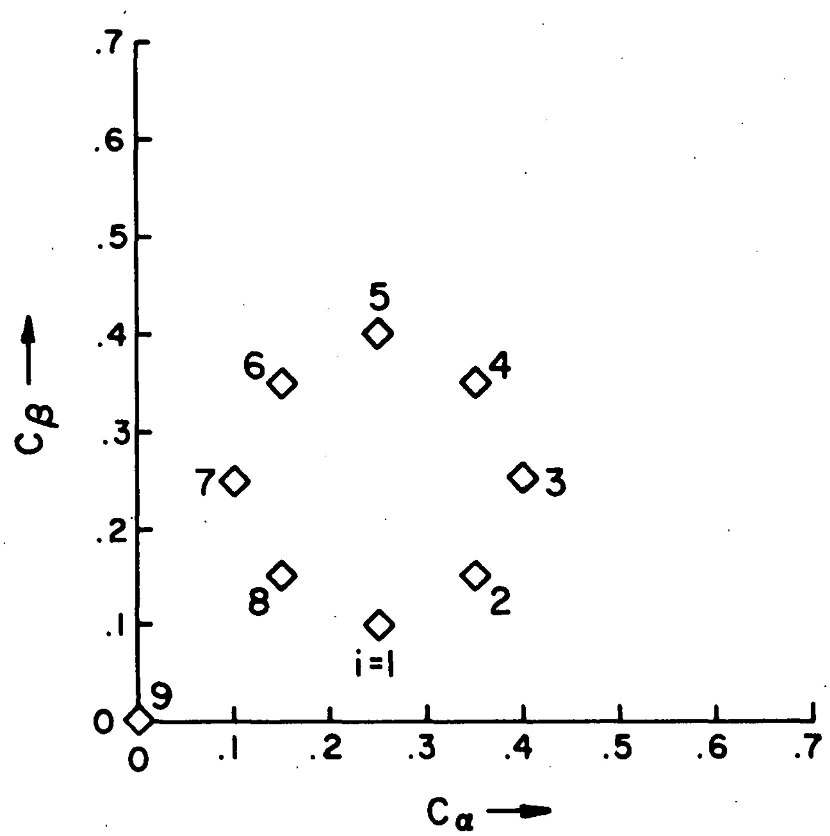

Figure 5. Joint distributions of (C_α, C_β) chosen to simulate chemical reaction rates immediately downwind of a roadway on which traffic is variably intermittent.

with equal frequency and we measure the intermittency of the traffic as the fraction of time there is a vehicle upwind of the observation line, t_i . The moment-generating model has been used to determine the chemical reaction rates as a function of kt for $t_i = 1.0, 0.5, 0.33, 0.2, 0.1$ ($t_i = 1.0$ corresponds to a steady, bumper-to-bumper stream of traffic). The values of $A_1 = \left(\frac{\overline{C'^2_\alpha}}{\overline{C}^2_\alpha} \frac{\overline{C'^2_\beta}}{\overline{C}^2_\beta}\right)^{\frac{1}{2}}$, $r = \frac{\overline{C'_\alpha C'_\beta}}{(\overline{C'^2_\alpha}\ \overline{C'^2_\beta})^{\frac{1}{2}}}$, and

$$A_2 = \frac{\overline{C'^2_\alpha C'_\beta}}{\overline{C}_\beta \overline{C'^2_\alpha} + \overline{C}_\alpha \overline{C'_\alpha C'_\beta}} \quad \text{at } kt = 1$$

and for each value of t_i are shown along with the observed ratios of $\partial\overline{C}_\alpha/\partial t$ to the reaction rates predicted assuming steady values of C_α and C_β , $(\partial\overline{C}_\alpha/\partial t)_s$, and to the rates predicted neglecting the third-order correlations, $(\partial\overline{C}_\alpha/\partial t)_I$, in Table 1. These results, which are now firmly grounded in reality, show clearly that the potential errors in the prediction of reaction rates neglecting the concentration fluctuations can be realized. Although the effects of concentration fluctuations are negligible for a steady stream of traffic, $t_i = 1$, chemical kinetics based on this assumption underestimate the initial depletion rate of $\overline{C}_\alpha$ and $\overline{C}_\beta$ by a factor of 9 when $t_i = 0.1$!

The effect of neglecting the third-order moments is not evident at $kt = 1$, however, since we started with the <u>correct</u> value of $\overline{C'_\alpha C'_\beta}$ and the integral effect of neglecting $\overline{C'^2_\alpha C'_\beta}$ and $\overline{C'_\alpha C'_\beta}$ is not yet large at $kt = 1$. Their integral effect on the predictions of $\overline{C}_\alpha$ and $\partial\overline{C}_\alpha/\partial t$ can be seen, however, in the time histories of these quantities when the third-order correlations are neglected. Values of $B_1 = \overline{C}_\alpha/\overline{C}_{\alpha I}$ and $B_2 = (\partial\overline{C}_\alpha/\partial t)/(\partial\overline{C}_\alpha/\partial t)_I$ for each value of t_i and $kt = 1, 5, 10, 16,$ and 20 are listed in Table 2. [( ) indicates $\overline{C}_{\alpha I}$ or $(\partial\overline{C}_\alpha/\partial t)_I$ has wrong sign.]

An inspection of this table shows that the first effect of neglecting the third-order correlations, while retaining the first- and second-order moments, is to produce significant errors in the reaction rate. This is, of course, the first integral effect on $\overline{C'_\alpha C'_\beta}$. The second effect is on the mean values predicted for the concentrations, an error which depends upon the time integral of $\overline{C'_\alpha C'_\beta}$. We also note that not only can the errors be large (for example, the reaction rate is over-predicted by a factor of 100 when $t_i = 0.1$ and $kt = 20$) but we get the totally erroneous results of positive values of $\partial\overline{C}_\alpha/\partial t$ and negative values of $\overline{C}_\alpha$!

From these results we conclude that a generally useful chemical kinetic model must include the representation of the moments of the concentration fluctuations through the third-order.

Summary

The various considerations and examples of the effects of concentration fluctuations on chemical reaction rates discussed above may be summarized as follows:

1. The effects of concentration fluctuations can be significant, to the point of dominating chemical reaction rates. The situations under which they are significant are characterized by joint distributions of the reactant concentrations which are skewed toward large values of these concentrations, since this is the condition under which the variance-to-mean-squared ratios can be large with respect to one.

2. The chemical reaction rate is significantly accelerated when the concentration fluctuations are positively correlated and is depressed when these fluctuations are negatively correlated. Combining these two requirements for significant effects of concentration fluctuations, we may sketch the general character of the joint distributions of C_α and C_β which require the inclusion of concentration fluctuations in chemical kinetic models. These are shown in Figure 6. The first, when $\overline{C_\alpha' C_\beta'} > 0$ is essentially the distribution of concentrations used for the intermittent traffic situation in the last section. The second, when $\overline{C_\alpha' C_\beta'} < 0$, may be quickly identified with the situation when the chemical reaction is retarded or stopped by local depletion of one of the reactants. This latter case depends strongly upon the relative rates of chemical reaction and of local diffusive mixing. Further study of this situation depends upon an appropriate coupling of the chemical and diffusion equations.

3. For strongly skewed distribution of C_α and C_β, the case when concentration fluctuations become dominant in the determination of the chemical reaction rate, the third-order correlations of these distributions <u>must</u> be included in the generalized chemical kinetic model. The neglect of these terms leads to the highly erroneous result that either the reactants are produced rather than depleted, or the mean concentrations go to negative values.

TABLE 1

t_i	A_1	r	A_2	$\frac{(\partial\bar{c}_\alpha/\partial t)}{(\partial\bar{c}_\alpha/\partial t)_s}$	$\frac{(\partial\bar{c}_\alpha/\partial c)}{(\partial\bar{c}_\alpha/\partial t)_I}$
1.0	0.19	-0.41	-0.04	0.92	1.0
0.50	1.40	0.61	0.02	1.86	1.0
0.33	2.7	0.67	0.50	2.80	1.0
0.20	5.0	0.74	1.48	4.70	1.0
0.10	11.0	0.75	4.00	9.25	1.0

TABLE 2

t_i	kt = 1		kt = 5		kt = 10		kt = 16		kt = 20	
	B_1	B_2	B_1	B_2	B_1	B_2	B_1	B_2	B_1	B_2
1.0	1.0	1.01	1.0	1.33	1.0	1.25	1.0	1.40	1.0	1.60
0.50	1.0	1.00	1.05	1.60	0.92	2.60	0.83	(-6.80)	0.77	(-2.35)
0.33	1.0	1.00	1.21	1.17	1.24	1.50	1.08	(-1.50)	0.96	(-0.50)
0.20	1.0	1.00	1.67	0.54	7.20	0.30	(-1.33)	0.09	(-0.50)	0.02
0.10	1.0	1.00	2.31	0.40	(-1.42)	0.41	(-0.30)	0.03	(-0.14)	0.01

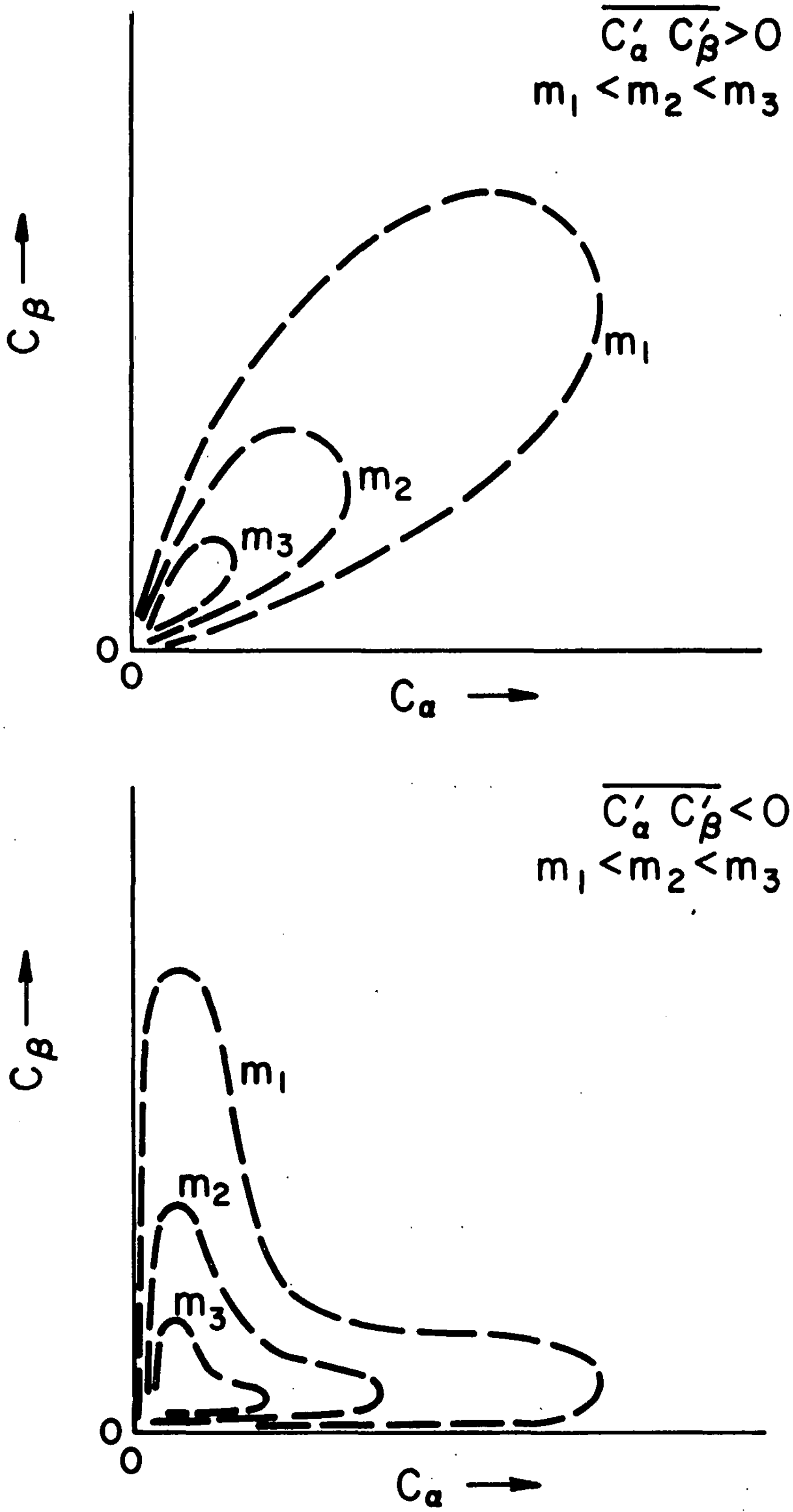

Figure 6. General types of joint frequency distributions of C_α and C_β for which concentration fluctuations are significant in determining chemical reaction rates.

4. CLOSURE OF THE CHEMICAL SUB-MODEL

Having demonstrated the need for a more general chemical kinetic model for reactions in inhomogeneous mixtures, we may proceed along either of two fronts. The more general of these is to write down prediction equations for the third-order correlations and seek closure by suitable assumptions regarding the fourth-order moments. If no such assumptions exist at the fourth order, we may proceed to higher-order moments until they are found. This line of inquiry has been pursued to the level of the fifth-order moments in the present study but has been set aside, primarily because the proliferation of simultaneous partial differential equations for the higher-order moments poses staggering computer requirements. This latter feature of higher-order closure becomes prohibitive when one considers the requirement for an equivalent level of closure of the diffusion equations with which this chemical sub-model is to be coupled.

With these facts in mind, we have turned attention to the development of approximate closure schemes in which maximum possible information regarding the third-order correlations is sought from the first- and second-order moments. As is noted later, such a closure scheme cannot be exact. We begin by reviewing the definitions of $\overline{C_\alpha' C_\beta'}$, $\overline{C_\alpha'^2 C_\beta'}$ and $\overline{C_\alpha' C_\beta'^2}$.

First, by definition,

$$\overline{C_\alpha' C_\beta'} = \frac{1}{N} \sum_i n_i (C_{\alpha i} - \overline{C}_\alpha)(C_{\beta i} - \overline{C}_\beta) \qquad (4.1)$$

where n_i is the frequency of occurrence of the joint values of $(C_{\alpha i}, C_{\beta i})$ and $N = \sum_i n_i$. Expanding Equation (4.1) and making use of the definitions of $\overline{C}_\alpha$ and $\overline{C}_\beta$, i.e., $\overline{C}_j = \frac{1}{N} \sum_i n_i C_{ji} (j = \alpha, \beta)$, one obtains

$$\frac{\overline{C'_\alpha C'_\beta}}{\overline{C}_\alpha \overline{C}_\beta} = \frac{1}{\overline{C}_\alpha \overline{C}_\beta N} \sum_i n_i C_{\alpha i} C_{\beta i} - 1 \tag{4.2}$$

We note in particular from Equation (4.2) that, since

$$\frac{1}{\overline{C}_\alpha \overline{C}_\beta N} \sum_i n_i C_{\alpha i} C_{\beta i} \geq 0 \tag{C7}$$

$\overline{C'_\alpha C'_\beta}/\overline{C}_\alpha \overline{C}_\beta = -1$ only when the lower limit of conditions (C7) is satisfied. This can occur only when any nonzero values of $C_{\alpha i}$ are coupled with zero values of $C_{\beta i}$, and vice versa. Then, when $\overline{C'_\alpha C'_\beta}/\overline{C}_\alpha \overline{C}_\beta = -1$, which is the condition for the termination of the chemical reaction, all joint moments of $n_i(C_{\alpha i}, C_{\beta i})$ about the origin must be zero.

Now consider the definition of $\overline{C'^2_\alpha C'_\beta}$.

$$\overline{C'^2_\alpha C'_\beta} = \frac{1}{N} \sum_i n_i (C_{\alpha i} - \overline{C}_\alpha)^2 (C_{\beta i} - \overline{C}_\beta) \tag{4.3}$$

or

$$\frac{\overline{C'^2_\alpha C'_\beta}}{\overline{C}^2_\alpha \overline{C}_\beta} = \frac{1}{\overline{C}^2_\alpha \overline{C}_\beta N} \sum_i n_i C^2_{\alpha i} C_{\beta i}$$

$$- \left[1 + \frac{\overline{C'^2_\alpha}}{\overline{C}^2_\alpha} + 2 \frac{\overline{C'_\alpha C'_\beta}}{\overline{C}_\alpha \overline{C}_\beta} \right] \tag{4.4}$$

using Equation (4.1) and the definitions of $\overline{C}_\alpha$ and $\overline{C}_\beta$. It is immediately evident from Equation (4.4) that our problem of approximating $\overline{C_\alpha'^2 C_\beta'}$ by first- and second-order moments reduces to finding a suitable approximation for the first term on the right-hand side of Equation (4.4) in terms of these moments. For convenience we denote this term by $A_{i\alpha}$, i.e.,

$$A_{i\alpha} = \frac{1}{\overline{C}_\alpha^2 \overline{C}_\beta N} \sum_i n_i \, C_{\alpha i}^2 C_{\beta i} \qquad (4.5)$$

In seeking this approximation we may note the following conditions which $A_{i\alpha}$ must satisfy

1. $A_{i\alpha} = 0$ when $\overline{C_\alpha' C_\beta'}/\overline{C}_\alpha \overline{C}_\beta = -1$

2. $A_{i\alpha} = 1$ when $\overline{C_\alpha'^2}/\overline{C}_\alpha^2 = 0$

3. $A_{i\alpha} = 1 + \dfrac{\overline{C_\alpha'^2}}{\overline{C}_\alpha^2} + 2\dfrac{\overline{C_\alpha' C_\beta'}}{\overline{C}_\alpha \overline{C}_\beta}$ when $\overline{C_\alpha'^2 C_\beta'} = 0$

4. $A_{i\alpha} \geq 0$ at all times. (C8)

Condition 4 in (C8) operates primarily to constrain the joint values which $\overline{C_\alpha'^2}/\overline{C}_\alpha^2$ and $\overline{C_\alpha' C_\beta'}/\overline{C}_\alpha \overline{C}_\beta$ may assume. For example, when conditions 3 and 4 in (C8) are applied jointly, we derive directly the further condition that

$$\left.\begin{aligned} &\frac{\overline{C'^2_\alpha}}{\overline{C}^2_\alpha} + 2\,\frac{\overline{C'_\alpha C'_\beta}}{\overline{C}_\alpha \overline{C}_\beta} \geq -1 \\ \text{or}\qquad & \\ &\frac{\overline{C'_\alpha C'_\beta}}{\overline{C}_\alpha \overline{C}_\beta} \geq -\tfrac{1}{2}\left[1 + \frac{\overline{C'^2_\alpha}}{\overline{C}^2_\alpha}\right] \end{aligned}\right\} \qquad \text{(C9)}$$

Finally, we must note that $\overline{C'^2_\alpha C'_\beta}$ and $\overline{C'_\alpha C'^2_\beta}$ cannot be specified exactly from first- and second-order moments alone. Consider, for example, the two distributions of $C_{\alpha i}$ and $C_{\beta i}$ shown in Figure 7. All of the first- and second-order moments are identical for these two distributions, but the third-order correlations are of opposite sign. Clearly, we are looking for useful approximations, not exact relationships, and any such approximations must be delimited as to their regions of applicability. The criteria for usefulness of these approximations must be based on the accuracy with which the chemical model within which they are incorporated predicts the chemical reaction rates. However, in this development stage we shall be primarily interested in the accuracy of specification of the third-order correlations.

Approximations of $A_{1\alpha}$ From First- and Second-Order Moments

Utilizing conditions (C8) and (C9), it is not difficult to formulate approximate expressions for $A_{1\alpha}$ and $A_{1\beta}$ from $\overline{C}_\alpha$, $\overline{C}_\beta$, $\overline{C'_\alpha C'_\beta}$, and $\overline{C'^2_\alpha}$ and $\overline{C'^2_\beta}$. For example, an early approximation which has been tested is

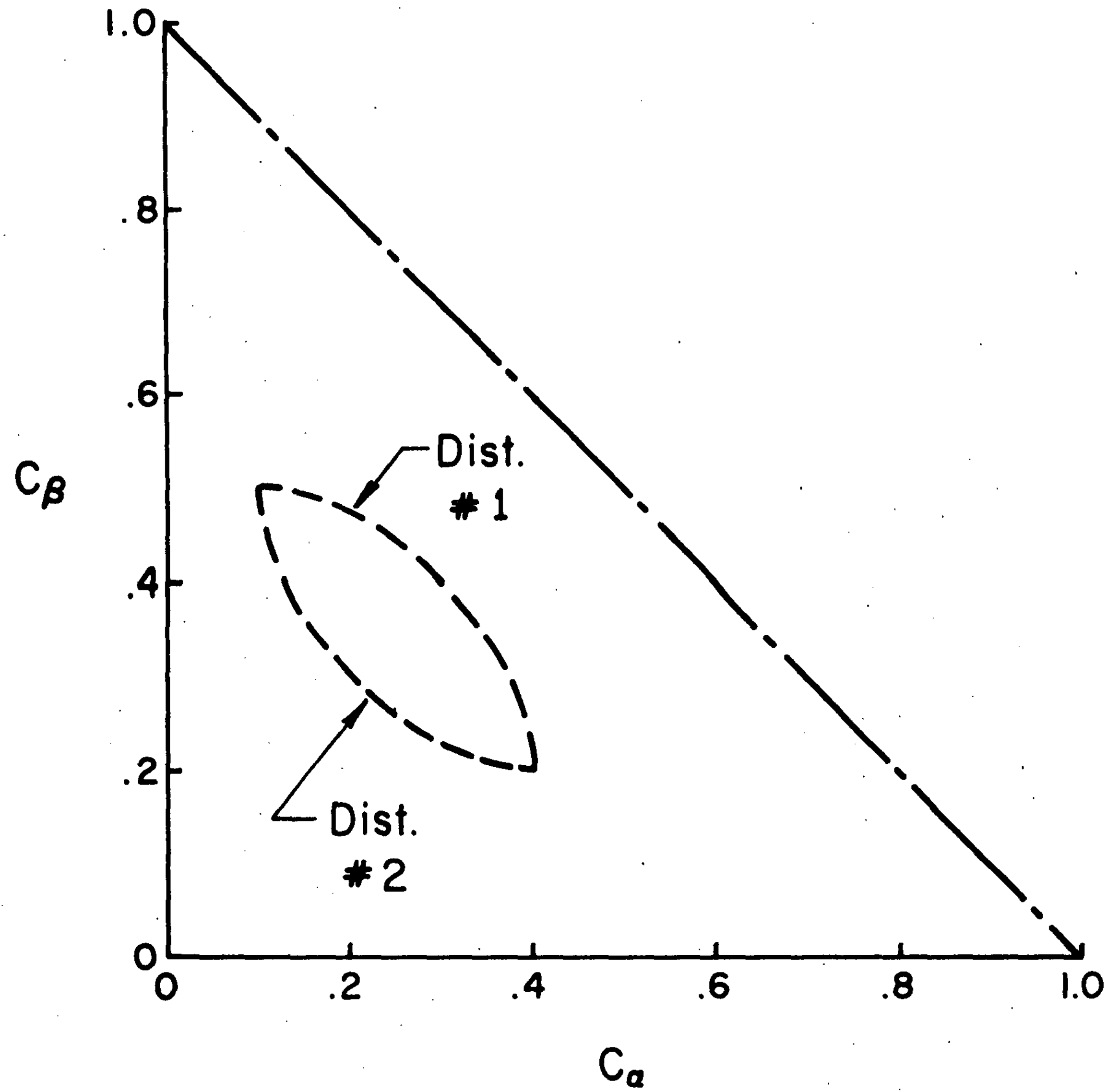

Figure 7. An example of two joint distributions of C_α and C_β for which all first- and second-order moments are equal but the third-order moments are not equal.

$$A_{i\alpha} = \left[1 + \frac{\overline{C'_\alpha C'_\beta}}{\overline{C}_\alpha \overline{C}_\beta}\right]\left[1 + \frac{\overline{C'^2_\alpha}}{\overline{C}^2_\alpha}\right] \tag{4.6}$$

Since $\overline{C'_\alpha C'_\beta} = 0$ when $\overline{C'^2_\alpha} = 0$ and $\overline{C'_\alpha C'_\beta}/\overline{C}_\alpha \overline{C}_\beta \geq -1$, it is evident from inspection of Equation (4.6) that this approximation satisfies conditions 1, 2, and 4 of (C8), but satisfies condition 3 only if $\overline{C'_\alpha C'_\beta} = 0$ when $\overline{C'^2_\alpha C'_\beta} = 0$. According to condition (C9), the latter result is admitted but is not required, i.e., $\overline{C'_\alpha C'_\beta}$ may be nonzero when $\overline{C'^2_\alpha C'_\beta} = 0$.

The development of an improved approximation of $A_{i\alpha}$, improved in the sense of more appropriate realization of condition 3 in (C8), proceeds as follows: Let

$$A_{i\alpha} = \left[1 + \frac{\overline{C'^2_\alpha}}{\overline{C}^2_\alpha} + 2\,\frac{\overline{C'_\alpha C'_\beta}}{\overline{C}_\alpha \overline{C}_\beta}\right] f_\alpha(\overline{C}_\alpha, \overline{C}_\beta, \overline{C'_\alpha C'_\beta}, \overline{C'^2_\alpha C'^2_\beta}) \tag{4.7}$$

where the function f_α satisfies the conditions

$$\left.\begin{aligned} f_\alpha &= 0 \text{ when } \overline{C'_\alpha C'_\beta}/\overline{C}_\alpha \overline{C}_\beta = -1 \\ f_\alpha &= 1 \text{ when } \overline{C'^2_\alpha C'_\beta} = 0 \end{aligned}\right\} \tag{C10}$$

A simple function which satisfies conditions (C10) is

$$f_\alpha = \frac{(\overline{C'_\alpha C'_\beta})/(\overline{C}_\alpha \overline{C}_\beta) + 1}{M + 1} \tag{4.8}$$

where M is defined as the value of $\overline{C'_\alpha C'_\beta}/\overline{C}_\alpha \overline{C}_\beta$ when $\overline{C'^2_\alpha C'_\beta} = 0$. We may note immediately that M as defined must satisfy condition (C9), i.e.,

$$M \geq -\tfrac{1}{2}\left[1 + \frac{\overline{C_\alpha'^2}}{\overline{C}_\alpha^2}\right] \tag{C11}$$

As a further measure of M, however, we may also note that since the ordinary correlation coefficient, $\overline{C_\alpha' C_\beta'}/(\overline{C_\alpha'^2}\,\overline{C_\beta'^2})^{\frac{1}{2}}$, must lie between ± 1 (condition (C3))

$$-\left[\frac{\overline{C_\alpha'^2}}{\overline{C}_\alpha^2}\;\frac{\overline{C_\beta'^2}}{\overline{C}_\beta^2}\right]^{\frac{1}{2}} \leq \frac{\overline{C_\alpha' C_\beta'}}{\overline{C}_\alpha \overline{C}_\beta} \leq \left[\frac{\overline{C_\alpha'^2}}{\overline{C}_\alpha^2}\;\frac{\overline{C_\beta'^2}}{\overline{C}_\beta^2}\right]^{\frac{1}{2}} \tag{C12}$$

and we expect M to be related to both $\overline{C_\alpha'^2}/\overline{C}_\alpha^2$ and $\overline{C_\beta'^2}/\overline{C}_\beta^2$. This expectation is reinforced by the fact that, as defined, M must have the same value for both $\overline{C_\alpha'^2 C_\beta'}$ and $\overline{C_\alpha' C_\beta'^2}$, although $\overline{C_\alpha'^2}/\overline{C}_\alpha^2$ is not necessarily equal to $\overline{C_\beta'^2}/\overline{C}_\beta^2$.

Some values of M versus $\left[\frac{\overline{C_\alpha'^2}}{\overline{C}_\alpha^2}\;\frac{\overline{C_\beta'^2}}{\overline{C}_\beta^2}\right]^{\frac{1}{2}}$, as determined from the moment generating model, are shown in Figure 8. (Each of these solutions was derived from a log-normal or a composite of log-normal distributions of $C_{\alpha i}$ and $C_{\beta i}$ which were skewed toward large values of C_α and C_β.) As can be seen from Figure 8, within the range tested, M is a relatively well-behaved function of $\left[\frac{\overline{C_\alpha'^2}}{\overline{C}_\alpha^2}\;\frac{\overline{C_\beta'^2}}{\overline{C}_\beta^2}\right]^{\frac{1}{2}}$. For our present stage of approximation, however, we have chosen a dichotomous relationship for M, namely,

$$\begin{aligned} M = 0 \text{ when } \left[\frac{\overline{C_\alpha'^2}}{\overline{C}_\alpha^2}\;\frac{\overline{C_\beta'^2}}{\overline{C}_\beta^2}\right]^{\frac{1}{2}} &\leq 1 \\ M = 1 \text{ when } \left[\frac{\overline{C_\alpha'^2}}{\overline{C}_\alpha^2}\;\frac{\overline{C_\beta'^2}}{\overline{C}_\beta^2}\right]^{\frac{1}{2}} &> 1 \end{aligned} \tag{C13}$$

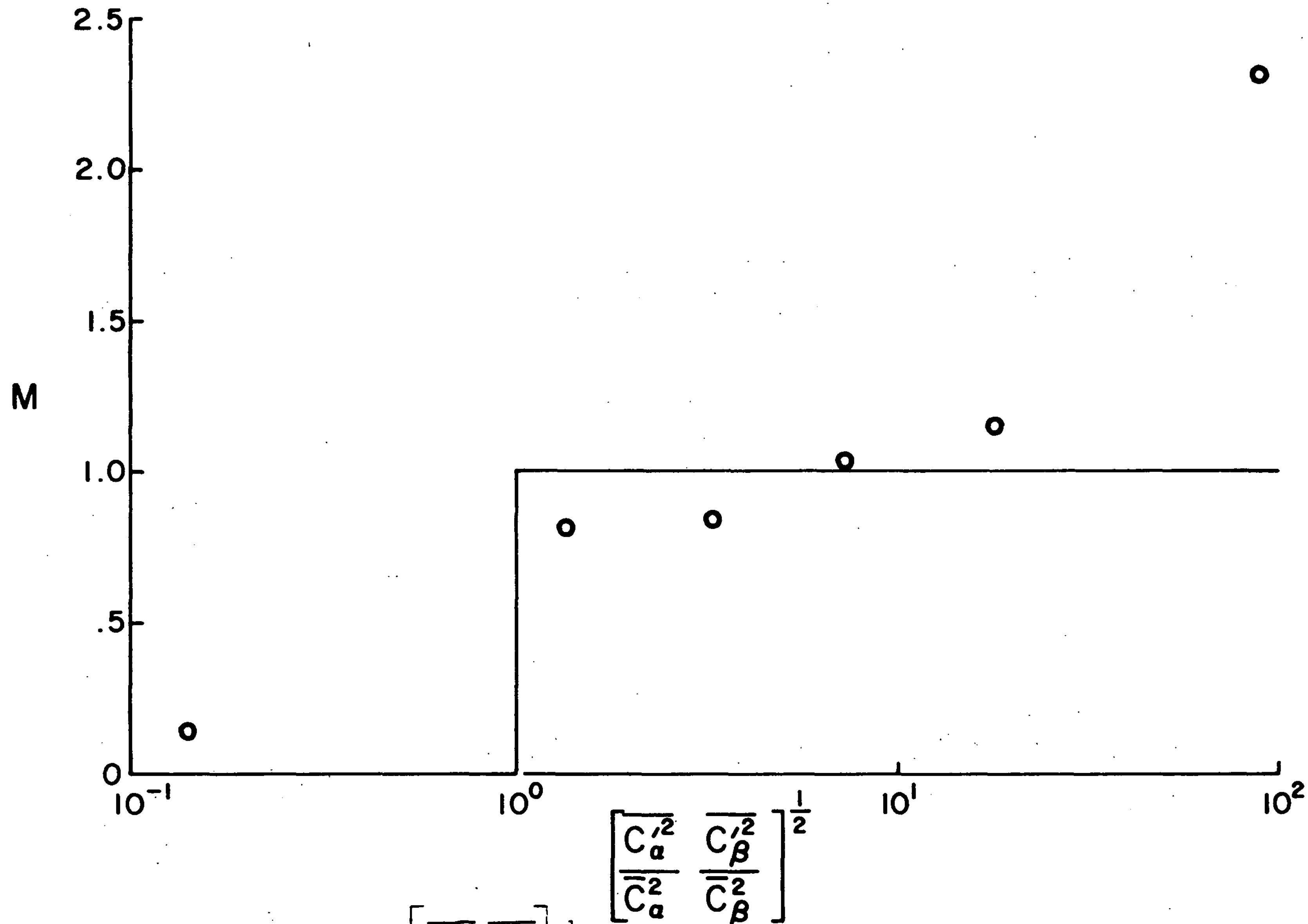

Figure 8. Values of M vs $\left[\frac{\overline{C_\alpha'^2}}{\overline{C}_\alpha^2}\ \frac{\overline{C_\beta'^2}}{\overline{C}_\beta^2}\right]^{\frac{1}{2}}$ as determined by solution of the basic chemical kinetics equations for various initial log-normal frequency distributions of C_α and C_β.

Using Equations (4.4), (4.7), and (4.8), our approximate predictor equations for $\overline{c_\alpha'^2 c_\beta'}$ and $\overline{c_\alpha' c_\beta'^2}$ are

$$\overline{c_\alpha'^2 c_\beta'} = \frac{\overline{C}_\alpha^2 \overline{C}_\beta}{M+1}\left[1 + \frac{\overline{c_\alpha'^2}}{\overline{C}_\alpha^2} + 2\,\frac{\overline{c_\alpha' c_\beta'}}{\overline{C}_\alpha \overline{C}_\beta}\right]\left[\frac{\overline{c_\alpha' c_\beta'}}{\overline{C}_\alpha \overline{C}_\beta} - M\right] \qquad (4.9)$$

and

$$\overline{c_\alpha' c_\beta'^2} = \frac{\overline{C}_\alpha \overline{C}_\beta^2}{M+1}\left[1 + \frac{\overline{c_\beta'^2}}{\overline{C}_\beta^2} + 2\,\frac{\overline{c_\alpha' c_\beta'}}{\overline{C}_\alpha \overline{C}_\beta}\right]\left[\frac{\overline{c_\alpha' c_\beta'}}{\overline{C}_\alpha \overline{C}_\beta} - M\right] \qquad (4.10)$$

and we specify M by conditions (C13) .

As a first, but severe test of this approximation, comparison of the predicted and observed values of $\overline{c_\alpha'^2 c_\beta'}$ for the most extreme value of $\left[\frac{\overline{c_\alpha'^2}}{\overline{C}_\alpha^2}\,\frac{\overline{c_\beta'^2}}{\overline{C}_\beta^2}\right]^{\frac{1}{2}}$ shown in Figure 8 (Run L24) is shown in Figure 9, and the predictions of $\partial\overline{C}_\alpha/\partial t$ from this model are compared with those predicted by 1) neglecting the fluctuations completely and 2) neglecting only the third-order correlations, in Figure 10.

The Approximate Chemical Sub-Model For Inhomogeneous Mixtures

Employing Equations (4.9) and (4.10) and conditions (C13), the chemical sub-model for two-body reactions in inhomogeneous mixtures is

$$\frac{\partial \overline{C}_\alpha}{\partial t} = -\,k_1\left[\overline{C}_\alpha \overline{C}_\beta + \overline{c_\alpha' c_\beta'}\right] \qquad (4.11)$$

$$\frac{\partial \overline{C}_\beta}{\partial t} = -\,k_2\left[\overline{C}_\alpha \overline{C}_\beta + \overline{c_\alpha' c_\beta'}\right] \qquad (4.12)$$

$$\frac{\partial \overline{c_\alpha' c_\beta'}}{\partial t} = -\,k_1\left[\overline{C}_\alpha \overline{c_\beta'^2} + \overline{C}_\beta \overline{c_\alpha' c_\beta'} + \overline{c_\alpha' c_\beta'^2}\right] - k_2\left[\overline{C}_\beta \overline{c_\alpha'^2} + \overline{C}_\alpha \overline{c_\alpha' c_\beta'} + \overline{c_\alpha'^2 c_\beta'}\right] \qquad (4.13)$$

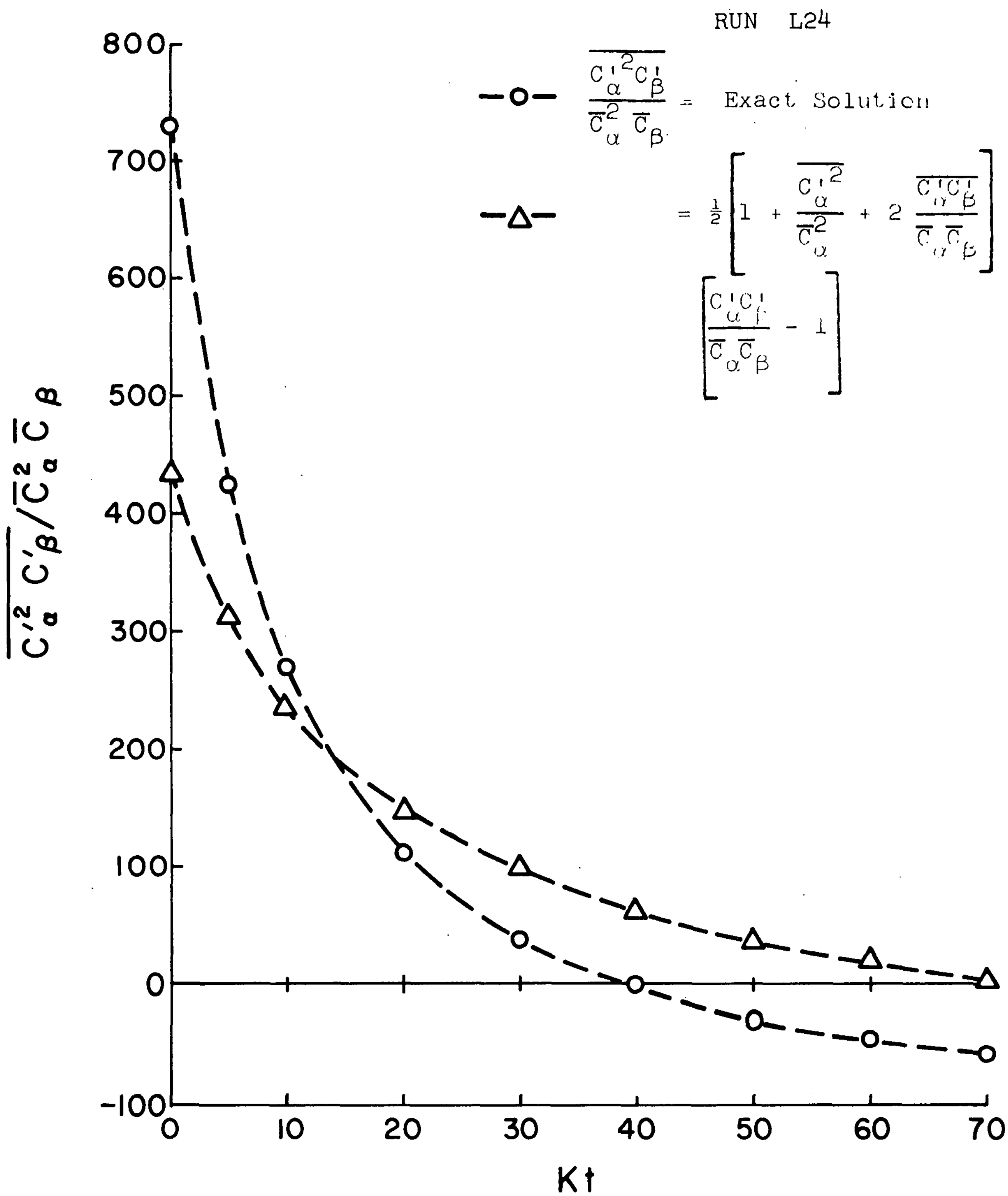

Figure 9. Approximation of the third-order correlation for an initial log-normal distribution with $\left[\frac{\overline{C'^2_\alpha}}{\overline{C}^2_\alpha} \frac{\overline{C'^2_\beta}}{\overline{C}^2_\beta}\right]^{\frac{1}{2}} = 90.$

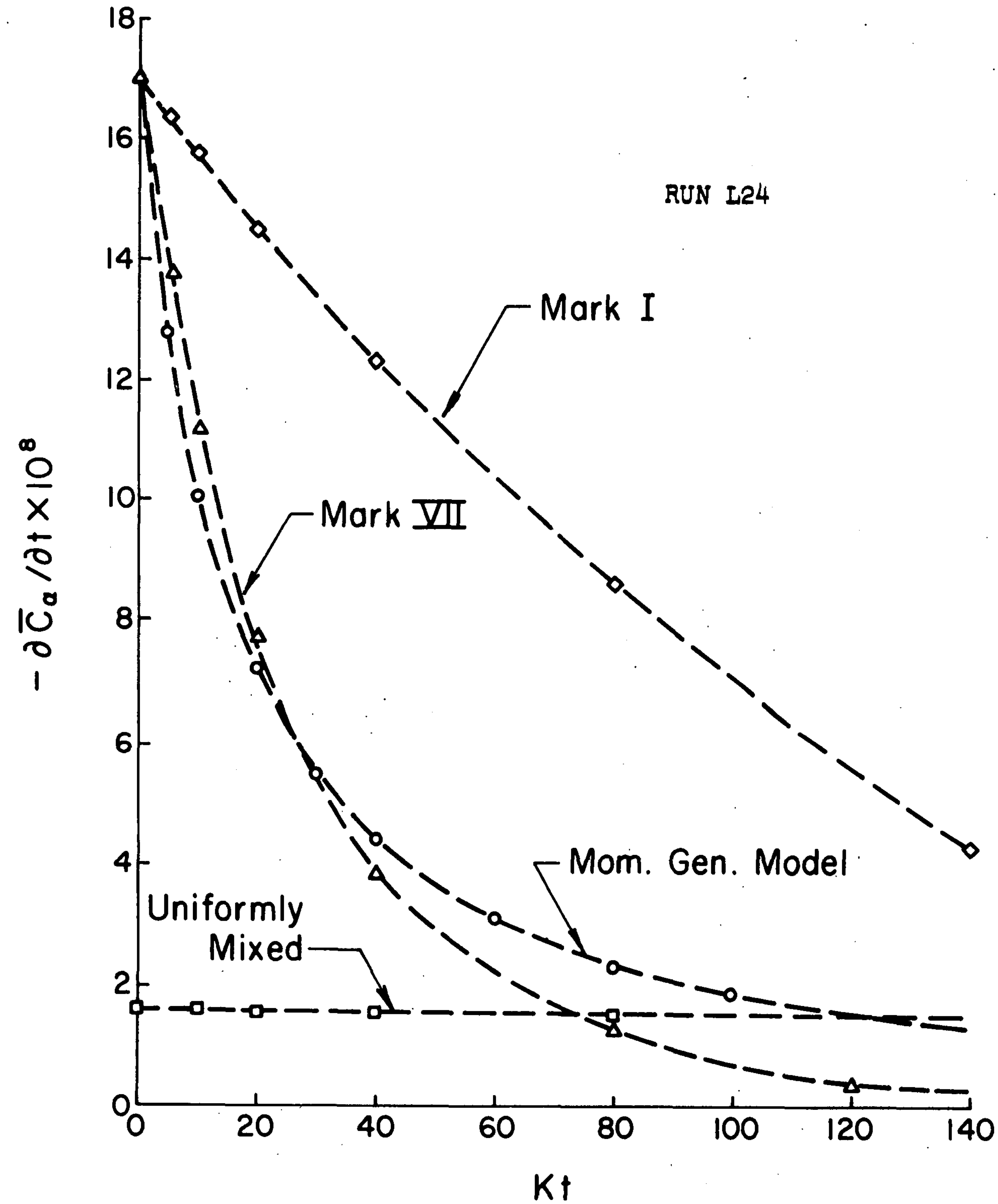

Figure 10. Comparison of predicted vs actual chemical reaction rates for Run L24 under the following assumptions:

1. Neglect of concentration fluctuations (uniformly mixed)
2. Neglect of third-order correlation (Mark I)
3. Inclusion of approximate estimates of third-order correlations (Mark VII)

$$\frac{\partial \overline{c_\alpha'^2}}{\partial t} = -2k_1 \left[\overline{C}_\beta \overline{c_\alpha'^2} + \overline{C}_\alpha \overline{c_\alpha' c_\beta'} + \overline{c_\alpha'^2 c_\beta'} \right] \tag{4.14}$$

$$\frac{\partial \overline{c_\beta'^2}}{\partial t} = -2k_2 \left[\overline{C}_\alpha \overline{c_\beta'^2} + \overline{C}_\beta \overline{c_\alpha' c_\beta'} + \overline{c_\alpha' c_\beta'^2} \right] \tag{4.15}$$

$$\overline{c_\alpha'^2 c_\beta'} = \frac{\overline{C}_\alpha^2 \overline{C}_\beta}{M+1} \left[1 + \frac{\overline{c_\alpha'^2}}{\overline{C}_\alpha^2} + 2 \frac{\overline{c_\alpha' c_\beta'}}{\overline{C}_\alpha \overline{C}_\beta} \right] \left[\frac{\overline{c_\alpha' c_\beta'}}{\overline{C}_\alpha \overline{C}_\beta} - M \right] . \tag{4.16}$$

$$\overline{c_\alpha' c_\beta'^2} = \frac{\overline{C}_\alpha \overline{C}_\beta^2}{M+1} \left[1 + \frac{\overline{c_\beta'^2}}{\overline{C}_\beta^2} + 2 \frac{\overline{c_\alpha' c_\beta'}}{\overline{C}_\alpha \overline{C}_\beta} \right] \left[\frac{\overline{c_\alpha' c_\beta'}}{\overline{C}_\alpha \overline{C}_\beta} - M \right] \tag{4.17}$$

$$\begin{aligned} M &= 0 \text{ when} \left[\frac{\overline{c_\alpha'^2}}{\overline{C}_\alpha^2} \frac{\overline{c_\beta'^2}}{\overline{C}_\beta^2} \right] \le 1 \\ M &= 1 \text{ when} \left[\frac{\overline{c_\alpha'^2}}{\overline{C}_\alpha^2} \frac{\overline{c_\beta'^2}}{\overline{C}_\beta^2} \right] > 1 \end{aligned} \tag{C14}$$

and the sub-model is closed at the level of the first- and second order moments.

The only rigorous test of this approximate model available to us now is a comparison with the exact solutions of the chemical kinetic equations, as a function of reaction time kt , and for various initial distributions of $(C_{\alpha i}, C_{\beta i})$. The much more realistic case of coupled chemical depletion and dilution by turbulent mixing must await the coupling of the chemical and diffusion sub-models. However, if the local diffusive mixing is very, very slow compared with chemical depletion, this sub-model must "track" the chemical depletion correctly. The following tests of the chemical sub-model are therefore restricted to this circumstance so far as any degree of reality is concerned.

Since our primary concern in the coupled chemistry-diffusion models will be accuracy in the prediction of the local mean reaction rates, we are particularly concerned with this facet of the chemistry sub-model. The comparison of interest is between the local depletion rates of the reacting chemical species as measured by $\partial \overline{C}_\alpha / \partial t$. From a variety of initial distributions for $n_i(C_{\alpha i}, C_{\beta i})$, we have chosen four which exhibit varying degrees of the effects of inhomogeneous mixing. Their initial distributions are shown in Figure 11 and the comparisons of reaction rates as a function of reaction time are shown in Figures 12 to 15, (including the initial reaction rates predicted when the concentration fluctuations are neglected).

These comparisons, although by no means exhaustive, show that the approximate chemical sub-model developed here captures a very large fraction of the effects of inhomogeneous mixing on chemical reaction rates. Over a very wide range of reaction rates, this model predicts the exact rate to within a factor of two, while the neglect of the fluctuation terms in the chemical kinetic equations incurs errors of up to a factor of 100. On this basis it seems safe to proceed to the coupling of this chemical sub-model and the invariant (second-order closure) diffusion sub-model.

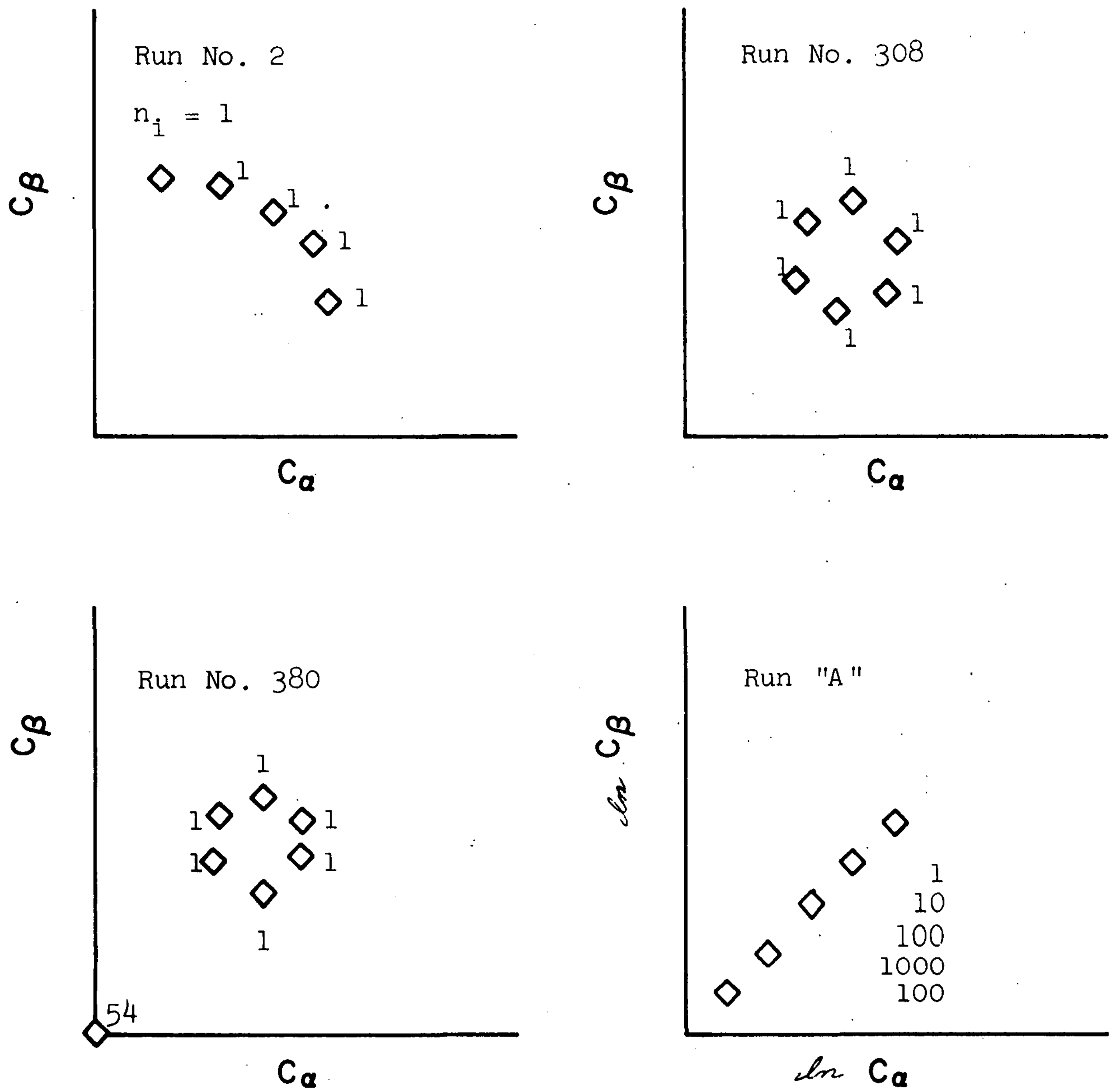

Figure 11. Schematic of four distributions used to test the approximate chemical model.

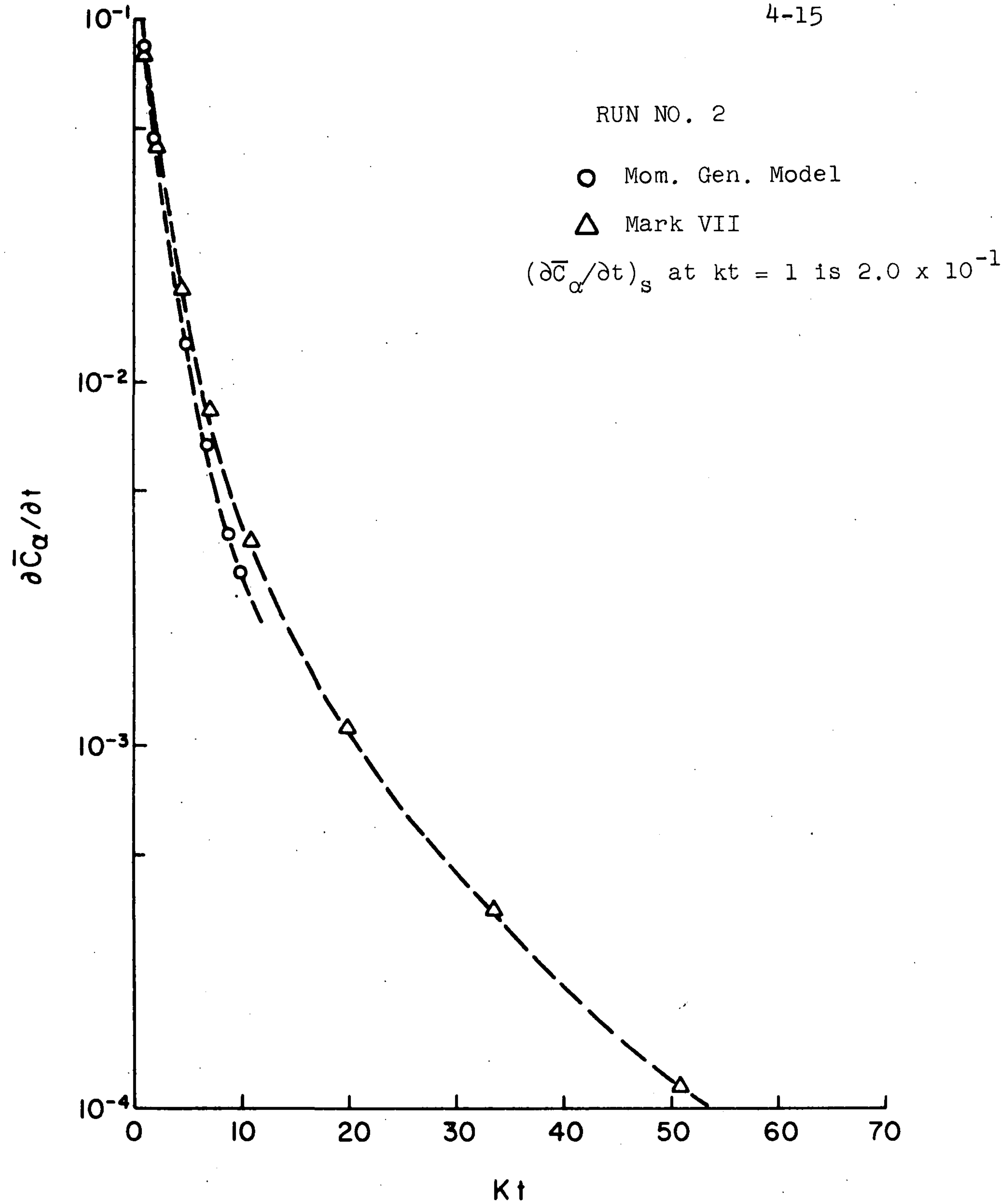

Figure 12. Comparison of reaction rates predicted by the chemical kinetic model (Mark VII) with exact solution for initial distribution of (C_α, C_β) shown in Figure 11.

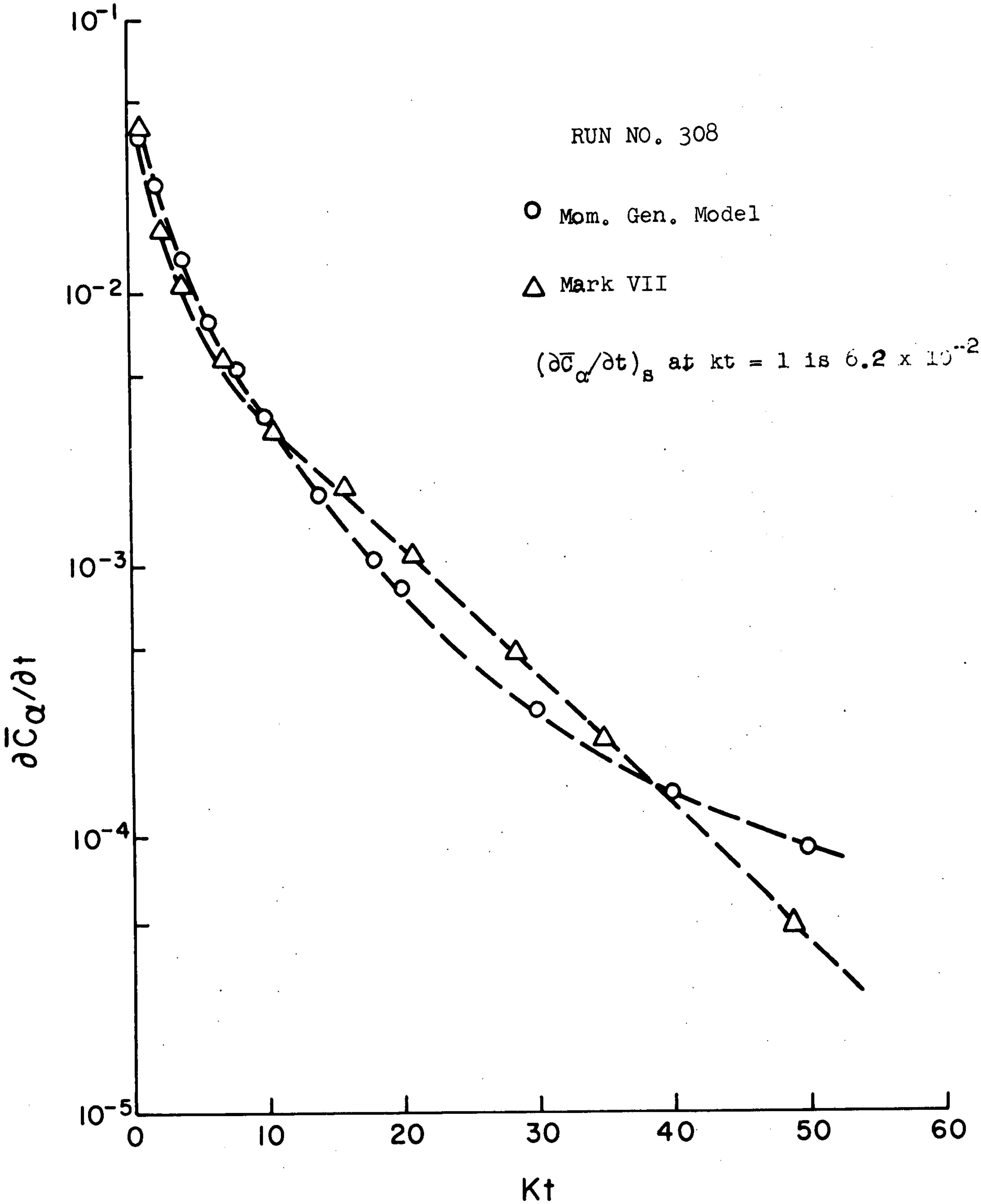

Figure 13. Comparison of reaction rates predicted by the chemical kinetic model (Mark VII) with exact solution for initial distribution of (C_α, C_β) shown in Figure 11.

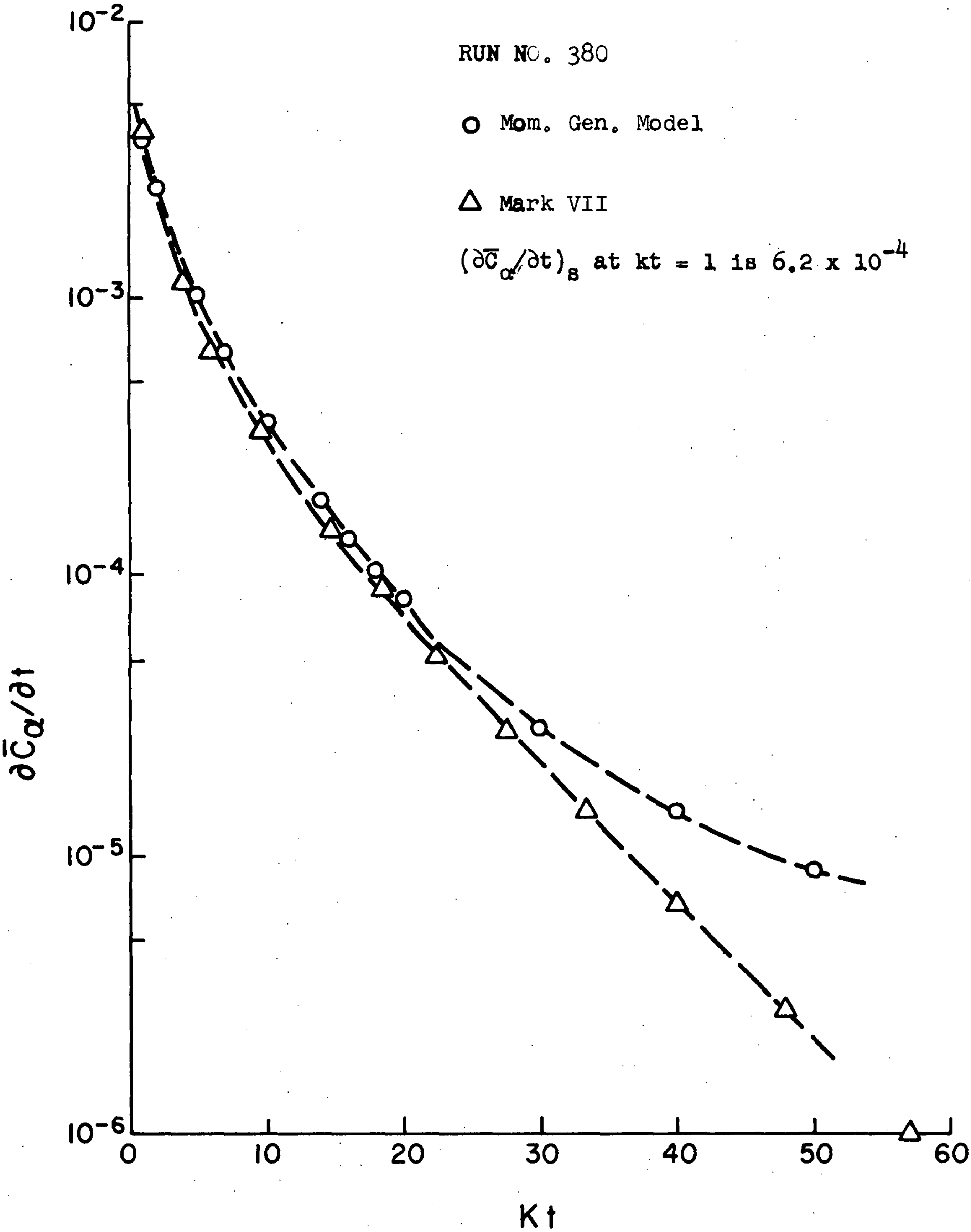

Figure 14. Comparison of reaction rates predicted by the chemical kinetic model (Mark VII) with exact solution for initial distribution shown in Figure 11.

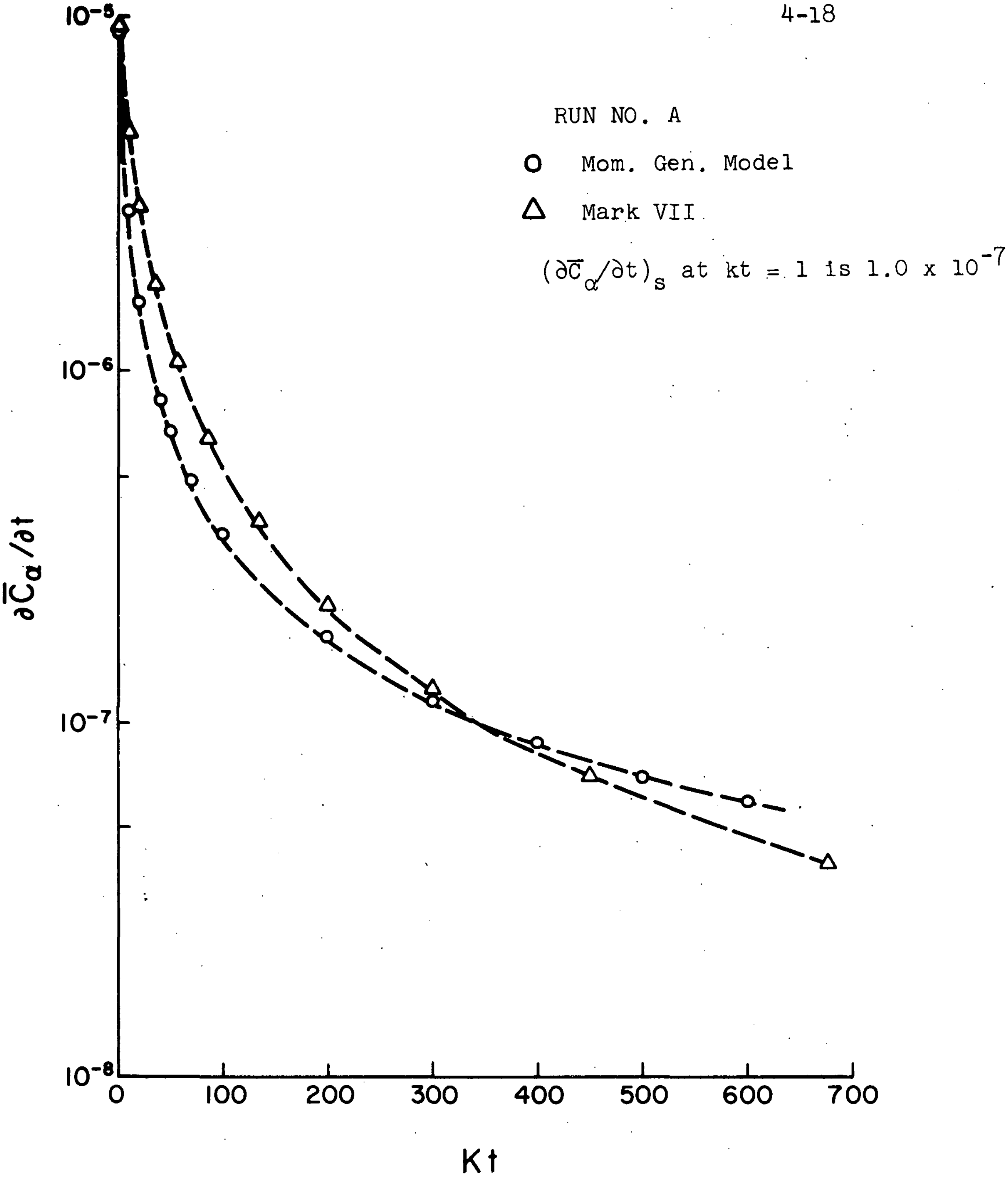

Figure 15. Comparison of reaction rates predicted by the chemical kinetic model (Mark VII) with exact solution for initial distribution shown in Figure 11.

5. THE CONSTRUCTION OF A TWO-DIMENSIONAL COUPLED DIFFUSION/CHEMISTRY MODEL FOR A BINARY REACTION SYSTEM

The development of the closure scheme for the chemical sub-model described in the previous section, coupled with the models for prediction of turbulence structure, fluxes, and turbulent diffusion of matter described in Volume I of this report, provides the necessary modules for a coupled diffusion/chemistry model, the objective of this program. In particular, these developments make possible coupled models which permit examination in detail of the processes of generation and decay of the fluctuating components, as well as the mean values, of turbulent diffusion and inhomogeneous reactions of a binary or two-body reactive system.

As a starting point for these coupled models we have chosen the relatively simple, but realistic, situation of two reactive but otherwise passive pollutants emanating from either common or separate cross-wind line sources. This choice reduces the diffusion calculations to two dimensions and permits the decoupling of the diffusion/chemistry model from the turbulence model, since there is no feedback into the turbulence field due to either pollutant density or exo- or endothermic reactions. The decoupled turbulence model is used to generate the field of turbulent motions and fluxes, which are then used, along with source specifications and reaction rate constants, as input to the coupled diffusion/chemistry model. As can be seen from the full derivation of the two-dimensional model presented in the next section, this system, involving as it does nine simultaneous partial differential equations, is already rather complicated. However, one of the primary reasons for starting at this basic level of complexity is to permit close examination of the interactions between turbulent diffusion and chemical reactions in the simplest realistic mode in which they could occur. When these interactions are understood, extension of the models to three-dimensional configurations, nonpassive pollutants, and three-body reactions can be undertaken with a much better appreciation of the complex nonlinear system within which they will operate.

Due to the limited time and funds for this project, only a few test calculations of the combined effects of turbulent diffusion and chemistry have been possible. Some basic calculations, which begin to define the effects of turbulence vis a vis chemical reaction rates, and two sets of calculations for the $NO_x - O_3$ patterns to be expected in a multiple freeway situation are presented and discussed in Section 6. Despite their limited number, these examples already point up sharply the effects of inhomogeneous mixing (produced by the turbulence field) and the effects of diffusion-limited conditions on fast reactions characteristic of photochemical chains.

Derivation of the Modeled Equations for the Mixing of Two Chemically Reacting Materials Emanating from Cross-Wind Line Sources

For an atmospheric shear layer in which the Schmidt number is equal to one and the adiabatic density is constant, we may follow Donaldson (Vol. I) and write the equation governing the diffusion and chemistry of a reacting species, α, as

$$\frac{\partial C_\alpha}{\partial t} = - u_j \frac{\partial C_\alpha}{\partial x_j} + \nu_o \frac{\partial^2 C_\alpha}{\partial x_j^2} - k_\alpha C_\alpha C_\beta \qquad (5.1)$$

where k_α is the reaction rate of the α species with a second species β. A similar equation may also be written for C_β, but this will not be done until the modeling is completed.

We may express our variables in terms of their mean and fluctuating parts as

$$C_\alpha = \overline{C}_\alpha + C'_\alpha$$

$$C_\beta = \overline{C}_\beta + C'_\beta$$

$$u_j = \overline{u}_j + u'_j \tag{5.2}$$

Substituting these expressions into Equation (5.1) and averaging, we obtain the mean local rate of change of concentration in terms of convection, molecular and turbulent diffusion and chemical reaction

$$\frac{\partial \overline{C}_\alpha}{\partial t} = - \overline{u}_j \frac{\partial \overline{C}_\alpha}{\partial x_j} - \frac{\partial}{\partial x_j} (\overline{u'_j C'_\alpha}) + \nu_o \frac{\partial^2 \overline{C}_\alpha}{\partial x_j^2}$$

$$- k_\alpha(\overline{C}_\alpha \overline{C}_\beta + \overline{C'_\alpha C'_\beta}) \tag{5.3}$$

In deriving Equation (5.3) we have used the continuity equation

$$\frac{\partial \overline{u}_j}{\partial x_j} = 0$$

$$\frac{\partial u'_j}{\partial x_j} = 0 \tag{5.4}$$

From Equation (5.3) we see that we now require expressions for $\overline{u'_j C'_\alpha}$ and $\overline{C'_\alpha C'_\beta}$. We first subtract Equation (5.3) from Equation (5.1) to obtain an equation for the fluctuation C'_α ,

$$\frac{\partial C'_\alpha}{\partial t} = -\bar{u}_j \frac{\partial C'_\alpha}{\partial x_j} - u_j \frac{\partial \bar{C}_\alpha}{\partial x_j} - u'_j \frac{\partial C'_\alpha}{\partial x_j} + \frac{\partial}{\partial x_j}\left(\overline{u'_j C'_\alpha}\right) + \nu_o \frac{\partial^2 C'_\alpha}{\partial x_j^2}$$

$$- k_\alpha\left(C'_\alpha \bar{C}_\beta + \bar{C}_\alpha C'_\beta + C'_\alpha C'_\beta - \overline{C'_\alpha C'_\beta}\right) \qquad (5.5)$$

Following Donaldson (Vol. I), we may write the expression for u'_i as

$$\frac{\partial u'_i}{\partial t} = \left\{ \bar{u}_j \frac{\partial u'_i}{\partial x_j} + u'_j \frac{\partial \bar{u}_i}{\partial x_j} + u'_j \frac{\partial u'_i}{\partial x_j} - \overline{u'_j \frac{\partial u'_i}{\partial x_j}} \right\}$$

$$+ \frac{1}{T_o}\, gT' + \nu_o \frac{\partial^2 u'_i}{\partial x_j^2} - \frac{\partial p'}{\partial x_i} \qquad (5.6)$$

Multiplying Equation (5.6) by C'_α and (5.5) by u'_i, adding, and averaging, we obtain an expression for $\overline{u'_i C'_\alpha}$,

$$\frac{\partial \overline{u'_i C'_\alpha}}{\partial t} = -\bar{u}_j \frac{\partial \overline{u'_i C'_\alpha}}{\partial x_j} - \overline{u'_i u'_j} \cdot \frac{\partial \bar{C}_\alpha}{\partial x_j} - \overline{u'_j C'_\alpha} \cdot \frac{\partial \bar{u}_i}{\partial x_j}$$

$$- \frac{\partial}{\partial x_j}\left(\overline{u'_i u'_j C'_\alpha}\right) + \frac{g}{T_o}\, \overline{C'_\alpha T'} + \nu_o \left\{ \frac{\partial^2 \overline{u'_i C'_\alpha}}{\partial x_j^2} - 2\, \overline{\frac{\partial u'_i}{\partial x_k} \frac{\partial C'_\alpha}{\partial x_k}} \right\}$$

$$- \frac{\partial \overline{p' C'_\alpha}}{\partial x_i} + \overline{p' \frac{\partial C'_\alpha}{\partial x_i}}$$

$$- k_\alpha \left\{ \bar{C}_\beta \overline{u'_i C'_\alpha} + \bar{C}_\alpha \overline{u'_i C'_\beta} + \overline{u'_i C'_\alpha C'_\beta} \right\} \qquad (5.7)$$

Equation (5.7) introduces various third-order correlations, pressure correlations and dissipation terms that have been modeled previously. We must, however, obtain an expression for $\overline{C'_\alpha T'}$. Returning to Volume I, we may write the equation governing the temperature fluctuation T' as

$$\frac{\partial T'}{\partial t} = -\left\{ \overline{u}_j \frac{\partial T'}{\partial x_j} + u_j' \frac{\partial \overline{T}}{\partial x_j} + u_j' \frac{\partial T'}{\partial x_j} - \overline{u_j' \frac{\partial T'}{\partial x_j}} \right\} + \nu_o \frac{\partial^2 T'}{\partial x_j^2} \tag{5.8}$$

We then multiply this equation by C_α' , Equation (5.5) by T' , add them together and average to obtain the equation governing the rate of change of $\overline{C_\alpha' T'}$

$$\begin{aligned} \frac{\partial \overline{C_\alpha' T'}}{\partial t} = & - \overline{u}_j \frac{\partial \overline{C_\alpha' T'}}{\partial x_j} - \overline{u_j' T'} \frac{\partial \overline{C}_\alpha}{\partial x_j} - \overline{C_\alpha' u_j'} \frac{\partial \overline{T}}{\partial x_j} \\ & - \frac{\partial}{\partial x_j} (\overline{u_j' C_\alpha' T'}) + \nu_o \left\{ \frac{\partial^2 \overline{C_\alpha' T'}}{\partial x_j^2} - 2 \overline{\frac{\partial C_\alpha'}{\partial x_k} \frac{\partial T'}{\partial x_k}} \right\} \\ & - k_\alpha \left\{ \overline{C}_\beta \overline{C_\alpha' T'} + \overline{C}_\alpha \overline{C_\beta' T'} + \overline{T' C_\alpha' C_\beta'} \right\} \end{aligned} \tag{5.9}$$

The triple correlation $\overline{u_j' C_\alpha' T'}$ and the dissipation term have already been modeled. The correlation $\overline{T' C_\alpha' C_\beta'}$ will be discussed below.

Returning to Equation (5.3), we see that we must determine the governing equation for $\overline{C_\alpha' C_\beta'}$. If we multiply Equation (5.5) by C_β' and add to it the equation obtained by multiplying C_α' by the fluctuation equation for C_β' - α replaced by β and β by α in (5.5) - then the average of that expression gives the equation for $\overline{C_\alpha' C_\beta'}$

$$\frac{\partial \overline{c'_\alpha c'_\beta}}{\partial t} = - \bar{u}_j \frac{\partial \overline{c'_\alpha c'_\beta}}{\partial x_j} - \overline{u'_j c'_\beta} \frac{\partial \bar{c}_\alpha}{\partial x_j} - \overline{u'_j c'_\alpha} \frac{\partial \bar{c}_\beta}{\partial x_j}$$

$$- \frac{\partial}{\partial x_j} (\overline{u'_j c'_\alpha c'_\beta}) + \nu_o \left\{ \frac{\partial^2 \overline{c'_\alpha c'_\beta}}{\partial x_j^2} - 2 \overline{\frac{\partial c'_\alpha}{\partial x_k} \frac{\partial c'_\beta}{\partial x_k}} \right\}$$

$$- k_\alpha \left\{ \bar{c}_\beta \overline{c'_\alpha c'_\beta} + \bar{c}_\alpha \overline{c'^2_\beta} + \overline{c'_\alpha c'^2_\beta} \right\}$$

$$- k_\beta \left\{ \bar{c}_\alpha \overline{c'_\alpha c'_\beta} + \bar{c}_\beta \overline{c'^2_\alpha} + \overline{c'^2_\alpha c'_\beta} \right\} \qquad (5.10)$$

We see from Equation (5.10) that we must model the third-order correlations $\overline{c'_\alpha c'^2_\beta}$ and $\overline{c'^2_\alpha c'_\beta}$, but also that we require expressions for $\overline{c'^2_\alpha}$ and $\overline{c'^2_\beta}$. These two equations are identical except for the transposition of α and β. The $\overline{c'^2_\alpha}$ equation is found by multiplying (5.5) by c'_α and averaging to obtain

$$\frac{\partial \overline{c'^2_\alpha}}{\partial t} = - \bar{u}_j \frac{\partial \overline{c'^2_\alpha}}{\partial x_j} - 2 \overline{c'_\alpha u'_j} \frac{\partial \bar{c}_\alpha}{\partial x_j}$$

$$- \frac{\partial \overline{u'_j c'^2_\alpha}}{\partial x_j} + \nu_o \left\{ \frac{\partial^2 \overline{c'^2_\alpha}}{\partial x_j^2} - 2 \overline{\frac{\partial c'_\alpha}{\partial x_k} \frac{\partial c'_\alpha}{\partial x_k}} \right\}$$

$$- 2k_\alpha \left\{ \bar{c}_\beta \overline{c'^2_\alpha} + \bar{c}_\alpha \overline{c'_\alpha c'_\beta} + \overline{c'^2_\alpha c'_\beta} \right\} \qquad (5.11)$$

Now, since we are dealing with an atmospheric shear layer, and our initial attention will be directed to cross-wind line sources of α and β, we expect that the only derivative of importance is the one normal to the mean flow $\bar{u}$ in the x cartesian direction. Thus, only $x_j = x_3 = z$ will be important in the equations. Also, we may set $t = x/\bar{u}$ without loss of generality. The modeling for the third-order correlations, pressure correlations, and dissipation terms is prescribed by Donaldson in Volume I as

$$\overline{u_j'u_k'C_\alpha'} = -\Lambda_{2_\alpha} q \left\{ \frac{\partial \overline{u_j'C_\alpha'}}{\partial x_k} + \frac{\partial \overline{u_k'C_\alpha'}}{\partial x_j} \right\}$$

$$\overline{u_j'C_\alpha'C_\beta'} = -\Lambda_{2_B} q \frac{\partial \overline{C_\alpha'C_\beta'}}{\partial x_j}$$

$$\overline{u_j'C_\alpha'T'} = -\Lambda_{2_\alpha} q \frac{\partial \overline{C_\alpha'T'}}{\partial x_j}$$

$$\overline{p' \frac{\partial C_\alpha'}{\partial x_k}} = -\frac{q}{\Lambda_{1_\alpha}} \overline{u_k'C_\alpha'}$$

$$\overline{p'C_\alpha'} = -\Lambda_{3_\alpha} q \frac{\partial \overline{u_i'C_\alpha'}}{\partial x_i}$$

$$\overline{\frac{\partial u_i'}{\partial x_k} \frac{\partial C_\alpha'}{\partial x_k}} = \frac{\overline{u_i'C_\alpha'}}{\lambda_\alpha^2} \qquad (5.12)$$

where $q \equiv (\overline{u'u'} + \overline{v'v'} + \overline{w'w'})^{\frac{1}{2}}$ and λ, Λ_1, Λ_2 and Λ_3 are length scales. Also, $\Lambda_{2_B} \equiv (\Lambda_{2_\alpha} \Lambda_{2_\beta})^{\frac{1}{2}}$ where α and β correspond to the species in question. When Equations (5.12) are substituted into Equations (5.3), (5.7), (5.9), (5.10), and (5.11), we obtain our final equation set governing the simultaneous diffusion and chemical reaction of α and β

$$\bar{u} \frac{\partial \bar{C}_\alpha}{\partial x} = \nu_o \frac{\partial^2 \bar{C}_\alpha}{\partial z^2} - \frac{\partial \overline{C_\alpha'w'}}{\partial z} - k_1 (\bar{C}_\alpha \bar{C}_\beta + \overline{C_\alpha'C_\beta'}) \qquad (5.13)$$

$$\bar{u} \frac{\partial \bar{C}_\beta}{\partial x} = \nu_o \frac{\partial^2 \bar{C}_\beta}{\partial z^2} - \frac{\partial \overline{C_\beta'w'}}{\partial z} - k_2 (\bar{C}_\alpha \bar{C}_\beta + \overline{C_\alpha'C_\beta'}) \qquad (5.14)$$

$$\bar{u}\,\frac{\partial\overline{C'_\alpha w'}}{\partial x} = -\,\overline{w'w'}\,\frac{\partial\bar{C}_\alpha}{\partial z} + \frac{g}{T_o}\,\overline{C'_\alpha T'} + \frac{\partial}{\partial z}\left\{(2\Lambda_{2_\alpha} + \Lambda_{3_\alpha})\,q\,\frac{\partial\overline{C'_\alpha w'}}{\partial z}\right\} - \frac{q}{\Lambda_{1_\alpha}}\,\overline{C'_\alpha w'} + \nu_o\,\frac{\partial^2\overline{C'_\alpha w'}}{\partial z^2} - 2\nu_o\,\frac{\overline{C'_\alpha w'}}{\lambda_\alpha^2} - k_1\left\{\bar{C}_\alpha\overline{C'_\beta w'} + \bar{C}_\beta\overline{C'_\alpha w'} - \Lambda_{2_B}\,q\,\frac{\partial\overline{C'_\alpha C'_\beta}}{\partial z}\right\} \tag{5.15}$$

$$\bar{u}\,\frac{\partial\overline{C'_\beta w'}}{\partial x} = -\,\overline{w'w'}\,\frac{\partial\bar{C}_\beta}{\partial z} + \frac{g}{T_o}\,\overline{C'_\beta T'} + \frac{\partial}{\partial z}\left\{(2\Lambda_{2_\beta} + \Lambda_{3_\beta})\,q\,\frac{\partial\overline{C'_\beta w'}}{\partial z}\right\} - \frac{q}{\Lambda_{1_\beta}}\,\overline{C'_\beta w'} + \nu_o\,\frac{\partial^2\overline{C'_\beta w'}}{\partial z^2} - 2\nu_o\,\frac{\overline{C'_\beta w'}}{\lambda_\beta^2} - k_2\left\{\bar{C}_\alpha\overline{C'_\beta w'} + \bar{C}_\beta\overline{C'_\alpha w'} - \Lambda_{2_B}\,q\,\frac{\partial\overline{C'_\alpha C'_\beta}}{\partial z}\right\} \tag{5.16}$$

$$\bar{u}\,\frac{\partial\overline{C'_\alpha T'}}{\partial x} = -\,\overline{w'T'}\,\frac{\partial\bar{C}_\alpha}{\partial z} - \overline{C'_\alpha w'}\,\frac{\partial\bar{T}}{\partial z} + \frac{\partial}{\partial z}\left\{\Lambda_{2_\alpha}\,q\,\frac{\partial\overline{C'_\alpha T'}}{\partial z}\right\} + \nu_o\,\frac{\partial^2\overline{C'_\alpha T'}}{\partial z^2} - 2\nu_o\,\frac{\overline{C'_\alpha T'}}{\lambda_\alpha^2} - k_1\left\{\bar{C}_\alpha\overline{C'_\beta T'} + \bar{C}_\beta\overline{C'_\alpha T'} + \overline{T'C'_\alpha C'_\beta}\right\} \tag{5.17}$$

$$\bar{u}\,\frac{\partial\overline{C'_\beta T'}}{\partial x} = -\,\overline{w'T'}\,\frac{\partial\bar{C}_\beta}{\partial z} - \overline{C'_\beta w'}\,\frac{\partial\bar{T}}{\partial z} + \frac{\partial}{\partial z}\left\{\Lambda_{2_\beta} q\,\frac{\partial\overline{C'_\beta t'}}{\partial z}\right\}$$

$$+\,\nu_o\,\frac{\partial^2\overline{C'_\beta T'}}{\partial z^2} - 2\,\nu_o\,\frac{\overline{C'_\beta T'}}{\lambda_\beta^2}$$

$$-\,k_2\left\{\bar{C}_\alpha\overline{C'_\beta T'} + \bar{C}_\beta\overline{C'_\alpha T'} + \overline{T'C'_\alpha C'_\beta}\right\} \qquad (5.18)$$

$$\bar{u}\,\frac{\partial\overline{C'_\alpha C'_\beta}}{\partial x} = -\,\overline{C'_\alpha w'}\,\frac{\partial\bar{C}_\beta}{\partial z} - \overline{C'_\beta w'}\,\frac{\partial\bar{C}_\alpha}{\partial z} + \frac{\partial}{\partial z}\left\{\Lambda_{2_B} q\,\frac{\partial\overline{C'_\alpha C'_\beta}}{\partial z}\right\}$$

$$+\,\nu_o\,\frac{\partial^2\overline{C'_\alpha C'_\beta}}{\partial z^2} - 2\nu_o\,\frac{\overline{C'_\alpha C'_\beta}}{\lambda_B^2}$$

$$-\,k_1\left\{\bar{C}_\alpha\overline{C'^2_\beta} + \bar{C}_\beta\overline{C'_\alpha C'_\beta} + \overline{C'_\alpha C'^2_\beta}\right\}$$

$$-\,k_2\left\{\bar{C}_\alpha\overline{C'_\alpha C'_\beta} + \bar{C}_\beta\overline{C'^2_\alpha} + \overline{C'^2_\alpha C'_\beta}\right\} \qquad (5.19)$$

$$\bar{u}\,\frac{\partial\overline{C'^2_\alpha}}{\partial x} = -\,2\overline{C'_\alpha w'}\,\frac{\partial\bar{C}_\alpha}{\partial z} + \frac{\partial}{\partial z}\left\{\Lambda_{2_\alpha} q\,\frac{\partial\overline{C'^2_\alpha}}{\partial z}\right\}$$

$$+\,\nu_o\,\frac{\partial^2\overline{C'^2_\alpha}}{\partial z^2} - 2\nu_o\,\frac{\overline{C'^2_\alpha}}{\lambda_\alpha^2}$$

$$-\,2k_1\left\{\bar{C}_\alpha\overline{C'_\alpha C'_\beta} + \bar{C}_\beta\overline{C'^2_\alpha} + \overline{C'^2_\alpha C'_\beta}\right\} \qquad (5.20)$$

$$\bar{u}\,\frac{\partial\overline{C'^2_\beta}}{\partial x} = -\,2\overline{C'_\beta w'}\,\frac{\partial\bar{C}_\beta}{\partial z} + \frac{\partial}{\partial z}\left\{\Lambda_{2_\beta} q\,\frac{\partial\overline{C'^2_\beta}}{\partial z}\right\}$$

$$+\,\nu_o\,\frac{\partial^2\overline{C'^2_\beta}}{\partial z^2} - 2\nu_o\,\frac{\overline{C'^2_\beta}}{\lambda_\beta^2}$$

$$-\,2k_2\left\{\bar{C}_\alpha\overline{C'^2_\beta} + \bar{C}_\beta\overline{C'_\alpha C'_\beta} + \overline{C'_\alpha C'^2_\beta}\right\} \qquad (5.21)$$

We have written $k_\alpha \equiv k_1$ and $k_\beta \equiv k_2$. Since we have decoupled the diffusion/chemistry model from the background turbulence model, a solution of Equations (5.13) - (5.21) requires knowledge of the initial distributions of $\overline{C}_\alpha$ and $\overline{C}_\beta$ and of the flow parameters $\overline{u}$, $\overline{T}$, T_o, $\overline{w'w'}$, q, and $\overline{w'T'}$. The macro scale lengths Λ and micro lengths λ must also be known as functions of the background turbulence or the plume characteristics.

Finally, the coupled diffusion/chemistry model is closed by modeling the third-order chemistry correlations as described in Section 4.

$$\overline{C_\alpha'^2 C_\beta'} = \frac{1}{1+M}\left\{\overline{C}_\alpha^2\overline{C}_\beta + 2\overline{C}_\alpha\overline{C_\alpha' C_\beta'} + \overline{C}_\beta\overline{C_\alpha'^2}\right\}\left\{\frac{\overline{C_\alpha' C_\beta'}}{\overline{C}_\alpha\overline{C}_\beta} - M\right\} \quad (5.22)$$

$$\overline{C_\alpha' C_\beta'^2} = \frac{1}{1+M}\left\{\overline{C}_\alpha\overline{C}_\beta^2 + \overline{C}_\alpha\overline{C_\beta'^2} + 2\overline{C}_\beta\overline{C_\alpha' C_\beta'}\right\}\left\{\frac{\overline{C_\alpha' C_\beta'}}{\overline{C}_\alpha\overline{C}_\beta} - M\right\} \quad (5.23)$$

where

$$M = 1 \text{ when } \frac{\overline{C_\alpha'^2}\,\overline{C_\beta'^2}}{\overline{C}_\alpha\overline{C}_\beta} > 1$$

$$M = 0 \text{ when } \frac{\overline{C_\alpha'^2}\,\overline{C_\beta'^2}}{\overline{C}_\alpha\overline{C}_\beta} \leq 1 \quad (5.24)$$

A generalization of (5.22) and (5.23) gives the appropriate modeling for $\overline{T'C_\alpha' C_\beta'}$

$$\overline{T'C_\alpha' C_\beta'} = \frac{1}{1+M}\left\{\overline{T}\,\overline{C}_\alpha\overline{C}_\beta + \overline{C}_\alpha\overline{C_\beta' T'} + \overline{C}_\beta\overline{C_\alpha' T'} + \overline{T}\,\overline{C_\alpha' C_\beta'}\right\} \cdot \left\{\frac{\overline{C_\alpha' C_\beta'}}{\overline{C}_\alpha\overline{C}_\beta} - M\right\} \quad (5.25)$$

With the properly modeled equations, we can now proceed to a discussion of some of the results of computer solutions of these equations.

6. SOME CALCULATIONS OF THE INTERACTIONS OF TURBULENT DIFFUSION AND CHEMISTRY

As must be evident from the derivation and recapitulation of the closed diffusion/chemistry equations (Section 5), it is virtually impossible to trace the effects of variations of any one variable through this simulation system. This being the case, the validation of the model must involve multiple iterations with a systematic, step-by-step variation of each of the input variables, and comparison of these model predictions with observed values of concentration patterns, chemical depletion rates, turbulent flux divergences, and the like. Neither time nor resources have permitted this validation of the model, of course, and the calculations presented here must be regarded as suggestive rather than authoritative as to how real chemically reactive and turbulent systems may operate. The verification of these predictions must be deferred, but the results which are presented here argue strongly that at least in some circumstances the interactions of turbulent diffusion and chemical reactions are highly significant and, if verified from observations, models of this type may also improve predictions of air quality in the lower atmosphere significantly.

An Illustrative Calculation

In view of novelty of simultaneous consideration of the turbulent diffusion of reactive chemical species and their reactivity in inhomogeneous mixtures, it appears highly desirable to examine in detail the individual processes by which turbulent diffusion and chemical reactions produce observed patterns of reactant concentrations and reactant depletion in a simple but realistic system. To this end we have chosen to calculate the combined processes of diffusion and chemistry for the case of a plane jet of reactant α

released continuously and isokinetically into a uniform environment of reactant β. The environment of β is characterized by a uniform transport speed $\overline{u} = 10$ m/sec and an isotropic and homogeneous field of turbulence characterized by the vertical intensity of turbulence $\overline{w'^2} = 1$ m^2/sec^2. The plane jet of the α species is oriented across the mean field of flow and the initial vertical distribution of the concentration of α, $\overline{C}_\alpha$, is taken as gaussian with a central value of one and standard deviation $\sigma_z = 0.4$ m. In view of the requirements that the mass fractions of α and β equal one, this "jet" of the α species displaces the ambient β species at the source in such a way that the initial distribution of the concentration of the β species is the complementary gaussian, $\overline{C}_{\beta 0} = 1 - \overline{C}_{\alpha 0}$. This geometry of the initial distributions of $\overline{C}_\alpha$ and $\overline{C}_\beta$ is shown in Figure 16. Note that no initial fluctuations of C_α and C_β are introduced at the source. Finally, we take $k_1 = k_2 = 1.0$.

In keeping with the constraints imposed in the construction of the model, we assume the reaction of α with β proceeds isothermally. For our present purposes we shall also assume that this reaction is irreversible, even though this assumption is not mandatory*. With these input conditions the model calculates the redistribution and the chemical depletion of α and β as a function of travel distance or time after emission.

As a first partial view of the coupled effects of diffusion and chemistry in this flow reactor, we may compare the predicted axial concentrations of the α species as a function of distance from the source and under the following conditions:

*The effects of reversibility of reactions and catalytic cycles may be accommodated to a certain extent by appropriate choices of the reaction rate constants, k_1 and k_2. Similarly, three body reactions of the type $-k_1\overline{C}_\alpha C_\beta C_M$ may also be simulated, if $\partial C_M/\partial t \simeq 0$, by taking $\overline{k} = k_1 C_M$, where M is the third body.

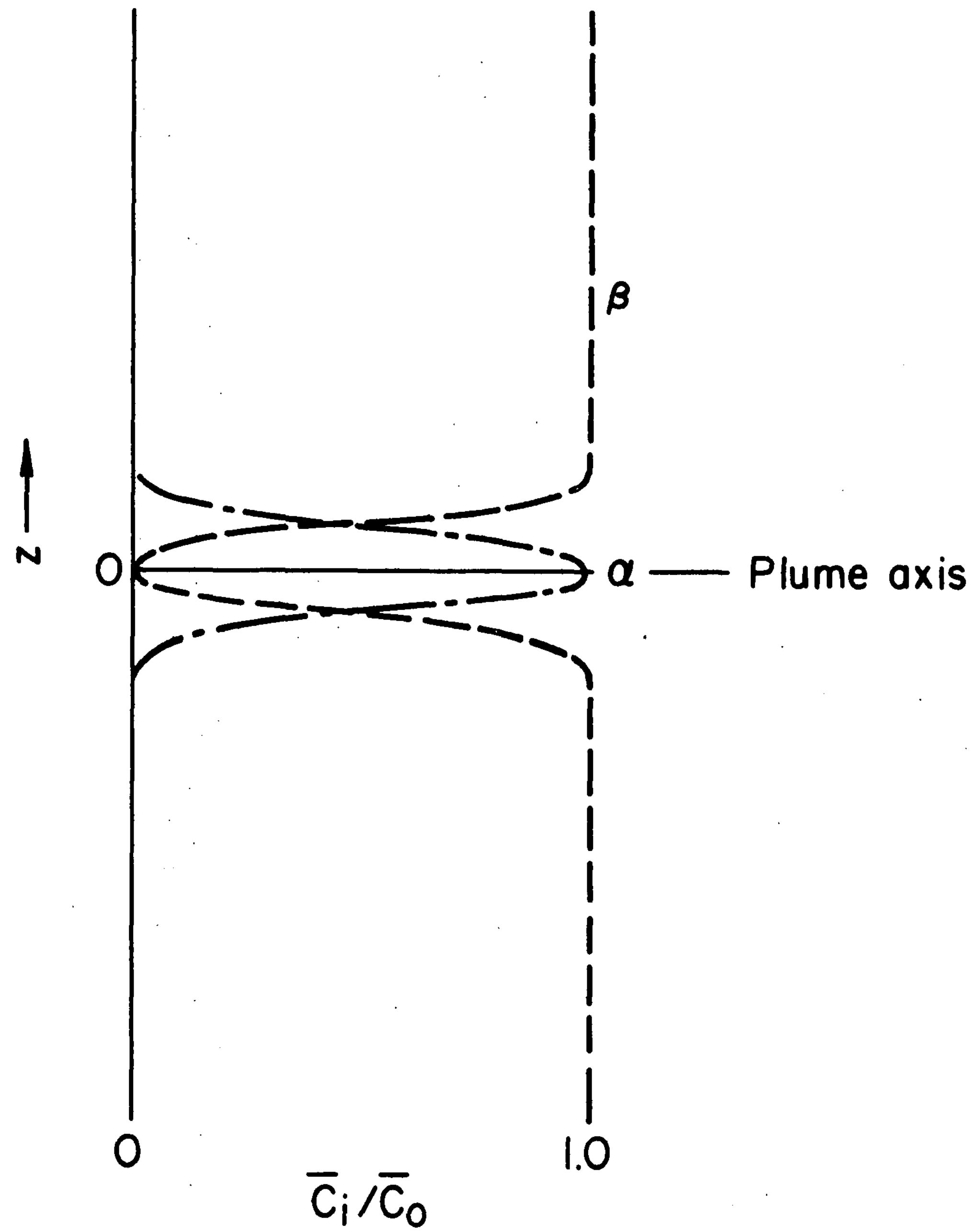

Figure 16. Source configuration for a plane jet of pure α species injected isokinetically into an environment of pure β species.

1. α does not react with β (diffusion only)
2. Diffusion and chemistry occur, but the chemical reaction rates are calculated on the basis of the local mean values of concentration only. (We have termed this "homogeneous chemistry" since $\overline{c'_\alpha c'_\beta}$ is neglected.)
3. Diffusion and inhomogeneous chemistry are operative. (The full model described in Section 5.)

This comparison is shown in Figure 17 and it is immediately evident that the neglect of $\overline{c'_\alpha c'_\beta}$ leads to a significant over prediction of the rate of decrease of the axial concentration of the α species. For example, the ratio of the predicted concentrations at $x = 40$ m is two, and, as is clear from Figure 17, this ratio is increasing with x. This result reflects primarily the effect of $\overline{c'_\alpha c'_\beta}$ on the chemical reaction rate. However, such a simple portrayal of the results of coupled chemistry and diffusion does not portray the balance of the diffusive and chemical processes at work. In order to gain this insight we must examine in detail the balance of turbulent diffusion and chemical reactions going on across the plume.

In order to examine this balance we have neglected the molecular diffusion terms and plotted each of the rates which determine $\partial\overline{c}_\alpha/\partial t$ and $\partial\overline{c}_\beta/\partial t$ as a function of distance from the plume centerline at $x = 37$ m or $t = 3.7$ sec. The profiles of mean concentrations of α and β are shown in Figure 18 and the diffusion and chemical reaction rates predicted by the model are shown in Figure 19. In order to discuss and interpret these results, we recall the balance equations for $\partial\overline{c}_\alpha/\partial t$ and $\partial\overline{c}_\beta/\partial t$.

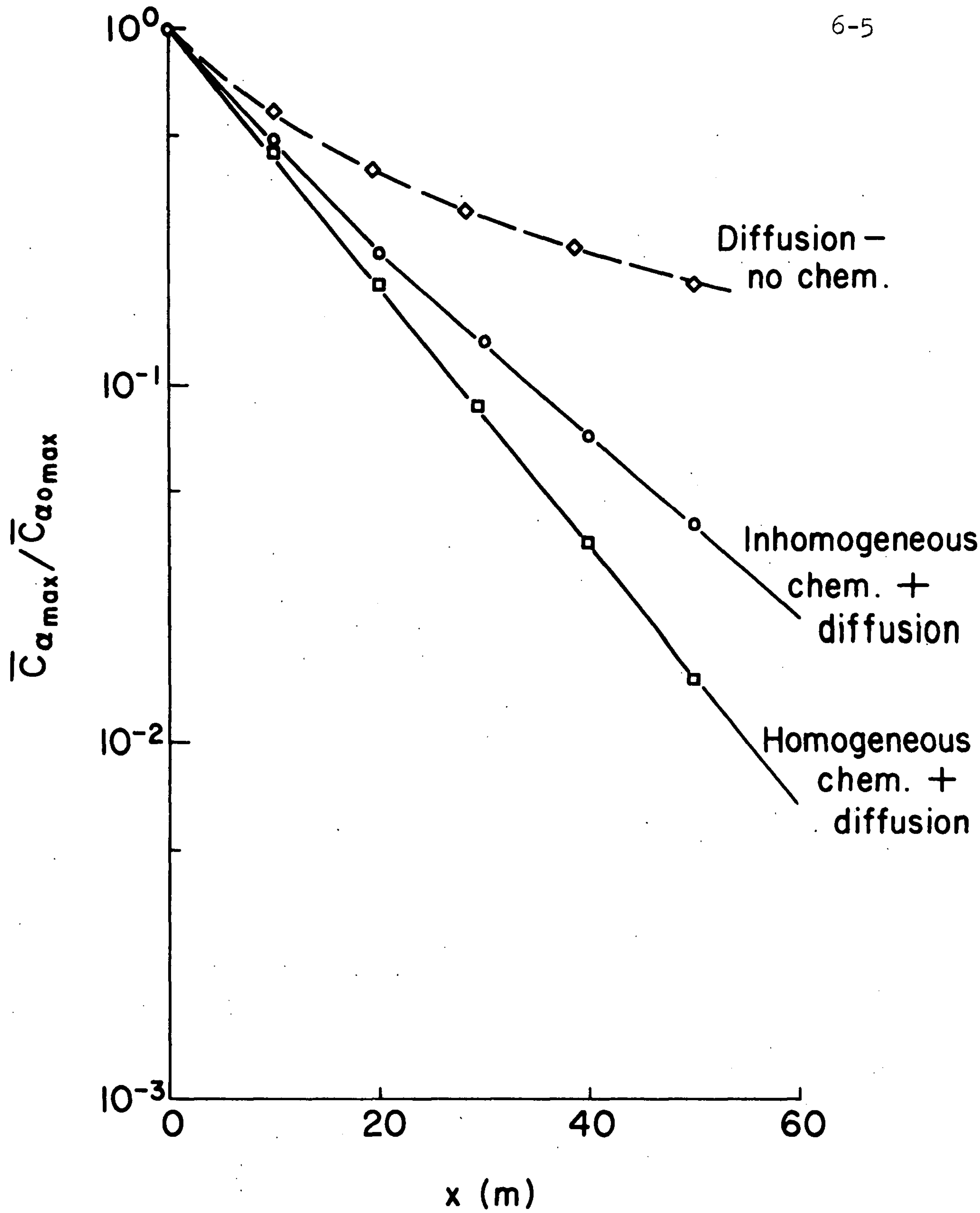

Figure 17. Comparison of the axial concentrations of the α species as a function of travel distance from the plane jet as estimated for 1) diffusion only, 2) inhomogeneous chemistry plus diffusion, and 3) homogeneous chemistry and diffusion. (See text for details.)

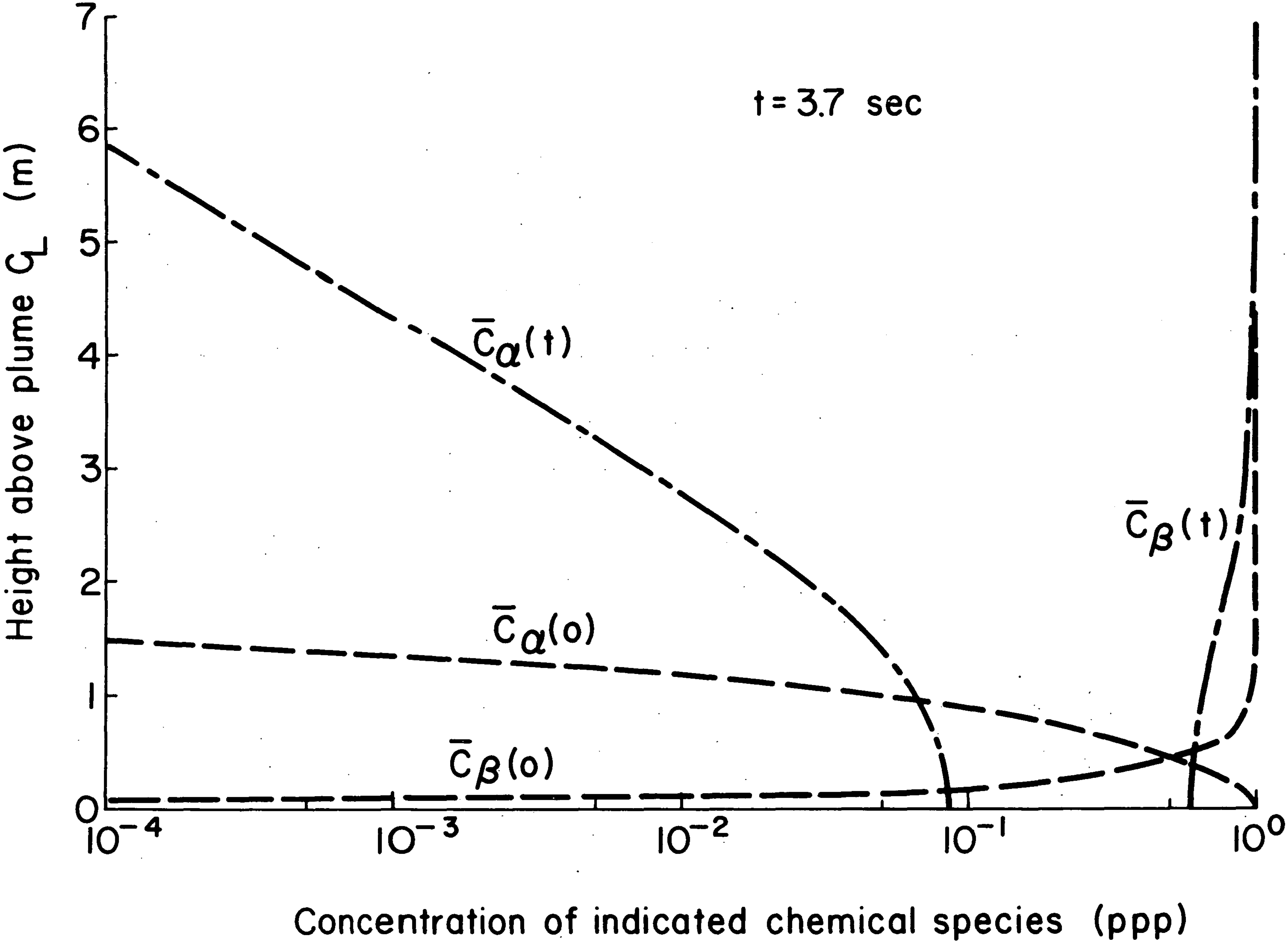

Figure 18. Vertical distributions of α and β species at source and at $x = 37$ m ($t = 3.7$ sec.) .

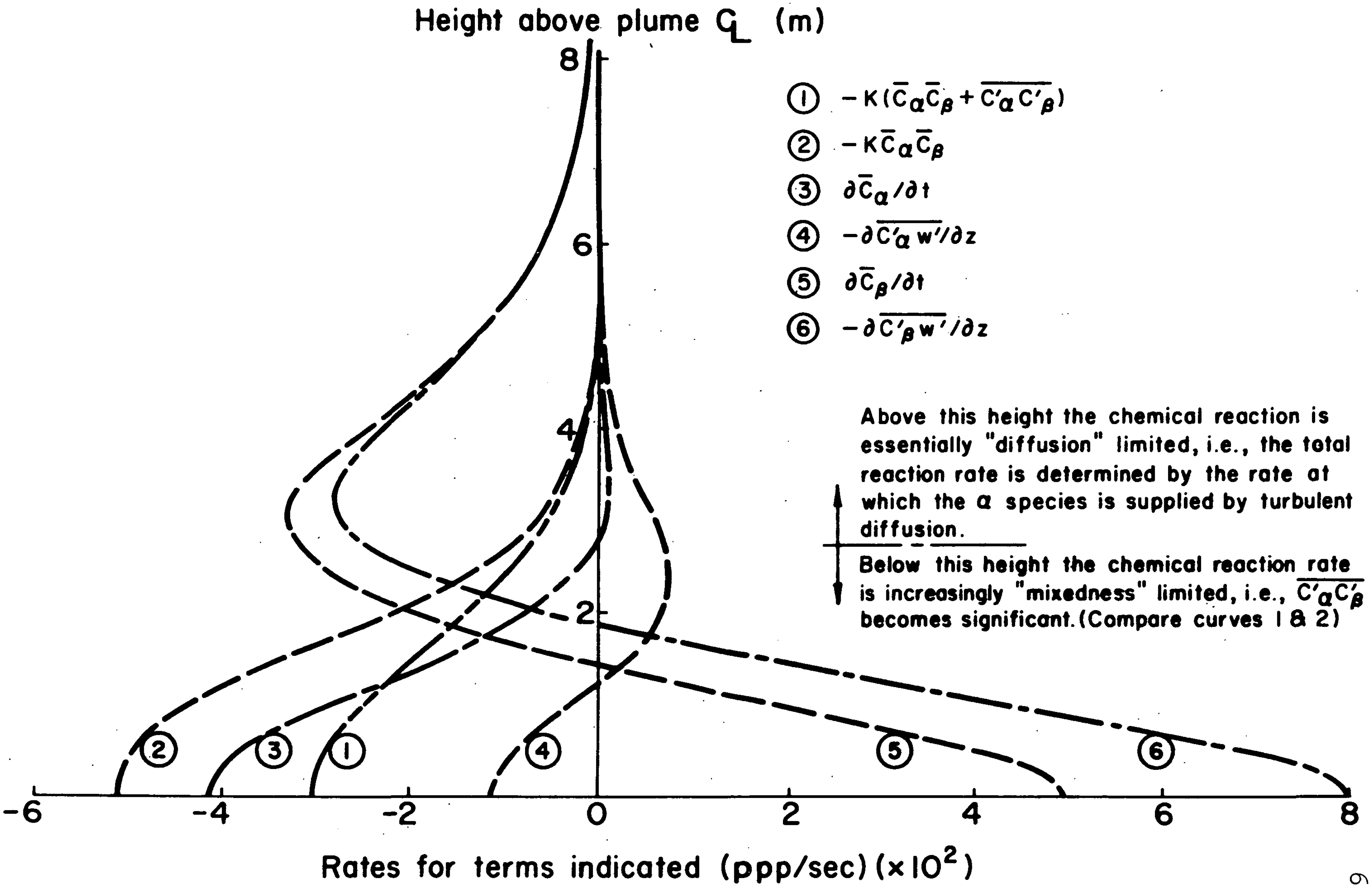

Figure 19. Calculated values of local rates of change of the concentrations of α and β due to diffusive flux divergence and to inhomogeneous chemical reactions.

$$\frac{\partial \overline{C}_\alpha}{\partial t} = - \frac{\partial}{\partial z} \overline{C'_\alpha w'} - k_1(\overline{C}_\alpha \overline{C}_\beta + \overline{C'_\alpha C'_\beta}) \qquad (6.1)$$

and

$$\frac{\partial \overline{C}_\beta}{\partial t} = - \frac{\partial}{\partial z} \overline{C'_\beta w'} - k_2(\overline{C}_\alpha \overline{C}_\beta + \overline{C'_\alpha C'_\beta}) \qquad (6.2)$$

where we have neglected $\nu_o \dfrac{\partial^2 \overline{C}_\alpha}{\partial z^2}$ and $\nu_o \dfrac{\partial^2 \overline{C}_\beta}{\partial z^2}$ as small in comparison with $\frac{\partial}{\partial z} \overline{C'_\alpha w'}$ and $\frac{\partial}{\partial z} \overline{C'_\beta w'}$. Each of the retained terms is plotted as a function of height above (or below) the plume centerline in Figure 19. (Recall that $\partial \overline{C}_\alpha / \partial t$ and $\partial \overline{C}_\beta / \partial t$ are the local rates of change of the mean concentration of α and β due to both turbulent diffusion and chemical reaction; $\frac{\partial}{\partial z} \overline{C'_\alpha w'}$ and $\frac{\partial}{\partial z} \overline{C'_\beta w'}$ are the local divergences of the turbulent flux of the α and β species; $-k(\overline{C}_\alpha \overline{C}_\beta)$ is the average local chemical reaction rate due to the local mean concentrations of α and β ; $-k \, \overline{C'_\alpha C'_\beta}$ is the average local chemical reaction rate due to correlated fluctuations of the concentrations of α and β .)

A patient inspection of Figure 19 reveals the following facts regarding the diffusion and chemistry processes through the plume:

1. The diffusion of the α species is removing α from the plume core from the center line to $z = 1.25$ m and is causing an accumulation of α from 1.25 to 5 m (Curve 4).

2. The diffusion of the β species into the plume is operating to remove β from the height zone 2 to 8 m and accumulate β in the height zone 0 to 2 m (Curve 6).

3. The chemical reaction is depleting both the α and β species between the plume center line and $z = 6$ m (Curve 1), the upper height being the limit of α penetration into the β environment at this time.

4. The chemical reaction diminishes the rate of increase of the concentration of β below $z = 1.5$ m and accelerates the decrease of concentration of β from 1.5 to 5 m (Curve 5).

5. Below 2.75 m the chemical reaction accelerates the depletion of α in the plume core, but above 2.75 m the reaction rate very nearly balances the diffusive transfer rate for α, i.e., above $z = 2.75$ m the chemical reaction is diffusion limited (Curve 3).

6. Below $z = 5$ m the diffusive mixing of β with α becomes increasingly inhomogeneous so that at the plume center line the chemical reaction rate is proceeding at only 60 per cent of the rate computed on the basis of mean values of β and α concentration at that height. (Comparison of Curves 1 and 2)

From these detailed comparisons we can immediately deduce that the α plume is not only being rapidly depleted by reaction with β but that it is also growing in vertical width only slowly because of the balance between diffusion and reaction rates in the outer limits of the plume. On the other hand, the β deficit in the initial plume is being filled in with only minor interference from the local chemical reaction with α. Further, the depletion of the α species in the core of the plume is significantly slower than would have been expected from mean-value chemical kinetics. In this region the chemistry is "mixedness" limited while above this region it is clearly "diffusion" limited.

This simple example is intended only to illustrate the balance of diffusive and chemical processes (and, incidentally, points to a laboratory experiment which may verify these predictions). However, the example does illustrate the model's power to simulate and portray complex chemistry/diffusion processes.

The Sensitivity of Chemical Reactions to Turbulent Diffusion Rates

The example discussed above is, of course, only one particular case and cannot provide any real insight into the sensitivity of the combined diffusion and chemical depletion of reactive species to variations in the input variables. Extensive sensitivity analyses have not been possible, but we have done a partial analysis of the effect of turbulence intensity on the chemical depletion rate of the α species for the flow reactor described above.

Returning to Equation (6.1) we note that since $\overline{u}$ is constant

$$\int_{-\infty}^{\infty} \overline{u} \frac{\partial \overline{C}_\alpha}{\partial x} dz = \frac{\partial}{\partial x} \int_{-\infty}^{\infty} \overline{u}\, \overline{C}_\alpha \, dz = \frac{\partial F_\alpha}{\partial x} \qquad (6.3)$$

where F_α is the horizontal flux of the α species at distance x . Then

$$\frac{\partial F_\alpha}{\partial x} = - \int_{-\infty}^{\infty} \frac{\partial \overline{C'_\alpha w'}}{\partial z} dz - k \int_{-\infty}^{\infty} (\overline{C}_\alpha \overline{C}_\beta + \overline{C'_\alpha C'_\beta}) \, dz \qquad (6.4)$$

and since the first term on the right of Equation (6.4) is zero, the rate of change of the flux of the α species is determined by the total reaction rate over the height of the plume at any distance x . In order to compare the model's prediction of this rate against a limiting condition, we may note that as

$\overline{C'_\alpha C'_\beta}$ goes to zero and $\overline{C}_\beta$ tends to be uniformly distributed through the α plume (a condition which can only be approached asymptotically), the basic chemical reaction goes over to a first-order reaction and for $\overline{u}$ = constant

$$\frac{1}{F_\alpha}\frac{\partial F_\alpha}{\partial x} = -\frac{k\overline{C}_{\beta 0}}{\overline{u}} \tag{6.5}$$

where $\overline{C}_{\beta 0}$ is the environmental concentration of the β species. We can rewrite Equation (6.4) as

$$\frac{1}{F_\alpha}\frac{\partial F_\alpha}{\partial x} = -k\int_{-\infty}^{\infty}(\overline{C}_\alpha\overline{C}_\beta + \overline{C'_\alpha C'_\beta})\,dz \Big/ \int_{-\infty}^{\infty}\overline{u}\,\overline{C}_\alpha\,dz \tag{6.6}$$

and compare Equations (6.5) and (6.6) from the model calculations using various values of $\overline{w'^2}$.

This comparison is shown for the flow reactor problem and at $x = 40$ m in Figure 20. As can be seen from Figure 20, the relative chemical depletion rate of the α species is quite sensitive to the intensity of turbulence for small values of $\overline{w'^2}$ but becomes quite insensitive to this input parameter when $\overline{w'^2}$ becomes large. We may also note that even with the vigorous turbulence of $\overline{w'^2} = 3\ m^2/sec^2$, the chemical depletion rate has only achieved about 60 per cent of the limiting, first-order reaction rate at $x = 40$ m or $kt = 4$ sec.

A Simulation of $NO - O_3$ Reactions and Diffusion Downwind of a Multiple Freeway System

The preceding calculations illustrate the basic capabilities of the A.R.A.P. coupled invariant diffusion/chemistry model and, of course, provide only a minimal excursion into the possible interactions of diffusion and chemistry processes in a turbulent flow reactor. The stage is set for in-depth analyses of this kind, but neither time nor resources have permitted the multiple

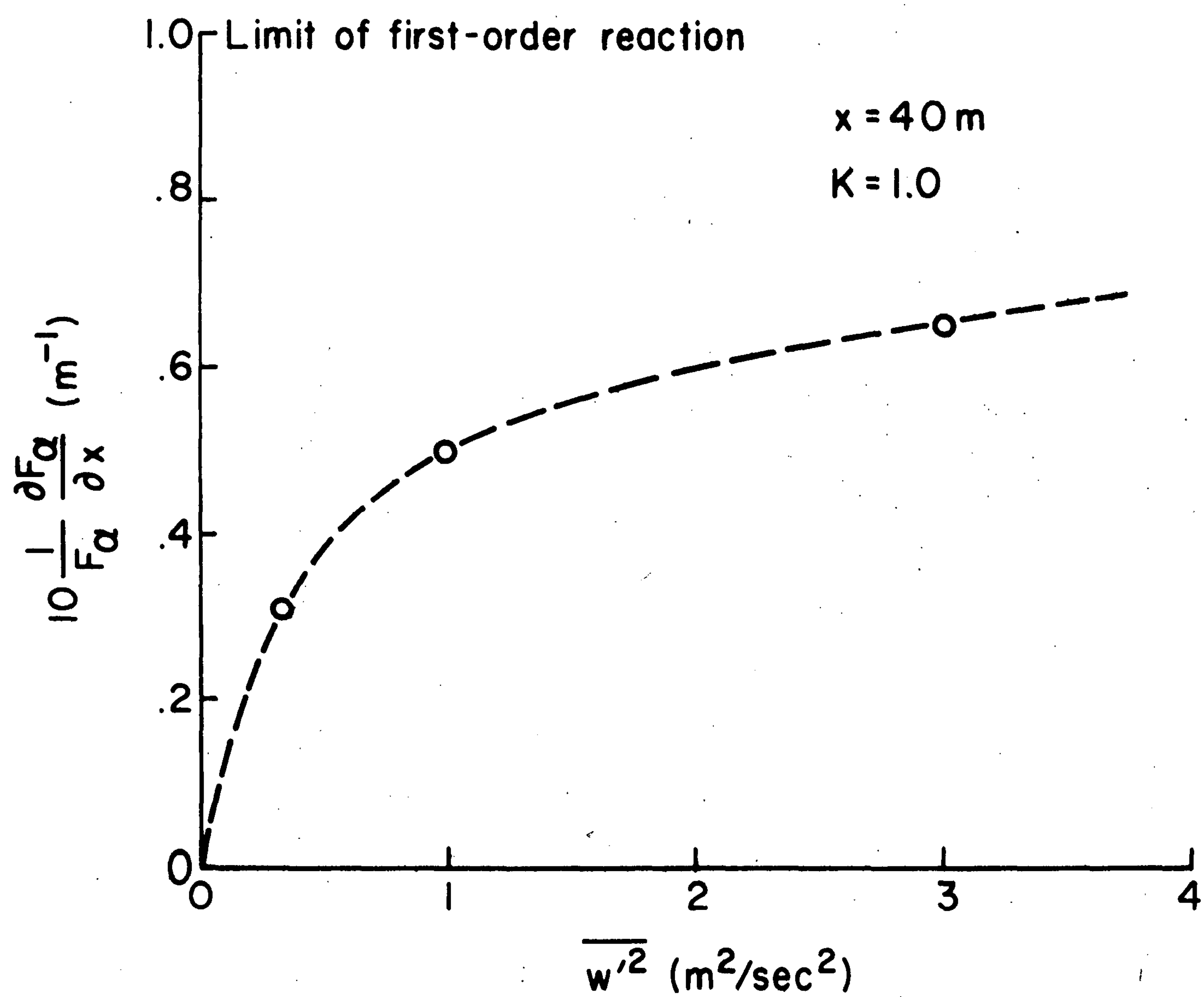

Figure 20. The partial dependence of the chemical depletion of the α species on the intensity of turbulence.

calculations which are required. However, as an exercise of the coupled dimensional model we have constructed an initial simulation of the diffusion and chemical reaction of NO (emitted from vehicles travelling on surface roads or freeways) with the ambient O_3 . In order to examine the effects of multiple sources of NO , we imagine four parallel freeways, oriented across the mean wind and separated by a distance of 300 m. Steady traffic is assumed on each freeway so that each represents a continuous line source of NO . The geometry of the freeways and the assumed initial source distribution of NO at each freeway are shown in Figure 21. Shown there also are the mean wind profiles and the potential temperature lapse rate chosen for this calculation (a neutral lapse rate and a realistic boundary layer wind profile). Just upwind of the first freeway (S_1) we assume that O_3 is uniformly distributed in the vertical at a concentration of 10 ppm. At the first freeway we displace O_3 with NO so that the initial street level value of O_3 immediately downwind of (S_1) is zero.

For the purposes of this calculation we assume that NO reacts with O_3 irreversibly so that the only sources of NO are the freeways (NO) and the reservoir of O_3 above the NO plumes. With this assumption (which, of course, denies the multiple reactions and catalytic cycles which enter into the photochemical problems associated with NO and O_3) we choose the value of the reaction rate constant as $k = 5 \times 10^5$ (1/ppm-sec). The calculation proceeds from the first upwind freeway to a distance of 1200 m (300 m downwind from the fourth and final freeway. From these calculations we can recover the predicted vertical profiles of the mean concentrations of NO and O_3 and of the diffusion and chemical rates at any distance downwind.

Before looking at some of the details of these calculations, we may see the general result by examining the mean

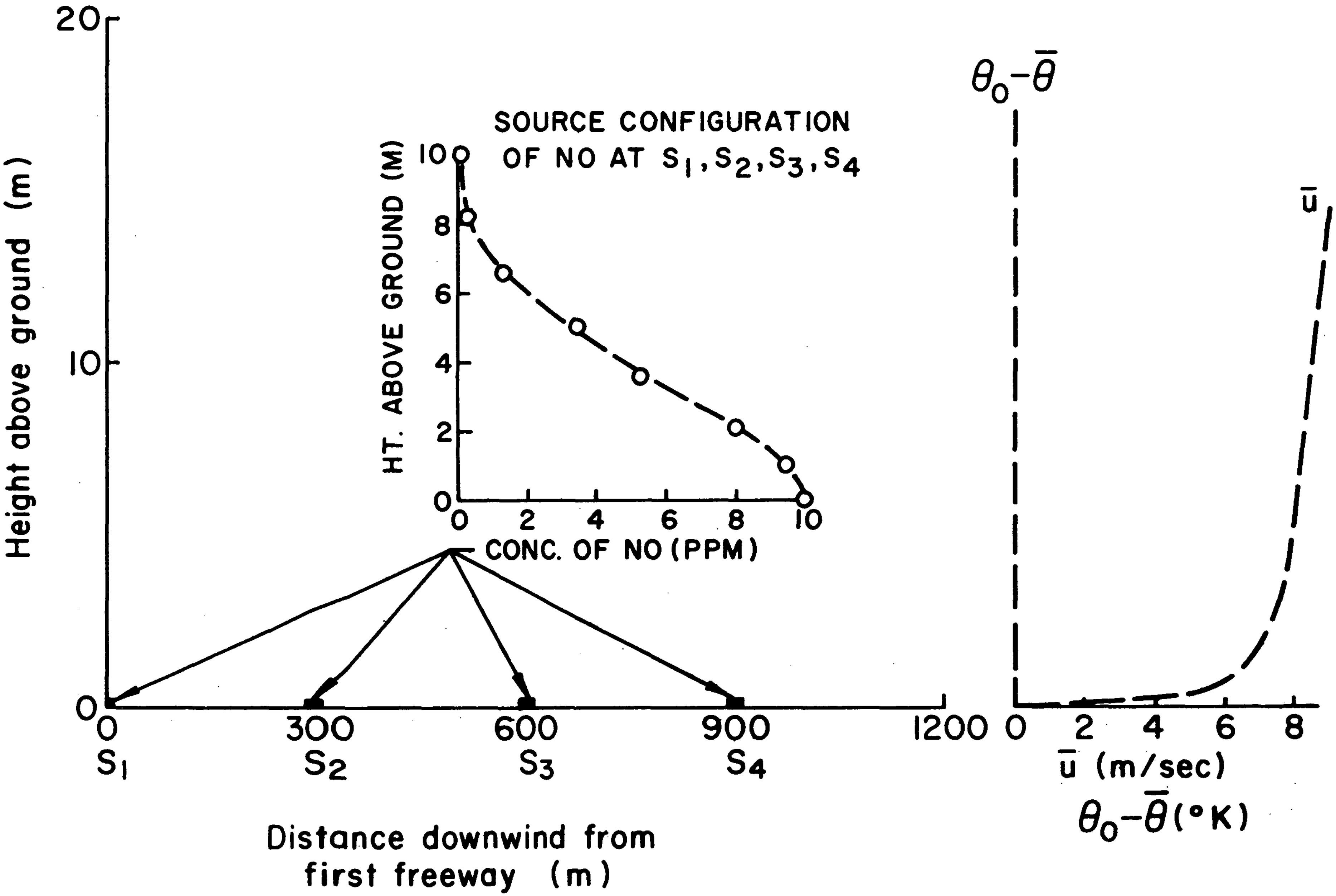

Figure 21. The source geometries and the boundary layer meteorological conditions chosen for simulation of a multiple freeway problem.

values of the concentration of NO and O_3 at 1.625 m above street level and as a function of distance downwind from the first freeway. These values are plotted in Figure 22 and we see immediately the gradual accumulation of NO and the depletion of O_3 in the surface layer as the air moves across multiple freeways.

A closer examination of Figure 22 also reveals the balance between diffusive mixing and chemical reactions as reflected in the surface layer concentrations of the O_3. Note that the residual O_3 entering each freeway is drastically depleted by reaction with the fresh NO during the first 50 m of travel, and then the O_3 concentration increases due to diffusive mixing from above at a rate which exceeds the chemical destruction rate. Recalling the illustrative calculation discussed in the previous sections, we see here the suggestion of a fine balance between diffusion of the reactants into each other and the chemical depletion rate. In this case the chemistry is restricted by the supply rate of O_3 to the NO plume.

With this general result in hand, we may turn attention to the details by examining the predicted vertical profiles of NO and O_3 concentration and of their reaction rates at selected positions in the array of freeways. For this purpose we have elected to plot these profiles at $x = 400$ and 1200 m ; these are shown in Figures 23 and 24 (Note the difference in height scales when comparing these two figures).

Examination of these figures shows immediately the surface layer depletion of O_3 and the inability of diffusive mixing to maintain a uniform distribution of O_3 with height. Even at 1200 m the surface layer concentration of O_3 is less than 1/10th its value outside the NO plume. And we may note in passing that this diffusion limitation can be

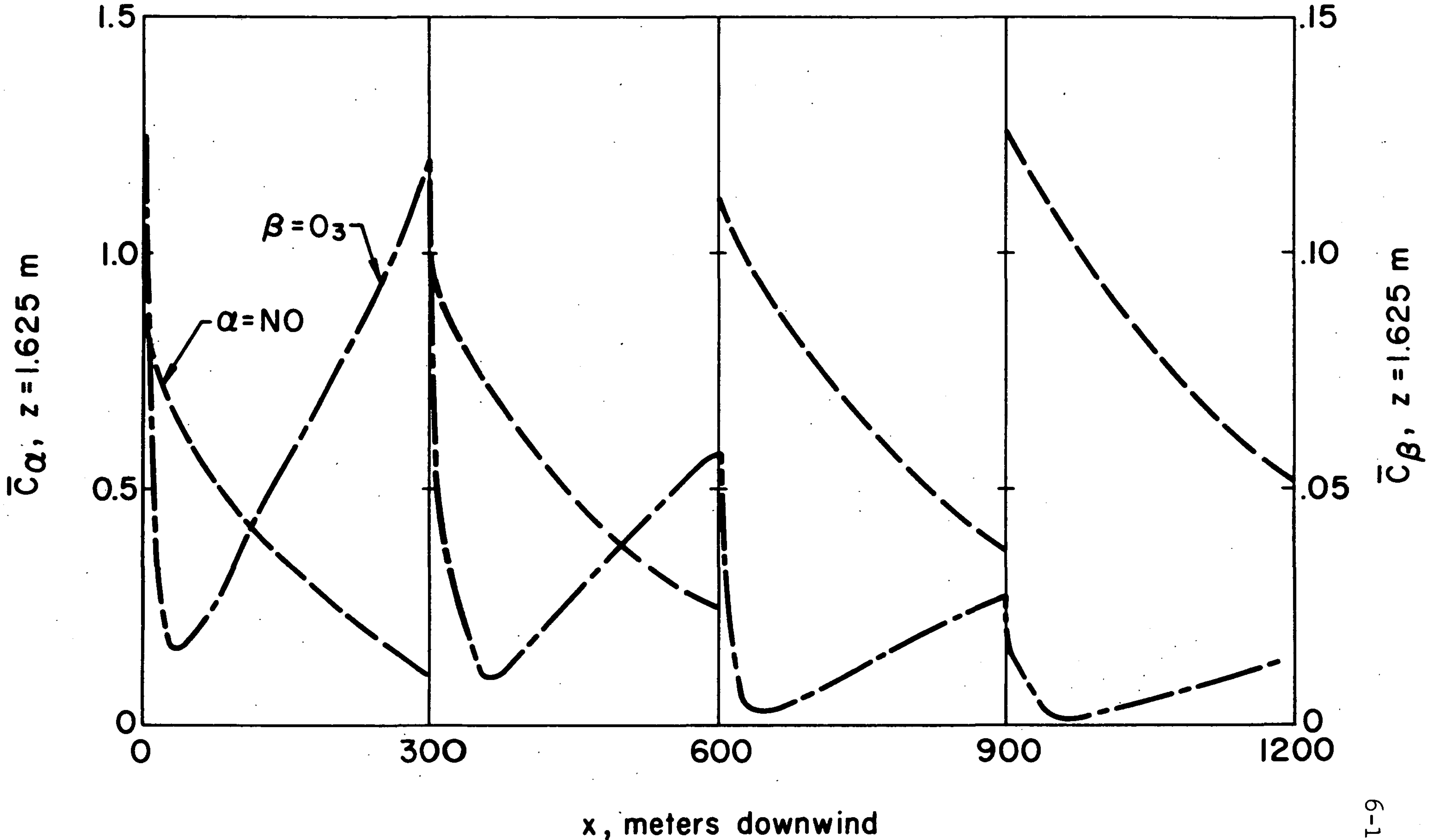

Figure 22. Surface layer concentrations of NO and O_3 predicted for multiple freeway simulation.

readily checked by vertical profile measurements of the concentrations of suitably chosen reactants.

Of considerably greater interest, however, is the portrayal of the chemical reaction rates with height at 400 and 1200 m. These are plotted on the right-hand side of Figures 23 and 24, and for comparison we have also plotted the rates determined by the local mean values of concentration alone. As is more than evident, these reactions are strongly "mixedness" limited; the total reaction rate over the plume height is only 19 per cent of the mean value rates at 400 m and 13 per cent at 1200 m. This result points to the "folding" nature of turbulent mixing, a process in which discreet volumes of each reactant are folded into one another, but are <u>not</u> intimately mixed and therefore react chemically at a much slower rate than their local average values of concentration suggest. The calculation also points to the maintenance and even enhancement of this "mixedness" limitation when we are dealing with multiple sources. Its true role in a complex photochemical system needs much further study, of course. But the portrayal of a diffusion/chemistry interaction which may alter the chemical reaction rates by a factor of five or more can hardly be ignored!

This demonstration of the potential significance of the correlations of concentration fluctuations in the determination of chemical reaction rates also points up the necessity for second-order closure models if these effects are to be simulated. The possibility that important multiple-source urban air pollution problems exist in which this effect will be significant commends second-order closure models, either for the direct simulation of these situations or for the development of correction factors which can be applied to first-order closure models.

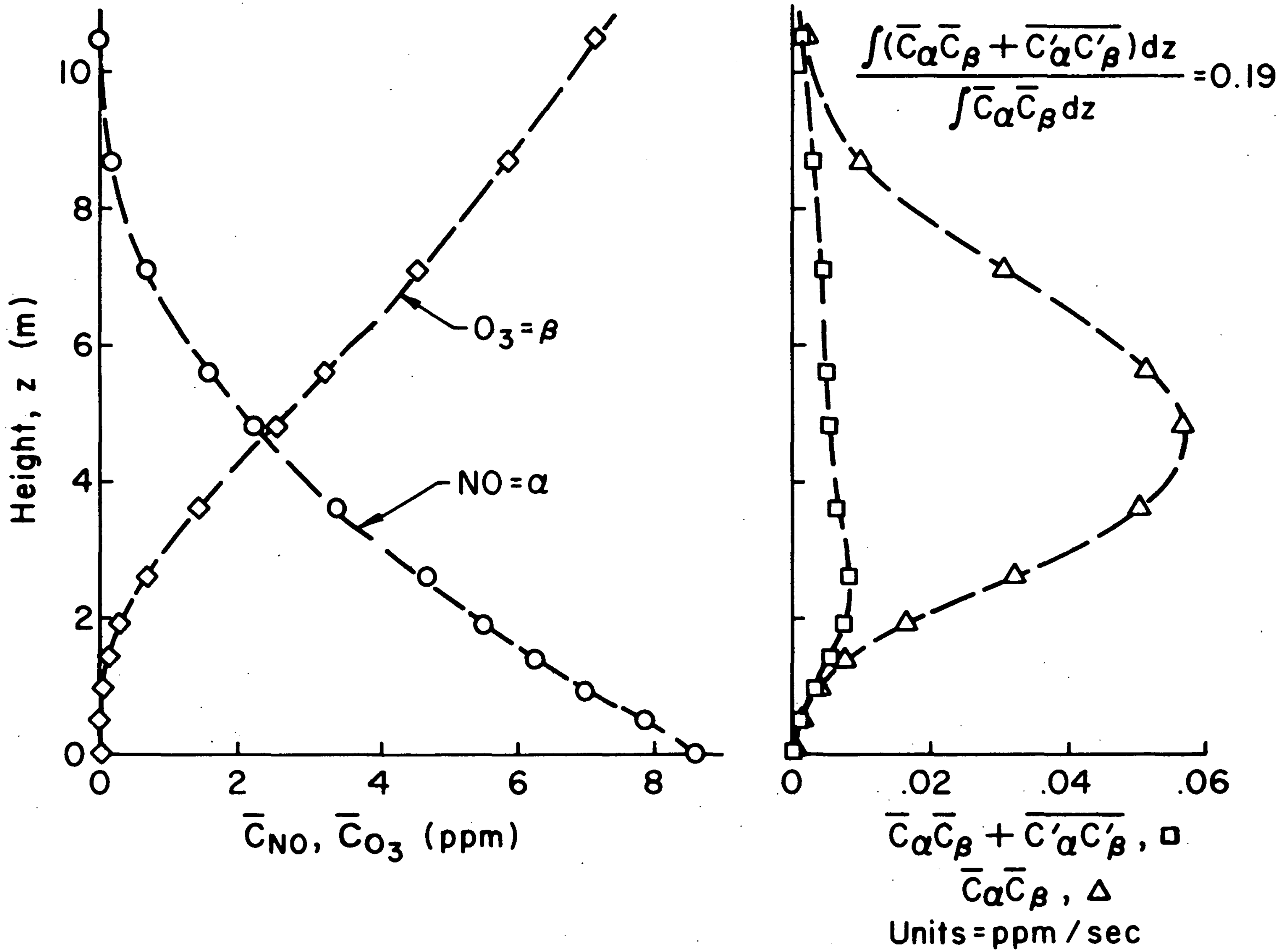

Figure 23. Vertical profiles of the concentration of NO and O_3. and of their chemical reaction rate at x = 400 m downwind from the first freeway.

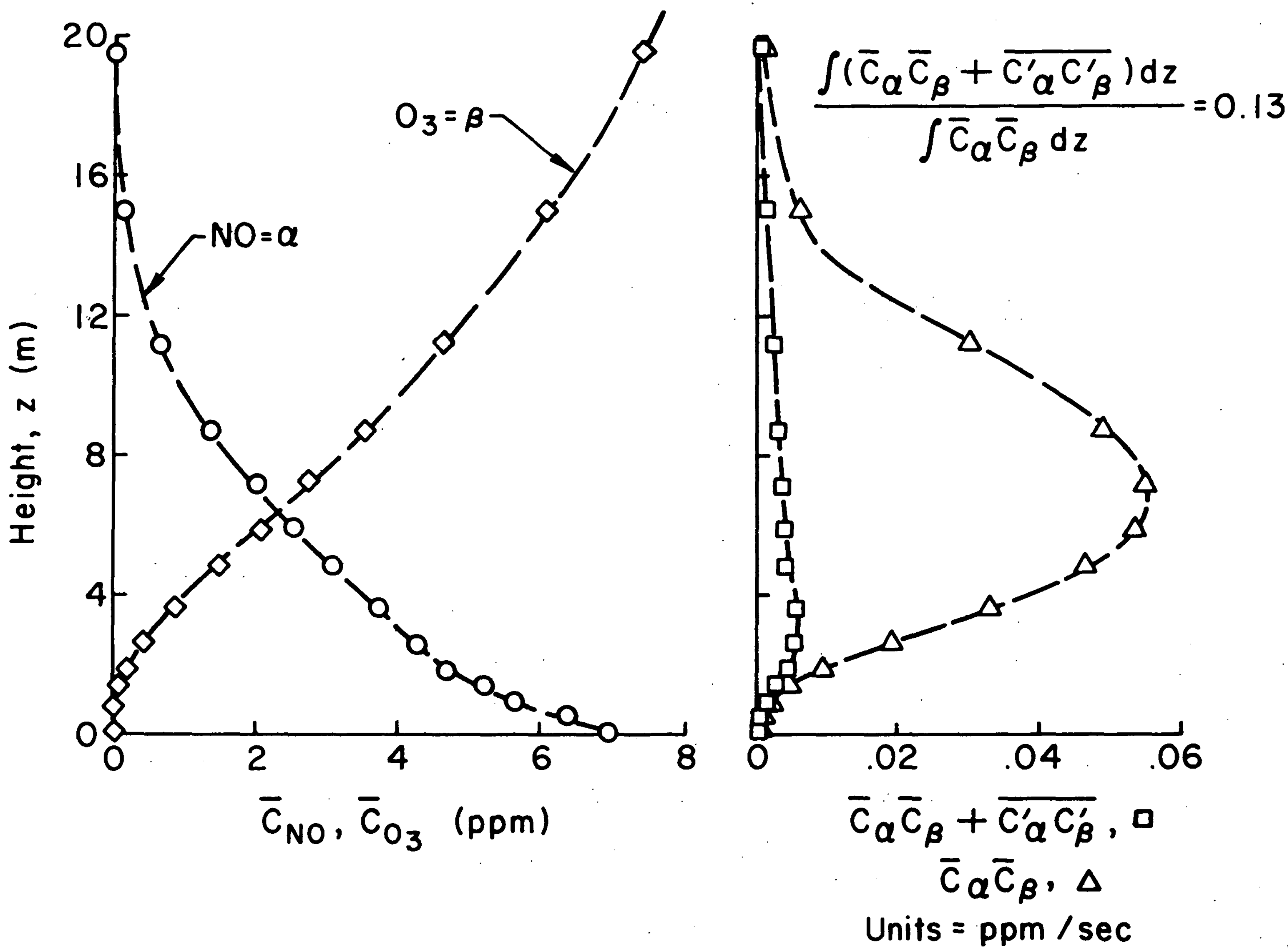

Figure 24. Same as Figure 23 except at $x = 1200$ m.

7. CONCLUSIONS AND RECOMMENDATIONS

Given the objectives of this program to construct a coupled invariant diffusion and chemistry model and to exercise such a model sufficiently to show its applicability and advantages in real-world situations, we can only conclude that this effort has been more than successful. This work has demonstrated the feasibility of incorporating the stochastic nature of turbulent diffusion and chemistry in dynamic models, and has provided the first working version of such a model.. Most importantly, perhaps, even this first and relatively simple version has revealed interactive effects between turbulent diffusion and chemical reactions which could not possibly be revealed by mean-value or first-order closure models. It seems clear to us that, on the one hand, the atmospheric chemists must reexamine their traditional assumptions of a well-mixed system in quasi-equilibrium, and on the other the atmospheric dynamicists must extend their considerations beyond the classical calculations of average values of pollutant concentrations. The further exercise and development of these second-order closure models can provide the tools necessary for the joint evaluation of turbulent, multi-source flow reactors, such as the atmospheric boundary layer in urban areas.

We make this latter recommendation with a full awareness of the complexities of the chemistry of urban air pollution and the proliferation of the invariant model equations as multiple or chain reactions are introduced. However, this increasing complexity need not deter the development and use of these concepts, since they may first be used to analyze critical turbulent reactions, then to define areas where simpler models are quite adequate, and finally to provide simulation capabilities for those situations where first-order closure models are demonstrably inadequate.

As a desirable prelude to further development of these models, such as their extension to coupled three-dimensional systems, the present model should be subjected to a rigorous sensitivity analysis wherein the input variables of the turbulence field, the initial plume geometries, and the chemical reaction coefficients are systematically varied and the outputs of reaction and diffusion rates and the concentration distributions are tested for sensitivity to these input variations. Second, critical experiments, first in the laboratory and then in the atmosphere, should be designed and conducted to verify and validate not only the basic model output such as mean values of concentration, but also the processes internal to the model's workings. In an atmospheric experiment, a minimum measurement program would require an array of towers oriented downwind from cross-wind line sources and equipped to measure the simultaneous means and fluctuations of at least two reacting chemical species (coming from well defined sources) and the turbulent flux of these materials, all as a function of height. The conduct of such an experiment within the broader measurements program of the EPA/RAPS appears particularly desirable.

APPENDIX A

EFFECT OF INHOMOGENEOUS MIXING ON ATMOSPHERIC PHOTOCHEMICAL REACTIONS

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Effect of Inhomogeneous Mixing on Atmospheric Photochemical Reactions

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■ The conventional assumption of local uniform mixing of reactive chemical species is reexamined by derivation of the chemical reaction equations to include the effect of locally inhomogeneous mixtures on the reaction rates. Preliminary solutions of a simplified version of these equations show that inhomogeneities in reactant concentration generally tend to slow the reaction rate. Estimates of the relative roles of local diffusive mixing and chemical reactions in inhomogeneous mixtures show that there are several relatively fast photochemical reactions which may be limited by local diffusive mixing. In these cases, the reaction proceeds much more slowly than would be predicted if the reactants were uniformly mixed.

In developing either mathematical simulation models or laboratory chambers for the study of chemical reactions in the atmosphere, it has been generally assumed that the reacting materials are uniformly mixed. However, observations of the time history of concentrations of trace materials show quite clearly that uniformly mixed materials are the exception rather than the rule in both air and water (Nickola et al., 1970 Singer et al., 1963; Csanady and Murthy, 1971). Local fluctuations of concentration are particularly significant during the early stages of atmospheric mixing, immediately following discharge of trace materials into the atmosphere, and when there are multiple point sources of pollutants. Our purpose here is to make a preliminary estimate of the importance of these fluctuations on atmospheric chemical reaction rates and determine, at least approximately, the relative roles of reaction rates and diffusive mixing in the control of atmospheric chemical reactions.

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The importance of chemical reactions in the atmosphere has been increasingly recognized in the problems of air pollution. These are probably most acute in dealing with photochemical smog formation (Worley, 1971). We have, therefore, drawn our examples from photochemistry, but we have not attempted to go beyond an examination of the possible importance of inhomogeneous mixing in these processes.

Basic Chemistry Model

We assume a bimolecular reaction

$$\alpha + \beta \rightarrow \gamma + \delta \qquad (1)$$

where α, β, γ, and δ denote chemical species and that the reaction of α with β to form γ and δ is stoichiometric and is governed by equations of the form

$$\frac{\partial[\alpha]}{\partial t} = -K[\alpha][\beta]$$
$$\frac{\partial[\beta]}{\partial t} = -K[\alpha][\beta] \qquad (2)$$

$[i]$ denotes the molar concentration of the ith chemical species and K is the reaction rate constant in units of (sec mol/cm^3)$^{-1}$. It is convenient to transform the concentration terms in Equations 2 to dimensionless mass fractions, C_i, by

$$\rho_o C_i = M_i[i] \qquad (3)$$

where ρ_o is the density of the mixture (g/cm^3) and M_i is the molecular weight of the ith chemical species. Then the depletion rates for the α and β species may be written

$$\frac{\partial C_\alpha}{\partial t} = -K_\alpha C_\alpha C_\beta \qquad (4)$$

and

$$\frac{\partial C_\beta}{\partial t} = -\frac{K_\alpha M_\beta}{M_\alpha} C_\alpha C_\beta \qquad (5)$$

where $K_\alpha = K\rho_0/M_\beta$ and has dimensions (sec-ppm)$^{-1}$ when C_α and C_β are expressed in parts per million (ppm) by wt.

We may now examine the relative contributions of the means and fluctuations of C_α and C_β to the chemical reaction rate by assuming the time history of these quantities at a fixed point constitutes a stationary time series and that

$$\left.\begin{aligned} C_\alpha &= \bar{C}_\alpha + C_\alpha' \\ C_\beta &= \bar{C}_\beta + C_\beta' \end{aligned}\right\} \tag{6}$$

where the overbar indicates a time average and the prime indicates the instantaneous fluctuation about the average. Noting that $\overline{C_\alpha'} = \overline{C_\beta'} = 0$ and that

$$\frac{\partial C_i}{\partial t} = \frac{\partial \bar{C}_i}{\partial t} + \frac{\partial C_i'}{\partial t} \tag{7}$$

we obtain directly from Equations 4–6

$$\frac{\partial \bar{C}_\alpha}{\partial t} = -K_\alpha\,(\bar{C}_\alpha\bar{C}_\beta + \overline{C_\alpha'C_\beta'}) \tag{8}$$

and

$$\frac{\partial \bar{C}_\beta}{\partial t} = -\frac{K_\alpha M_\beta}{M_\alpha}\,(\bar{C}_\alpha\bar{C}_\beta + \overline{C_\alpha'C_\beta'}) \tag{9}$$

where we have suppressed the dependence of K_α on the temperature and pressure. (This analysis can be extended to include the fluctuations of K_α owing to significant fluctuations of temperature and pressure. For our present purposes, we shall assume an isothermal reaction at ambient pressure.)

The role of concentration fluctuations in chemical reactions is immediately evident from Equations 8 or 9. The second-order correlation in the joint fluctuations of C_α and C_β either enhances the reaction rate (when the correlation is positive) or suppresses the reaction when $\overline{C_\alpha'C_\beta'}$ is negative. *Only when these fluctuations either do not exist or are uncorrelated is the average reaction rate governed by the average concentrations.* As a simple example of the importance of this correlation term, imagine that the materials α and β pass the point of observation at different times—i.e., they are never in contact with each other. Values of $\bar{C}_\alpha$ and $\bar{C}_\beta$ would be observed, but it is readily seen that $\bar{C}_\alpha\bar{C}_\beta = -\overline{C_\alpha'C_\beta'}$ in this case, a result which correctly predicts no chemical reaction.

If we assume no diffusive mixing of the reacting materials, we may model the chemical reactions by noting that

$$\frac{\partial C_i'^2}{\partial t} = 2\,C_i'\,\frac{\partial C_i'}{\partial t} \tag{10}$$

$$\frac{\partial C_i'}{\partial t} = \frac{\partial C}{\partial t} - \frac{\partial \bar{C}}{\partial t} \tag{11}$$

and

$$\frac{\partial C_\alpha'C_\beta'}{\partial t} = C_\alpha'\,\frac{\partial C_\beta'}{\partial t} + C_\beta'\,\frac{\partial C_\alpha'}{\partial t} \tag{12}$$

Performing the necessary operations and time-averaging, we get, repeating Equations 8 and 9,

$$\frac{\partial \bar{C}_\alpha}{\partial t} = -K_\alpha(\bar{C}_\alpha\bar{C}_\beta + \overline{C_\alpha'C_\beta'}) \tag{13}$$

$$\frac{\partial \bar{C}_\beta}{\partial t} = -\frac{K_\alpha M_\beta}{M_\alpha}\,(\bar{C}_\alpha\bar{C}_\beta + \overline{C_\alpha'C_\beta'}) \tag{14}$$

$$\frac{\partial \overline{C_\alpha'C_\beta'}}{\partial t} = -K_\alpha\left[\frac{M_\beta}{M_\alpha}\,(\bar{C}_\alpha\overline{C_\alpha'C_\beta'} + \bar{C}_\beta\overline{C_\alpha'^2} + \overline{C_\alpha'^2C_\beta'}) + (\bar{C}_\beta\overline{C_\alpha'C_\beta'} + \bar{C}_\alpha\overline{C_\beta'^2} + \overline{C_\alpha'C_\beta'^2})\right] \tag{15}$$

$$\frac{\partial \overline{C_\alpha'^2}}{\partial t} = -2\,K_\alpha(\bar{C}_\alpha\overline{C_\alpha'C_\beta'} + \bar{C}_\beta\overline{C_\alpha'^2} + \overline{C_\beta'C_\alpha'^2}) \tag{16}$$

$$\frac{\partial \overline{C_\beta'^2}}{\partial t} = -\frac{2\,K_\alpha M_\beta}{M_\alpha}\,\bar{C}_\beta\overline{C_\alpha'C_\beta'} + \bar{C}_\alpha\overline{C_\beta'^2} + \overline{C_\alpha'C_\beta'^2}) \tag{17}$$

Equations 13–17 provide a closed set, except for the third-order correlation terms $\overline{C_\alpha'C_\beta'^2}$ and $\overline{C_\beta'C_\alpha'^2}$.

The appearance of the third-order correlations complicates the modeling problem very considerably since the statistical description now requires consideration of the distribution functions for C_α and C_β. In an independent study, O'Brien (1971) has proceeded from Equations 13–17 by assuming the form of these distribution functions. Another approach, which we are pursuing, is to model the third-order correlations in terms of the second-order correlations. However, for our present purpose of determining whether or not the effects of inhomogeneous mixtures on chemical reactions may be significant, we may neglect the third-order correlations by assuming C_α' and C_β' are symmetrically distributed about $\bar{C}_\alpha$ and $\bar{C}_\beta$, respectively. This assumption is, of course, untenable for more general cases but it does permit a solution of Equations 13–17 by numerical techniques.

For an initial test of the significance of inhomogeneities in chemical reactions, we assume a reaction box in which the initial concentration distributions of α and β are arbitrarily specified by $\bar{C}_\alpha$, $\bar{C}_\beta$, $\overline{C_\alpha'^2}$, $\overline{C_\beta'^2}$, and $\overline{C_\alpha'C_\beta'}$. As a further constraint which isolates the chemical reaction process, we assume there is no mixing in the reaction vessel and no wall effects.

As a reference case, let us assume a completely uniform

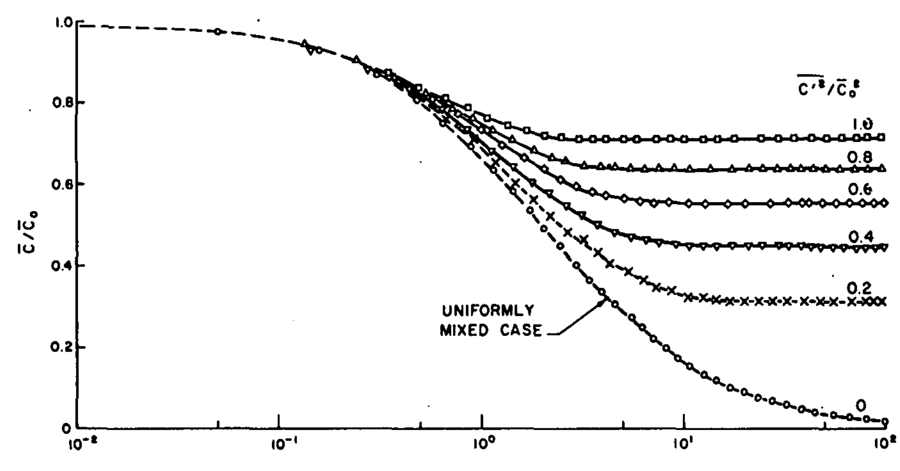

Figure 1. Chemical depletion of randomly mixed reactants ($\overline{C_\alpha'C_\beta'} = 0$) for various initial degrees of inhomogeneity, as measured by $\overline{C'^2}/\bar{C}_0^2$

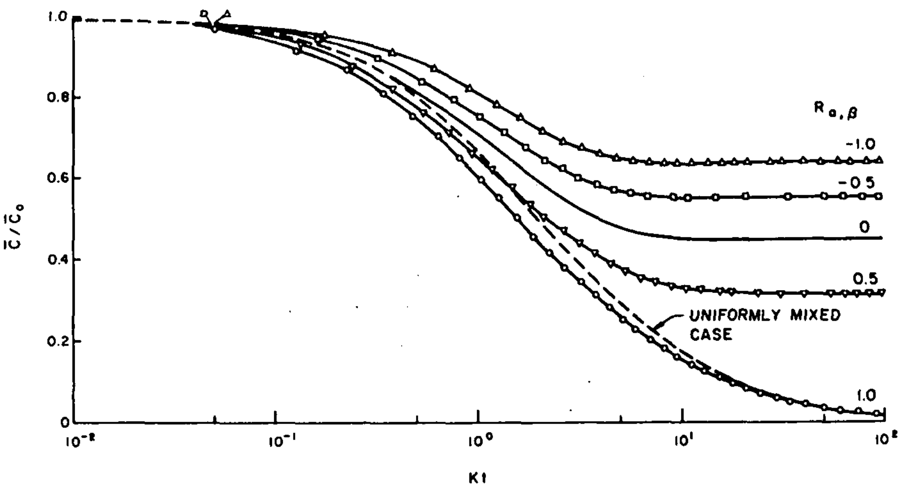

Figure 2. Chemical depletion of initially inhomogeneously mixed reactants ($\overline{C'^2}/\overline{C}_o^2 = 0.40$) for various degrees of initial correlation between C_α' and C_β', as measured by

$$R_{\alpha,\beta} = \frac{\overline{C_\alpha'C_\beta'}}{(\overline{C_\alpha'^2}\overline{C_\beta'^2})^{1/2}}$$

mixture of α and β—i.e., no fluctuations in concentration, $M_\alpha \simeq M_\beta$, and initially $\overline{C}_\alpha = \overline{C}_\beta = \overline{C}_o$. The predicted values of $\overline{C}_\alpha$ are shown in Figure 1 as a function of time normalized by the reaction rate constant. As can be seen, the reaction proceeds to exhaustion of the reacting materials.

Now let us assume that α and β are initially inhomogeneously mixed but that there is no initial correlation between C_α' and C_β'—i.e., initially $\overline{C_\alpha'C_\beta'} \equiv 0$. As a measure of these fluctuations, we take $\overline{C_i'^2}/\overline{C_i}^2 = 0.2, 0.4, 0.6, 0.8$, and 1.0. The results of these calculations are also shown in Figure 1, and it is immediately evident that any inhomogeneities operate to suppress the chemical reaction rate and to stop it completely before the reacting materials are exhausted. Mathematically, the model predicts that, in the absence of mixing, initial inhomogeneities operate to produce values of $\overline{C_\alpha'C_\beta'}$ which eventually become equal to $-\overline{C}_\alpha\overline{C}_\beta$ and the reaction ceases. Physically, the local reactions have everywhere proceeded to exhaustion of one of the reactants, leaving a residue of the other reactant and products at that site.

It is of special interest to note, from Equation 15, that the suppression of the reaction rate by $\overline{C_\alpha'C_\beta'}$ depends only on one of the reactants being nonuniformly distributed initially. A negative rate of change of $\overline{C_\alpha'C_\beta'}$ can be generated by nonzero values of either $\overline{C_\alpha'^2}$ or $\overline{C_\beta'^2}$, since the terms $\overline{C}_\beta\overline{C_\alpha'^2}$ and $\overline{C}_\alpha\overline{C_\beta'^2}$ are positive definite. The presence of concentration inhomogeneities in one of the reactants generates inhomogeneities in the other.

The effect of an initial correlation between C_α' and C_β' may now be examined by assigning initial nonzero values to $\overline{C_\alpha'C_\beta'}$, $\overline{C_\alpha'^2}$, and $\overline{C_\beta'^2}$. To illustrate this effect, we have chosen $\overline{C_\alpha'^2}/\overline{C}_o^2 = \overline{C_\beta'^2}/\overline{C}_o^2 = 0.4$ and $\overline{C_\alpha'C_\beta'}/(\overline{C_\alpha'^2}\overline{C_\beta'^2})^{1/2} = +1.0, +0.5, 0.0, -0.5$, and -1.0 where $\overline{C_\alpha'C_\beta'}/(\overline{C_\alpha'^2}\overline{C_\beta'^2})^{1/2} \equiv R_{\alpha,\beta}$, the ordinary correlation coefficient. The resulting predictions of $\overline{C}/\overline{C}_o$ are shown in Figure 2 and are again compared with the uniformly mixed case. As might have been expected, initial positive correlation accelerated the reaction rate, but only when this initial positive correlation was perfect did the reaction go to exhaustion of the reacting materials. In this case, although there were concentration fluctuations, stoichiometrically equal amounts of α and β were initially placed in each local volume. In all other cases, the reaction was again halted when one of the reactants was exhausted locally, leaving a residue of the other reactants and products of the reaction.

The combined effects of initial inhomogeneities and correlations between the fluctuations are summarized in Figure 3 by plotting the depletion of $\overline{C}$ during the first normalized time step as a function of $R_{\alpha,\beta}$ and $\overline{C'^2}/\overline{C}_o^2$. The effect of the magnitude of the fluctuations, as measured by $\overline{C'^2}$, reverses as one goes from large positive toward small positive and negative values of $\overline{C_\alpha'C_\beta'}$.

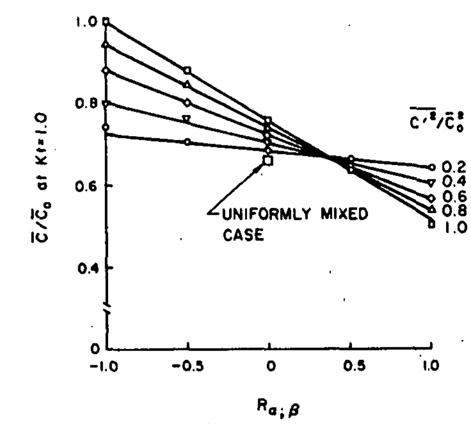

Figure 3. Joint effect of initial correlation and inhomogeneity on depletion of reacting materials at $Kt = 1.0$

These results point toward an important role for fluctuations of concentration in controlling chemical reaction rates. For example, if two reacting materials are discharged simultaneously from a point source, during their initial mixing with the atmosphere their concentration fluctuations should be large and positively correlated. We would then expect, on the basis of this effect, that their reaction rate would be considerably faster than if they were uniformly mixed from the start. The emission of hydrocarbon and NO_x from auto exhausts is a case in point. Discharge of SO_2 and particulate matter from power plant stacks is another.

On the other hand, if reacting materials are randomly mixed or if positive fluctuations in one are associated with negative fluctuations in the other, the reaction should be suppressed, compared to the uniformly mixed case. Both of these cases could be important, but their true importance depends critically on the rate at which atmospheric diffusion tends to mix chemical species and, hence, to diminish these fluctuations, as compared with the rate of chemical reaction produced by the concentration fluctuations.

Estimates of Local Mixing Rates in the Atmosphere

The only way in which the correlation $\overline{C_\alpha'C_\beta'}$ can be eliminated, if it exists, in given flow situations is by the process of molecular diffusion. To estimate the rate at which this can occur, we may write the expressions for the contribution of molecular diffusion to the time rate of change of C_α' and C_β'. They are

$$\left(\frac{\partial C_\alpha'}{\partial t}\right)_{\text{diff}} = D_\alpha \nabla^2 C_\alpha' = D_\alpha \frac{\partial^2 C_\alpha'}{\partial y_i \partial y_i} \tag{18}$$

$$\left(\frac{\partial C_\beta'}{\partial t}\right)_{\text{diff}} = D_\beta \frac{\partial^2 C_\beta'}{\partial y_i \partial y_i} \tag{19}$$

Multiplying Equations 18 and 19 by C_β' and C_α', respectively, adding, and time-averaging gives

$$\left(\frac{\partial \overline{C_\alpha' C_\beta'}}{\partial t}\right)_{\text{diff}} = D \frac{\partial^2 \overline{C_\alpha' C_\beta'}}{\partial y_i^2} - 2D \frac{\partial \overline{C_\alpha'}}{\partial y_i} \frac{\partial \overline{C_\beta'}}{\partial y_i} \tag{20}$$

(We have assumed $D_\alpha \simeq D_\beta = D$, consistent with the assumption $M_\alpha \simeq M_\beta$. See O'Brien (1971) for a discussion of this assumption.) The first term on the right-hand side of Equation 20 is nondissipative—i.e., it measures the transfer of the $\overline{C_\alpha' C_\beta'}$ correlation by gradients in the value of this correlation within the field. The second term is dissipative—i.e., it measures the local diminution of $\overline{C_\alpha' C_\beta'}$ by the action of molecular diffusion. The appropriate expression for this term is

$$2D \frac{\partial \overline{C_\alpha'}}{\partial y} \frac{\partial \overline{C_\beta'}}{\partial y} = \frac{2D\, \overline{C_\alpha' C_\beta'}}{\lambda^2} \tag{21}$$

In this expression, the dissipative scale length λ must be chosen as it is chosen for the calculation of other turbulent correlations when performing calculations of the structure of turbulence (Donaldson, 1969).

For such calculations, $1/\lambda^2$ is given approximately by

$$\frac{1}{\lambda^2} \simeq \frac{0.05\, \rho_o q}{\mu_o \Lambda}$$

where ρ_o is the atmospheric density, $q^2 = \overline{u'^2} + \overline{v'^2} + \overline{w'^2}$, μ_o is the molecular viscosity of air, and Λ is a length scale related to the integral scale of the atmosphere, and is of the order of 1000 cm in the earth's boundary layer.

If we choose typical values of the parameters involved in evaluating the magnitude of the expression for $(\partial \overline{C_\alpha' C_\beta'}/\partial t)_{\text{diff}}$ given in Equation 20, we have

$$\begin{aligned} \Lambda &= 1000 \text{ cm} \\ \rho_o &= 10^{-3} \text{ g/cm}^3 \\ \mu_o &= 1.7 \times 10^{-4} \text{ g/cm-sec} \\ D &= 1.7 \times 10^{-1} \text{ cm}^2\text{/sec} \\ q &= 30 \text{ cm/sec} \end{aligned}$$

These numbers give for the magnitude of the dissipative scale

$$\lambda = 10 \text{ cm}$$

From this result, we obtain, finally,

$$\frac{2D}{\lambda^2} = 3.4 \times 10^{-3} \text{ sec}^{-1}$$

The rate of destruction of $\overline{C_\alpha' C_\beta'}$ by molecular diffusion is of the order of magnitude of $3.4 \times 10^{-3} \overline{C_\alpha' C_\beta'}$ and is tending to drive $\overline{C_\alpha' C_\beta'}$ to zero. If this diffusion dissipation of $\overline{C_\alpha' C_\beta'}$ is dominant, $\overline{C_\alpha' C_\beta'}$ will remain close to zero and the chemical reaction will proceed according to the product of the mean concentrations. In this case, the chemical reaction rate is controlled by the reaction rate constant and the mean concentrations in the traditional way.

On the other hand, if the change of $\overline{C_\alpha' C_\beta'}$ is dominated by chemical reactions—i.e., the reaction proceeds more rapidly than species diffusion, $\overline{C_\alpha' C_\beta'}$ will tend to the value $-\overline{C}_\alpha \overline{C}_\beta$ and the reaction rate will be suppressed. In this case, the reaction is controlled by the rate of species mixing and will depend on parameters other than K_α and $\overline{C}_\alpha \overline{C}_\beta$.

Table I. Reaction Rate Constant K_α for Various Photochemical Reactions and Associated Estimates of N Using $\overline{C}_\alpha = 1$ ppm

Reaction	K (ppm-sec)$^{-1}$	N
1. $O_3 + NO = NO_2 + O_2$	8.3×10^{-4}	4
2. $NO_2 + O_3 = NO_3 + O_2$	1.7×10^{-5}	2×10^2
3. $NO_3 + NO = 2NO_2$	4.8	7×10^{-4}
4. $NO + HO_2 = NO_2 + OH$	1.7×10^{-1}	2×10^{-2}
5. $OH + O_3 = HO_2 + O_2$	1.7	2×10^{-3}
6. $OH + CO = H + CO_2$	5.0×10^{-2}	7×10^{-3}
7. $CH_3O_2 + NO = CH_3O + NO_2$	1.7	2×10^{-3}
8. $C_2H_3O_2 + NO = C_2H_3O + NO_2$	1.7	2×10^{-3}
9. $C_2H_4O_2 + NO = CH_3CHO + NO_2$	1.7	2×10^{-3}
10. $CH_3O + O_2 = HCHO + HO_2$	1.7	2×10^{-3}
11. $C_3H_6 + O = CH_3 + C_2H_3O$	6.0×10^{-1}	6×10^{-3}
12. $C_3H_6 + O_3 = HCHO + C_2H_4O_2$	8.3×10^{-3}	4×10^{-1}
13. $C_3H_6 + O_2 = CH_3O + C_2H_3O$	1.7×10^{-2}	2×10^{-1}
14. $C_3H_6 + HO_2 = CH_3O + CH_3CHO$	3.4×10^{-2}	10^{-1}
15. $C_2H_3O + M = CH_3 + CO + M$	1.7×10^{-1}	2×10^{-2}

We may estimate which two-body reactions will proceed as though $\overline{C'_\alpha C_\beta'} \simeq 0$—i.e., in the usual manner, and which will be modified by having values of $|\overline{C_\alpha' C_\beta'}|$ of the same order as $|\overline{C}_\alpha \overline{C}_\beta|$ by forming the ratio

$$N = \frac{\left(\frac{\partial \overline{C_\alpha' C_\beta'}}{\partial t}\right)_{\text{diff}}}{\left(\frac{\partial \overline{C_\alpha' C_\beta'}}{\partial t}\right)_{\text{ch}}} = \frac{2D}{\lambda^2 K_\alpha \overline{C}_\alpha} = \frac{3.4 \times 10^{-3}}{K_\alpha \overline{C}_\alpha} \tag{22}$$

When $N \gg 1.0$, $\overline{C_\alpha' C_\beta'}$ will tend to zero and the reaction will be controlled by the reaction rate constant and the mean concentrations; when $N \ll 1.0$, $\overline{C_\alpha' C_\beta'}$ will tend to and remain close to $-\overline{C}_\alpha \overline{C}_\beta$ and the reaction will proceed at a rate determined largely by the rate at which one reactant can be mixed with another and will depend on the scale of the patches of unmixed reactants.

Typical values of K_α for various reactions which enter into the photochemical chains are listed in Table I along with estimates of N. For these two-body reactions, only the first and second are sufficiently slow for conventional kinetic models to apply. The propylene reactions with O_3, O_2, and HO_2 (numbers 12, 13, and 14 in Table I) tend to represent a transition stage between diffusive mixing control and chemical reaction control of the reaction rate. The remaining reactions are all clearly diffusion-limited in inhomogeneous mixtures and should proceed at a rate which is much slower than conventional chemical kinetics would predict.

Conclusion

These results indicate there are clearly reactions in the photochemical chain which will be suppressed by the inability of the atmosphere to mix the reacting materials rapidly enough to prevent serious local depletion of one of the reacting materials. In these cases, conventional models of the reaction will tend to seriously overestimate the reaction rate, and, therefore, the production rate of the chemical species which enters into the next reaction in the photochemical chain. On the other hand, the enhancement of the reaction rate for two materials emanating from a common source and, therefore, occupying the same volume of the atmosphere, during the initial period of incomplete mixing, may also represent a significant departure from conventional simulation models.

It is hoped that this brief and necessarily incomplete discussion will serve to demonstrate the importance of turbulent fluctuations of concentrations in atmospheric chemical reactions. Consideration of these effects in refining simulation models of these reactions appears to be important.

Nomenclature

C_i = mass fraction of ith chemical species, ppm
D_i = molecular diffusion coefficient for ith chemical species, cm^2/sec
K = chemical reaction rate constant, cm^3/sec-mol
K_α, K_β = chemical reaction rate constants, 1/ppm-sec
M_i = molecular weight of ith chemical species, g/mol
N = nondimensional ratio of characteristic times
q^2 = $\overline{u'^2} + \overline{v'^2} + \overline{w'^2}$, cm^2/sec^2
$R_{\alpha,\beta}$ = ordinary second-order correlation coefficient
t = time, sec
u', v', w' = orthogonal components of turbulent fluid motion, cm/sec
y_i = length along ith direction of a cartesian coordinate system, cm
[ ], = averaged quantity
$'$ = departure from the average of the primed quantity

GREEK LETTERS

$\alpha, \beta, \gamma, \delta$ = chemical species
λ = dissipation scale length, cm
Λ = macroscale of atmospheric turbulence, cm
μ_o = dynamic viscosity for air, g/cm-sec
ρ_o = fluid density, g/cm^3

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APPENDIX B

CHEMICAL REACTIONS IN INHOMOGENEOUS MIXTURES: THE EFFECT OF THE SCALE OF TURBULENT MIXING

CHEMICAL REACTIONS IN INHOMOGENEOUS MIXTURES: THE EFFECT OF THE SCALE OF TURBULENT MIXING

Coleman duP. Donaldson* and Glenn R. Hilst**

ABSTRACT

Recent studies by O'Brien [1] and the authors of this paper [2] have provided a theoretical framework for the assessment of chemical reaction rates when the reactants are embedded in a turbulent fluid and are inhomogeneously mixed. The results of these studies, which are reviewed here, point towards a profound effect on chemical production and depletion rates when the characteristic reaction time, as measured by the product of the chemical kinetic reaction rate constants and the average and fluctuating concentrations of the reactions, is short compared with the characteristic molecular diffusion time. The latter time is measured by the ratio of the molecular diffusion coefficient and the square of the dissipation scale length, and is, therefore, dependent upon the scale of the turbulent motions. Both the fact of inhomogeneous mixtures and this dependence upon turbulent scales of motion pose significant problems when extending laboratory results to other scales of motion, such as the free atmosphere.

These theoretical results, which are partially substantiated by observations, point towards the need for simultaneous measurements of turbulence and chemical reaction rates over a range of turbulence scales and reaction rate constants. If substantiated by such new experimental measurements, the theoretical results point towards a clear requirement for joint consideration of the chemical reactions <u>and</u> the scale of turbulence in such diverse but critical problems as the design of large combustion apparatus and the calculation of photochemical reactions in the atmosphere.

INTRODUCTION

Although the effects of inhomogeneous mixing of reacting chemical species on the reaction rate, as measured by either the depletion of reacting species or the production of new species, have been recognized for at least ten years [3], methods for accounting for this effect have only recently emerged [1,2]. Neither of these methods are as yet fully developed, but they are sufficiently advanced that we may make some preliminary estimates of the situations under which the effects of inhomogeneous mixing will be pronounced or perhaps even completely dominate the reaction.

In particular, we find for the case of an irreversible two-body reaction at constant temperature that the following limitations are imposed by inhomogeneous mixing of either or both of the reacting species:

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- If the chemical reaction rate is slow compared with the molecular diffusion rate, no effect is noticed, and the reaction proceeds according to conventional chemical kinetics.

- If the chemical reaction rate is fast compared with the molecular diffusion rate, the reaction rate is limited by the diffusive mixing rate, tending, in the limit of very slow diffusive mixing, to zero before the reactants are exhausted.

A large number of reactions in combustion processes and photochemical smog formation fall within this latter category. It is, therefore, of considerable interest to investigate further just how much the reaction rate is curtailed by inhomogeneous mixing under such circumstances. In the following pages, we derive the basic equations for prediction of the joint effects of chemical reactions and molecular diffusion, examine the effects of the dissipation scale length of the turbulent motions, and identify, on a preliminary basis, the two-body reactions inherent in photochemical smog formation for which inhomogeneous mixing is a limiting condition.

MODELING OF CHEMICALLY REACTING FLOWS

For most computations of chemically reacting turbulent flows, it has been customary for engineers to proceed with the calculation according to the following scheme. First, the engineer develops by some method (mixing length, eddy diffusivity, or other method) equations for the time-averaged or mean values of the concentrations of the reacting species of interest (say, species α and β) at each point in the turbulent flow under consideration. He also obtains an equation for the mean value of the temperature that is expected at each point in this flow. It is then customary, if the equations that generally govern the reaction between α and β , are

$$\frac{DC_\alpha}{Dt} = -k_1 C_\alpha C_\beta \tag{1}$$

$$\frac{DC_\beta}{Dt} = -k_2 C_\alpha C_\beta \tag{2}$$

to assume that valid equations for the time rates of change of the mean values of the mass fractions of α and β are

$$\frac{D\bar{C}_\alpha}{Dt} = -\bar{k}_1 \bar{C}_\alpha \bar{C}_\beta \tag{3}$$

$$\frac{D\bar{C}_\beta}{Dt} = -\bar{k}_2 \bar{C}_\alpha \bar{C}_\beta \tag{4}$$

In these equations, $\bar{C}_\alpha$ and $\bar{C}_\beta$ are the time-averaged mass fractions of the two species and $\bar{k}_1$ and $\bar{k}_2$ are the reaction rates k_1 and k_2 evaluated at the mean temperature $\bar{T}$, i.e.,

$\bar{k}_1 = k_1(\bar{T})$ and $\bar{k}_2 = k_2(\bar{T})$.

Although equations such as (3) and (4) are used extensively at the present time, it is not difficult to show that they are incorrect when reaction rates are fast and the scale of the turbulence is large. This may be done by considering the proper forms of Eqs. (1) and (2) when they are averaged. The well-known results are*

$$\frac{D\bar{C}_\alpha}{Dt} = -\bar{k}_1\left(\bar{C}_\alpha\bar{C}_\beta + \overline{C'_\alpha C'_\beta}\right) - \left[\bar{C}_\alpha\overline{k'_1C'_\beta} + \bar{C}_\beta\overline{k'_1C'_\alpha} + \overline{k'_1C'_\alpha C'_\beta}\right] \tag{5}$$

and

$$\frac{D\bar{C}_\beta}{Dt} = -\bar{k}_2\left(\bar{C}_\alpha\bar{C}_\beta + \overline{C'_\alpha C'_\beta}\right) - \left[\bar{C}_\alpha\overline{k'_2C'_\beta} + \bar{C}_\beta\overline{k'_2C'_\alpha} + \overline{k'_2C'_\alpha C'_\beta}\right] \tag{6}$$

To demonstrate the character of these equations, let us discuss them under the assumption that $k'_1 = k'_2 = 0$. Equations (5) and (6) then reduce to

$$\frac{D\bar{C}_\alpha}{Dt} = -\bar{k}_1\left(\bar{C}_\alpha\bar{C}_\beta + \overline{C'_\alpha C'_\beta}\right) \tag{7}$$

and

$$\frac{D\bar{C}_\beta}{Dt} = -\bar{k}_2\left(\bar{C}_\alpha\bar{C}_\beta + \overline{C'_\alpha C'_\beta}\right) \tag{8}$$

It is clear from these equations that, if one wishes to calculate the reaction of α with β , it will be necessary to have an equation for the second-order correlation $\overline{C'_\alpha C'_\beta}$ unless one can show that $\overline{C'_\alpha C'_\beta} \ll \bar{C}_\alpha\bar{C}_\beta$ for the particular flow in question. The conditions required for $\overline{C'_\alpha C'_\beta} \ll \bar{C}_\alpha\bar{C}_\beta$ can be derived in the following way. First, by following the method used by Reynolds for the derivation of the equation for the turbulent stress tensor, one finds the following equation for the substantive derivative of the correlation $\overline{C'_\alpha C'_\beta}$:**

$$\frac{D\overline{C'_\alpha C'_\beta}}{Dt} = \left(\frac{D\overline{C'_\alpha C'_\beta}}{Dt}\right)_{chem} - \overline{u^{j\prime}C'_\alpha}\,\bar{C}_{\beta,j} - \overline{u^{j\prime}C'_\beta}\,\bar{C}_{\alpha,j} - \overline{u^{j\prime}C'_\alpha C'_\beta}_{,j} + \mathcal{D}g^{mn}(\overline{C'_\alpha C'_\beta})_{,mn} - 2\mathcal{D}g^{mn}(\overline{C'_{\alpha,m}C'_{\beta,n}})\ \dagger \tag{9}$$

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* For a discussion of these equations that is related to the present treatment, reference should be made to O'Brien [1] which was published after this work on the modeling of chemically reacting turbulent flows was started.

** For the purposes of this illustrative discussion, the flow is treated as incompressible.

† The notation is that of general tensor analyses. g^{mn} is the contravariant form of the metric tensor g_{mn} .

where the term $(D\overline{c'_\alpha c'_\beta}/Dt)_{chem}$ is the contribution of chemical kinetics alone to the substantive derivative of $\overline{c'_\alpha c'_\beta}$. This expression can be found from Eqs. (1) and (2), and is

$$\left(\frac{D\overline{c'_\alpha c'_\beta}}{Dt}\right)_{chem} = -k_1\left(\bar{c}_\alpha\overline{c'^2_\beta} + \bar{c}_\beta\overline{c'_\alpha c'_\beta} + \overline{c'_\alpha c'^2_\beta}\right) -k_2\left(\bar{c}_\alpha\overline{c'_\alpha c'_\beta} + \bar{c}_\beta\overline{c'^2_\alpha} + \overline{c'^2_\alpha c'_\beta}\right) \tag{10}$$

It is instructive to discuss the behavior of the correlation $\overline{c'_\alpha c'_\beta}$ for the case of turbulent reactions in the absence of any appreciably large gradients. In this case, Eq. (9) becomes

$$\frac{D\overline{c'_\alpha c'_\beta}}{Dt} = \left(\frac{D\overline{c'_\alpha c'_\beta}}{Dt}\right)_{chem} - 2\mathscr{D}g^{mn}(\overline{c'_{\alpha,m}c'_{\beta,n}}) \tag{11}$$

The second term on the right of Eq. (11) is the destruction of the correlation $\overline{c'_\alpha c'_\beta}$ by the action of molecular diffusion. In line with our previous work [5], we will model this term by means of a diffusion scale length λ so that Eq. (11) becomes

$$\frac{D\overline{c'_\alpha c'_\beta}}{Dt} = \left(\frac{D\overline{c'_\alpha c'_\beta}}{Dt}\right)_{chem} - 2\mathscr{D}\frac{\overline{c'_\alpha c'_\beta}}{\lambda^2} \tag{12}$$

The diffusion term in this equation is such that $\overline{c'_\alpha c'_\beta}$ tends to approach zero with a characteristic time that is

$$\tau_{diff} = \lambda^2/2\mathscr{D} \tag{13}$$

What is the overall effect of the first term on the right-hand side of Eq. (12)? The effect is difficult to see from an inspection of Eq. (11), but we may derive an expression for what this term accomplishes from Eqs. (7) and (8). First, multiply (7) by $\bar{c}_\beta$ and (8) by $\bar{c}_\alpha$ and then add the resulting equations. The result is

$$\left(\frac{D\bar{c}_\alpha\bar{c}_\beta}{Dt}\right)_{chem} = -\left(k_1\bar{c}_\beta + k_2\bar{c}_\alpha\right)\left(\bar{c}_\alpha\bar{c}_\beta + \overline{c'_\alpha c'_\beta}\right) \tag{14}$$

This equation can be interpreted by saying that the effect of chemistry alone is to drive $\bar{c}_\alpha\bar{c}_\beta$ to the negative of $\overline{c'_\alpha c'_\beta}$ (or $\overline{c'_\alpha c'_\beta}$ to the negative of $\bar{c}_\alpha\bar{c}_\beta$) with a characteristic time

$$\tau_{chem} = \frac{1}{k_1\bar{c}_\beta + k_2\bar{c}_\alpha} \tag{15}$$

Equation (14) states that the reaction between α and β will always stop, i.e., $\bar{c}_\alpha\bar{c}_\beta + \overline{c'_\alpha c'_\beta}$ will become zero, short of the exhaustion of α or β unless α and β are perfectly mixed wherever they occur in the turbulent flow under consideration. The physical reason for this is that, in the absence of diffusion, if α and β are not perfectly mixed to start with, the final state of the gas in any volume element will be α and products, β and products, α alone, or β alone, but never any region containing both α and β. It is easy to see that, no matter what the values taken on by C_α and C_β are as a function of time, if C_α is never nonzero when C_β is nonzero and vice versa so that no reaction is possible, it is mathematically true that $\overline{C}_\alpha \overline{C}_\beta + \overline{C'_\alpha C'_\beta} = 0$. Thus, Eqs. (7) and (8) state that no reactions are possible as required by the physics of the problem.

An actual example may make the meaning of $\overline{C'_\alpha C'_\beta}$ more clear. Consider that the flow of material by a given point is such that alternate blobs of α and β pass the point. Let us suppose that half the time the flow is all α and half the time it is all β. The resulting concentrations are sketched in Figure 1. If this pattern keeps repeating, the average values of C_α and C_β are obviously $\overline{C}_\alpha = 1/2$ and $\overline{C}_\beta = 1/2$. Whenever the flow is all α, $C'_\alpha = +1/2$ and $C'_\beta = -1/2$. Whenever the flow is all β, $C'_\alpha = -1/2$ and $C'_\beta = +1/2$. We find then that the average value of $\overline{C'_\alpha C'_\beta}$ must be $\overline{C'_\alpha C'_\beta} = -1/4$. Since $\overline{C'_\alpha C'_\beta} = \overline{C}_\alpha \overline{C}_\beta$, no reaction is possible according to Eqs. (7) and (8) and obviously no reaction should occur.

THE EFFECT OF SCALE LENGTH

We may now return to Eq. (12). If, in this equation, the scale λ is small enough and the reaction rates are slow enough, the second term on the right-hand side of the equation will be dominant and the flow will be such that $\overline{C'_\alpha C'_\beta}$ is always almost zero. This means that molecular diffusion is always fast enough to keep the two species well mixed. On the other hand, if the reaction rates are very fast and λ is very large, the first term on the right-hand side of Eq. (12) will be dominant and $\overline{C'_\alpha C'_\beta}$ will tend to be approximately equal to $-\overline{C}_\alpha \overline{C}_\beta$ and the two species will be poorly mixed. The rate of removal from the flow of α and β by reaction will then not be governed by reaction rates but will be limited by molecular diffusion. To put these notions into quantitative form, let us consider the ratio of the two characteristic times

$$N = \frac{\tau_{diff}}{\tau_{chem}} = \frac{\lambda^2}{2\mathcal{D}}\left(k_1 \overline{C}_\beta + k_2 \overline{C}_\alpha\right) \tag{16}$$

and a contact index

$$I = \frac{\overline{C}_\alpha \overline{C}_\beta + \overline{C'_\alpha C'_\beta}}{\overline{C}_\alpha \overline{C}_\beta} = 1 + \frac{\overline{C'_\alpha C'_\beta}}{\overline{C}_\alpha \overline{C}_\beta} \tag{17}$$

We note that if N is much smaller than one, diffusion will be very rapid and the two species α and β will be in intimate contact with each other. In this case $\overline{C'_\alpha C'_\beta}/\overline{C}_\alpha\overline{C}_\beta$ will be small and the contact index will approach one. If, on the other hand, N is much larger than one, mixing will be poor and $\overline{C'_\alpha C'_\beta}$ will approach $-\overline{C}_\alpha\overline{C}_\beta$. The contact index will then approach zero. In this case the reaction will be diffusion-limited.

In many laboratory flows, the dissipative or diffusive scale of turbulence is very small and N is, indeed, small so that the neglect of $\overline{C'_\alpha C'_\beta}$ in the kinetic equations is permissible. On the other hand, if the laboratory experiment is just increased in size, holding all other parameters such as velocity, temperature, etc., constant, one soon finds that the character of the flow changes. This may be seen by examining the expression for the dimensionless quantity N in more detail.

Let us assume the diffusive scale of a turbulent flow is of the order of the dissipative scale so that we may relate λ to the integral scale length of the turbulence Λ_1 by (cf. Ref. [5])

$$\lambda^2 = \Lambda_1^2/(a + b\rho q\Lambda_1/\mu) \tag{18}$$

where a and b are constants and $\rho q\Lambda_1/\mu$ is the turbulent Reynolds number. Substituting this expression into Eq. (16) gives

$$N = \frac{\Lambda_1^2}{2\mathscr{D}}\left(\frac{k_1\overline{C}_\beta + k_2\overline{C}_\alpha}{a + b\rho q\Lambda_1/\mu}\right) \tag{19}$$

For relatively high Reynolds numbers, this expression becomes

$$N = \frac{1}{2b}\cdot\frac{\mu}{\rho\mathscr{D}}\cdot\frac{\Lambda_1}{q}\left(k_1\overline{C}_\beta + k_2\overline{C}_\alpha\right) \tag{20}$$

If an experiment is performed in the laboratory and a value of N for this experiment is determined or estimated and is found to be small compared to one, then we know that the diffusive mixing of the flow is such that the species α and β are in contact. The reaction rate of these species is then chemically controlled. Now if the apparatus is just scaled up in size, all other things being equal, N will increase linearly with size since the scale Λ_1 increases linearly with the size of the apparatus. When the scale has been increased sufficiently, so that N is no longer very small compared to one, the nature of the flow in the device must change, for the species α and β will no longer be in intimate contact at equivalent positions in the apparatus.

The turbulent atmospheric boundary layer is a good example of a flow in which it is essential to keep track of the correlation $\overline{C'_\alpha C'_\beta}$ if one is to be able to make sense of the reaction of species which are introduced into the flow. To demonstrate this, we list in the table some of the second-order reactions responsible for the production of photochemical smog. We have also listed in this table the reaction rate recommended for each reaction [4] and an estimate of the number N for each reaction if it occurs in the atmospheric boundary layer where a typical value for λ is 10 centimeters. It is interesting to note that it is, in general, those reactions listed in the table for which N is greater than one that investigators have found to proceed more slowly than predicted by formulas such as Eqs. (3) and (4) when the reaction rate determined from laboratory experiments is used. This difficulty has led some investigators to search for other chemical reactions that might be considered which would explain this discrepancy.

CONCLUSION

It certainly appears unwise to follow this course until such time as one has at least developed a viable scheme for properly computing turbulent reacting flows. It is the authors' opinion that an acceptable method of computing such flows can be developed through the use of second-order correlation equations such as Eqs. (9) and (10). Methods of modeling the third-order correlations that appear in these equations can be found that are similar to those used to study the generation of turbulence and turbulent transport [5]. The development of a viable method for computing chemically reacting turbulent flows according to such a scheme is under active development by the authors. It is important to note in this connection that it is essential in developing this general method to consider fluctuations in density and in the reaction rate constants when the chemical rate equations are considered.

NOMENCLATURE

a, b	= constants
$\overline{C}_i$, C_i'	= concentration of subscript species, expressed as a mass fraction
$\mathcal{D}$	= molecular diffusion coefficient
I	= contact index (Eq. (17))
k_1, k_2	= chemical reaction rate constants
N	= dimensionless ratio of characteristic times for molecular diffusion and chemical reaction
q	= rms value of turbulent kinetic energy
Λ_1	= integral scale length of turbulence
λ	= dissipative scale length
μ	= viscosity
ρ	= density of the fluid
τ	= characteristic time

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Some Second-Order Reactions Responsible for Photochemical Smog [4]

Reaction	k $(\text{ppm-sec})^{-1}$	N
$O_3 + NO = NO_2 + O_2$ *	8.3×10^{-4}	0.25 *
$NO_2 + O_3 = NO_3 + O_2$	1.7×10^{-5}	5.0×10^{-3}
$NO_3 + NO = 2NO_2$	4.8	1.4×10^{3}
$NO + HO_2 = NO_2 + OH$	1.7×10^{-1}	50.0
$OH + O_3 = HO_2 + O_2$	1.7	5.0×10^{2}
$OH + CO = H + CO_2$	5.0×10^{-2}	1.5×10^{2}
$CH_3O_2 + NO = CH_3O + NO_2$	1.7	5.0×10^{2}
$C_2H_3O_2 + NO = C_2H_3O + NO_2$	1.7	5.0×10^{2}
$C_2H_4O_2 + NO = CH_3CHO + NO_2$	1.7	5.0×10^{2}
$CH_3O + O_2 = HCHO + HO_2$	1.7	5.0×10^{2}
$C_3H_6 + O = CH_3 + C_2H_3O$	6.0×10^{-1}	1.8×10^{2}
$C_3H_6 + O_3 = HCHO + C_2H_4O_2$	8.3×10^{-3}	2.5
$C_3H_6 + O_2 = CH_3O + C_2H_3O$	1.7×10^{-2}	5.0
$C_3H_6 + HO_2 = CH_3O + CH_3CHO$	3.4×10^{-2}	10.0
$C_2H_3O + M = CH_3 + CO + M$	1.7×10^{-1}	50.0

*Those reactions for which N is small compared to one are those which can be treated using mean quantities in the basic equations of chemical change, i.e., correlations in fluctuating quantities may be neglected.

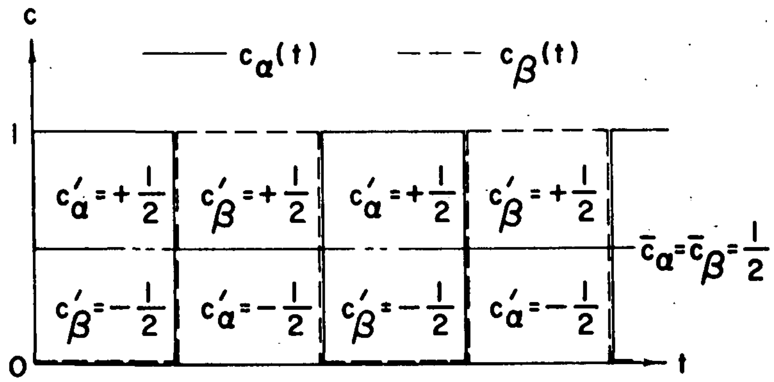

Figure 1. Simple problem illustrating $\overline{C'_\alpha C'_\beta} = -\overline{C}_\alpha \overline{C}_\beta$ when no reactions are possible