ON TURBULENT MIXING OF TWO RAPIDLY REACTING

CHEMICAL SPECIES

by

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KEY WORDS

ABSTRACT

This paper describes the evolution of moments of the concentration of each of the species in a two species, very rapid, isothermal, irreversible, second order, chemical reaction in a homogeneous turbulence in terms of an assumed initial distribution of the concentration fields. The fields decay in two stages. In the stage dominated by chemical kinetics, exact stochastic solutions are derived for a class of initial distributions. These solutions exhibit asymptotic concentration fields having an extremely high relative intensity and skewness associated with the spatial segregation of the species. In the second or diffusion controlled stage exact solutions are obtained in terms of the turbulent mixing of a nonreacting species when the molecular diffusivities of each species are equal. An approximate solution is proposed when they are unequal. In both cases the time scale of decay in the second stage is entirely characterized by turbulent mixing parameters. It is shown that in final period turbulence the reactants decay with an effective diffusivity of the same order as the smaller of the two diffusivities.

1. INTRODUCTION

The rate of a homogeneous reaction depends on the rate of encounter between reactant molecules. When the reactants are not distributed homogeneously the encounter rate and hence the reaction may be significantly altered. One extreme situation which has been carefully analyzed using singular perturbation techniques[1] is that of the diffusion of one substance into a semi-infinite medium containing a second substance with which it reacts according to a second-order equation. The distinction between the homogeneous kinetic rate and that obtained in the two species diffusion example just referred to is most pronounced in the case of a very rapid reaction, when the reactive time scale is orders of magnitude shorter than the time scale of diffusion. The latter time scale is clearly the determining one when the two species are initially segregated as in the above example. Furthermore, there is ample experimental evidence[2,3] suggesting that for very fast reactions in turbulence the asymptotic reaction rate is of the same order as the rate of turbulent mixing, and not of the kinetic rate for homogeneous reactions. Again, for very rapid reactions, there is a theory[4] in the case of two reactants with equal diffusivities which estimates the evolution of mean concentrations in a turbulent pipe flow reactor in terms of the mixing characteristics of the same reactor and these predictions are in general agreement with measurements. In the case of stochastically distributed reactants which are approximately homogeneous in the large, such as one may encounter in turbulently stirred chemical reactors, the fluctuations represent inhomogeneities on a small scale which may also have a profound influence on reaction rate. It is to the exploration of such a phenomena that this paper is addressed. Specifically, we should pose the following problem. Given an initial statistical description of the distribution of each species in a fully described turbulent fluid and assuming that the local instantaneous rate of reaction obeys the normal laws of homogeneous

chemical kinetics, determine the probability laws describing the distribution of each species at subsequent times. In fact, however, we address ourselves to a much simpler question. Determine the probability laws describing the distribution of each of the above species in terms of the probability laws describing the evolution of a single species in a turbulent fluid from an arbitrary, statistically prescribed, initial state (the turbulent mixing problem). For practical reasons these probability laws are most usefully presented in terms of the evolution of low order moments of the concentration field.

In order to isolate the role of small scale fluctuations from other effects we shall assume statistical homogeneity of the random concentration fields of the two species, a second order irreversible isothermal reaction and an extremely rapid reaction rate as compared to any diffusive or convective time scale in the turbulence. That is, the reaction is 'instantaneous'. We will also assume that the turbulence itself is homogeneous and we will ignore any dynamic or chemical role that the product or products might play.

2. MOMENT FORMULATION

A reaction of the type, $A + n\ B \rightarrow$ product, obeys the following equations

$$\frac{\partial \Gamma_A}{\partial t} + \frac{\partial}{\partial x_i} (u_i\ \Gamma_A) = D_A\ \nabla^2 \Gamma_A - C\ \Gamma_A \Gamma_B \tag{2.1}$$

$$\frac{\partial \Gamma_B}{\partial t} + \frac{\partial}{\partial x_i} (u_i\ \Gamma_B) = D_B\ \nabla^2 \Gamma_B - C\ \Gamma_A \Gamma_B \tag{2.2}$$

$$\frac{\partial u_i}{\partial x_i} = 0 \tag{2.3}$$

Where Γ_A represents n Γ_A, $u_i(x,t)$ is an isotropic stationary turbulent velocity field, Γ_A and Γ_B are random concentration fields, C is the kinetic reaction rate assumed constant, and D_A and D_B are the diffusivities of species A and B respectively. Decay equations for single point moments up to the second order can be deduced.

$$\frac{d\overline{\Gamma}_A}{dt} = \frac{d\overline{\Gamma}_B}{dt} = - C \, \overline{\Gamma_A \Gamma_B} \tag{2.4}$$

$$\frac{d\overline{\Gamma_A^2}}{dt} = 2D_A \, \overline{(\nabla\Gamma_A)^2} - 2C \, \overline{\Gamma_A^2 \Gamma_B} \tag{2.5}$$

$$\frac{d\overline{\Gamma_B^2}}{dt} = 2D_B \overline{(\nabla\Gamma_B)^2} - 2C \, \overline{\Gamma_A \Gamma_B^2} \tag{2.6}$$

$$\frac{d\overline{\Gamma_A \Gamma_B}}{dt} = (D_A + D_B) \, \overline{\nabla\Gamma_A \nabla\Gamma_B} - C(\overline{\Gamma_A^2\Gamma_B} + \overline{\Gamma_A\Gamma_B^2}) \tag{2.7}$$

The existence of triple concentration moments in equations (2.4) to (2.7) demonstrates the unclosed nature of the moment formulation and the necessity of resorting, in general, to approximation techniques. It is well known from studies of mixing in the absence of reaction that the role of the turbulence is buried in the gradient terms of (2.5) (2.6) and (2.7) and that it too leads to a very difficult stochastic non-linearity for which closure approximation techniques are required.

In this paper we wish to point out that in the case of very rapid reactions the random fields decay in two distinct stages. There is an initial stage which is entirely dominated by the reaction and for which exact stochastic solutions are possible if the appropriate initial statistical descriptions are provided. These solutions are valid for times much shorter than the time scales of turbulent

convection and diffusion, say τ_T , and if C is large enough they will hold for times very much greater than the **reactive** time scale C^{-1}. This is the condition, $C^{-1} \ll \tau_T$, we imply by the term very rapid reaction. Asymptotic behavior of the initial stage of a very rapid reaction is used to provide explicit initial stochastic information for the second or final stage of decay. In this final stage we exhibit exact stochastic solutions for each of the species concentrations in the case of equal diffusivities, $D_A = D_B$. Finally, approximate solutions are obtained in cases where $D_A \neq D_B$, the approximation being determined by an assumption based on a property of the exact solutions of the equal diffusivity case. The solutions in the second stage are to be interpreted in the sense mentioned in the introduction. That is, if the probability laws of the non-reacting turbulent mixing problem are known the solutions for the reacting species can be constructed.

3. INITIAL STAGE OF THE REACTION

For a very rapid reaction of the kind we have described the kinetic equations valid in the initial period up to a time much greater than C^{-1} are

$$\frac{\partial \Gamma_A}{\partial t} = - C \, \Gamma_A \Gamma_B \tag{3.1}$$

$$\frac{\partial \Gamma_B}{\partial t} = - C \, \Gamma_A \Gamma_B \tag{3.2}$$

If the initial concentrations $\Gamma_A(0)$, $\Gamma_B(0)$ are prescribed deterministically then the solution of (3.1) and (3.2) is

$$\Gamma_A(t) = \frac{\Gamma_A(0) \exp \{C(\Gamma_A(0) - \Gamma_B(0))t\}}{1 + [\Gamma_A(0) - \Gamma_B(0)]^{-1} \Gamma_A(0)[\exp\{C(\Gamma_A(0) - \Gamma_B(0))t\}-1]} \tag{3.3}$$

$$\Gamma_B(t) = \frac{\Gamma_B(0) \exp \{C(\Gamma_B(0) - \Gamma_A(0))t\}}{1 + [\Gamma_B(0) - \Gamma_A(0)]^{-1} \Gamma_B(0)[\exp\{C(\Gamma_B(0) - \Gamma_A(0))t\}-1]} \tag{3.4}$$

If the initial concentrations are prescribed stochastically in terms of a joint probability density, exact expressions for concentration moments can be derived.

For example:

$$\overline{\Gamma}_A = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{x \exp\{C(x-y)t\}P(x,y)\ dx\ dy}{1 + [x-y]^{-1}\ x\ [\exp\{C(x-y)t\}-1]} \tag{3.5}$$

where $P(\Gamma_A(0), \Gamma_B(0)]$ is the joint probability density of the initial distribution of $\Gamma_A(0)$ and $\Gamma_B(0)$.

Of special interest for our purposes are the following asymptotic results which follow directly from (3.5). These are, of course, not the values attained asymptotically by the system described by (2.1), (2.2) and (2.3) but they are approached in a time τ such that $C^{-1} \ll \tau \ll \tau_T$, where τ_T is the time scale of turbulent mixing of the system.

$$\text{Lim}_{t \to \infty} \overline{\Gamma}_A(t) = \overline{\Gamma}_A(\infty) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} (x-y)\ P(x,y)\ dy \tag{3.6},$$

where we have used the fact that, from (3.3),

$$\Gamma_A(\infty) = \begin{cases} \Gamma_A(0) - \Gamma_B(0)\ , & \Gamma_A(0) > \Gamma_B(0) \\ 0 & \Gamma_A(0) \le \Gamma_B(0) \end{cases}$$

Similarly

$$\overline{\Gamma}_B(\infty) = \int_{-\infty}^{\infty} dy \int_{-\infty}^{y} (y-x)\ P(x,y)dx \tag{3.7}.$$

We also note the following results for second moments

$$\overline{\Gamma_A^2}(\infty) = \int_{\infty}^{+\infty} dx \int_{\infty}^{x} (x-y)^2\ P(x,y)\ dy \tag{3.8},$$

$$\overline{\Gamma_B^2}(\infty) = \int_{\infty}^{+\infty} dy \int_{-\infty}^{y} (y-x)^2\ P(x,y)\ dx \tag{3.9},$$

$$\overline{\Gamma_A \Gamma_B}(\infty) = 0 \tag{3.10}.$$

Although (3.1) and (3.2) do not contain spatial operators it may be

useful to have correlation and cross correlation information to use as input information for the diffusion controlled final stage of the turbulently mixed reaction. In this case one will require joint probability densities $P[\Gamma_A(x,0)\ \Gamma_B(x,0);\ \Gamma_A(x',0)\ \Gamma_B(x',0)]$ and use of formulas such as

$$\overline{\Gamma_A \Gamma_A'}(r,t) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \left[\frac{x\ \exp\{C(x-y)t\}}{1+(x-y)^{-1}\ x[\exp\{C(x-y)t\}-1}\right]$$

(3.11)

$$\left[\frac{x'\ \exp\{C(x'-y')t\}}{1+(x'-y')^{-1}\ x'[\exp\{C(x'-y')t\}-1]}\right]\ P(x,y;x',y')\ dxdy\ dx!dy'$$

In particular,

$$\overline{\Gamma_A \Gamma_A'}(r,\infty) = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{x}(x-y)dy \int_{-\infty}^{\infty} dx' \int_{-\infty}^{x'}(x'-y')\ P(x,y';x',y')dy' \quad (3.12)$$

and

$$\overline{\Gamma_A \Gamma_B'}(r,\infty) = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{x}(x-y)dy \int_{-\infty}^{+\infty} dy' \int_{-\infty}^{y'}(y'-x')\ P(x,y;\ x',y')dx' \quad (3.13)$$

In the circumstance that $P(x,y;x',y')$ exhibits statistical independence of all four variables then the above equations reduce to

$$\overline{\Gamma_A \Gamma_A'}(r,t) = \overline{\Gamma_A}^2(t); \quad \overline{\Gamma_B \Gamma_B'} = \overline{\Gamma_B}^2(t); \quad \overline{\Gamma_A \Gamma_B'}(t) = \overline{\Gamma_A}(t)\overline{\Gamma_B}(t)$$

That is, no correlations are induced at non-coincident points by the reaction where there were none initially.

On the other hand under the same assumption of initial statistical independence whereby $\overline{\Gamma_A \Gamma_B}(0) = \overline{\Gamma_A}(0)\overline{\Gamma_B}(0)$ equation (3.10) shows that

$$\overline{\Gamma_A \Gamma_B}(\infty) = 0$$

This suggests that the asymptotic state of the initial period may exhibit large relative intensity of concentration fluctuations even if the initial

stochastic state did not. In situations where r.m.s. fluctuations are of the same order as the mean or larger it has been shown that the non-negativeness of concentration as a random variable plays a crucial role in the dynamics of decay and cannot be disregarded, for example, by approximating concentration as normally distributed.[5] Furthermore, probability density function measurements for a rapid second order reaction in the wake of a sphere have produced curves with qualitative resemblance to a log-normal distribution.[6] Therefore in order to make the simplest relevant computations on the asymptotic state of the initial period we will assume that each species concentration is initially log-normally distributed and statistically independent of the concentration of the second species at the same point and of all concentrations at non-coincident points in space. Furthermore all concentrations are assumed to be identically distributed, that is, if $F(\Gamma_A(0), \Gamma_B(0); \Gamma_A'(0), \Gamma_B'(0))$ is the initial joint distribution function for the concentration fields then $F(x,y; x',y') = F_1(x)F_1(y)F_1(x')F_1(y')$, where $\dfrac{dF_1}{dx} = \dfrac{1}{x\sigma\sqrt{2\pi}} \exp\{-\dfrac{1}{2\sigma^2}(\log x-\mu)^2\}$, $0 < x < \infty$, $\sigma > 0$. Thus

$$\overline{\Gamma}(0) = \exp\{\mu + \frac{1}{2}\sigma^2\}$$

$$\overline{\Gamma^2}(0) = \overline{\Gamma}^2(0) \exp\{\sigma^2\}$$

$$\overline{\gamma^2}(0)\,\overline{\Gamma}^{-2}(0) = \exp\{\sigma^2\} - 1$$

and

$$\overline{\gamma_a\gamma_b}(0) = 0$$

where σ and μ are the usual parameters of the log normal distribution and γ indicates a fluctuation in concentration about the mean. For example $\gamma_a = \Gamma_A - \overline{\Gamma}_A$. Since the distributions of species A and B are identical the label A or B has been dropped except in the case of cross moments.

Under the above circumstances the following asymptotic relationships can be developed using (3.6), (3.7), (3.8), (3.9) and (3.10)

$$\overline{\Gamma}(\infty) = \overline{\Gamma}(0) \left\{ 2N \left(\frac{\sigma}{\sqrt{2}} \mid 0,1 \right) - 1 \right\}$$

$$\overline{\Gamma^2}(\infty) = \overline{\gamma^2}(0),$$

$$\overline{\gamma^2}(\infty) \, \overline{\Gamma}^{-2}(\infty) = \frac{\exp\{\sigma^2\} - 1}{\left\{ 2N \left(\frac{\sigma}{\sqrt{2}} \mid 0,1 \right) - 1 \right\}}, \tag{3.14}$$

$$\overline{\gamma_a \gamma_b}(\infty) = - \overline{\Gamma^2}(\infty),$$

where $N \left(\frac{\sigma}{\sqrt{2}} \mid 0,1 \right)$ is the probability that $Y \leq \frac{\sigma}{\sqrt{2}}$ when Y is normally distributed with zero mean and has a variance of unity.

Equation (3.14) is of special interest since it indicates that indeed the asymptotic relative intensity can be as large as one pleases simply by choosing σ for the initial distribution large enough. Furthermore, it is easy to show from (3.14) that there is a lower bound on the relative intensity of fluctuation under the circumstances developed here. Namely, $\overline{\gamma^2}(\infty) \, \overline{\Gamma}^{-2}(\infty) \geq \pi - 1$, the lower bound being obtained in the limit $\sigma \to 0$. In a similar manner, large positive numbers are also predicted as lower bounds for the asymptotic skewness and kurtosis of the concentration fields. The general picture which emerges of the asymptotic state of the initial period is one in which the fluctuations are highly intense compared to the mean and the probability distribution of the concentration field cannot be considered even approximately normal. These are of course the characteristics one expects from a state in which the two species are segregated spatially. In the limit of an instantaneous reaction (or no molecular diffusion) segregation is the physical situation which arises, unless the two reacting species are perfectly correlated or in concentrations far from the stoichiometric balance assumed in this calculation.

4. THE DIFFUSION CONTROLLED STAGE OF THE REACTION

The asymptotic conditions derived in the previous section are not true asymptotic states for the system described by (2.1) (2.2) and (2.3). As spatial segregation of the two species is obtained through the reaction, molecular diffusion of each species into the other through interface surfaces becomes more significant, enhanced as always by the line and surface stretching characteristic of turbulent motions. The true asymptotic state of the irreversible reactions considered here will be the total depletion of one or both of the reacting species, the later condition occurring when the initial proportions are stoichiometric. For very rapid reactions it is necessary to solve the full set of equations

$$\frac{\partial \Gamma_A}{\partial t} + \underline{u} \cdot \nabla \Gamma_A = D_A \nabla^2 \Gamma_A - C \Gamma_A \Gamma_B \tag{2.1}$$

$$\frac{\partial \Gamma_B}{\partial t} + \underline{u} \cdot \nabla \Gamma_B = D_B \nabla^2 \Gamma_B - C \Gamma_A \Gamma_B \tag{2.2}$$

$$\nabla \cdot \underline{u} = 0 \tag{2.3},$$

where the initial conditions to be used are just the asymptotic conditions of the kinetically driven first stage derived in section 3. In spatial terms the derivation of section 3 can be considered the outer solution of a singular perturbation problem. The inner solution accounts for the role of molecular diffusivity in bringing reactive molecules together across the interfaces.

The determination of the evolution of concentration fields from the segregated state clearly requires that the velocity field $\underline{u}$ be fully described statistically. Even then any attempt at a moment formulation encounters the notorious difficulties of the turbulence mixing problem[7] as well as the nonlinearity associated with the reaction. It will be shown in the following paragraphs that when the diffusivities of the two species are equal the solution of the problem

posed by (2.1) (2.2) and (2.3) can be determined entirely in terms of solutions to the turbulent mixing problem. Specifically, let $P[X,t]$ be the probability density of $X(\underset{\sim}{x},t)$ where $X(\underset{\sim}{x},t)$ satisfies

$$\frac{\partial X}{\partial t} + \underline{u}.\nabla X = D\nabla^2 X \qquad (4.1)$$

$$\nabla \cdot \underline{u} \equiv 0$$

and both $\underset{\sim}{u}(\underset{\sim}{x},t)$ and $X(\underset{\sim}{x},o)$ have an arbitrary specific stochastic description. Then the probability densities $P[\Gamma_A,t]$, $P[\Gamma_B,t]$ for the reactant concentrations described by (2.1) (2.2) and (2.3) can be determined from $P[X,t]$ provided that $D_A = D_B = D$.

(A) The Case of equal diffusivities

When $D_A = D_B = D$ it is evident that $\Gamma_A - \Gamma_B$ satisfies equation (4.1) with $X = \Gamma_A - \Gamma_B$. Hence a knowledge of $P[X,t]$ from (4.1) and the initial conditions $X(\underset{\sim}{x},o) = \Gamma_A(\underset{\sim}{x},o) - \Gamma_B(\underset{\sim}{x},o)$ is equivalent to a knowledge of $P[\Gamma_A - \Gamma_B,t]$. Furthermore, as has been pointed out elsewhere, since $\Gamma_A \geq 0$ $\Gamma_B \geq o$ and $\overline{\Gamma_A \Gamma_B} \to o$ for a very rapid reaction.

$$\Gamma_A = \begin{cases} X & , & Y>0 \\ 0 & , & Y<0 \end{cases}$$

$$\Gamma_B = \begin{cases} 0 & , & Y>0 \\ -X & , & Y<0 \end{cases}$$

except at the reaction surfaces the thicknesses of which approach molecular dimensions as the reaction rate becomes infinite.

Thus $\quad P[\Gamma_A,t] = P[X,t] + k_A(t)\delta(X) \quad$ for $\quad X>0 \qquad (4.2)$

and $\quad P[\Gamma_B,t] = P[X,t] + k_B(t)\delta(X) \quad$ for $\quad X<0 \qquad (4.3),$

where $\quad k_A(t) = \int_{-\infty}^{o} P[X,t]dX$

$\quad k_B(t) = \int_{o}^{\infty} P[X,t]dX = 1 - k_A(t)$

Some consequences of (4.2) and (4.3) can be listed as follows:

$$\overline{\Gamma_A} = \int_0^\infty XP[X,t]dX = \overline{\Gamma_B} = 1/2|\overline{X}|$$

$$\overline{\Gamma^2}_A(t) = \int_0^\infty X^2P[X,t]dX, \quad \overline{\Gamma^2}_B(t) = \int_{-\infty}^0 X^2P[X,t]dX \quad ,$$

where X satisfies (4.1) and $X(\underset{\sim}{x},o) = \Gamma_A(\underset{\sim}{x},o) - \Gamma_B(\underset{\sim}{x},o)$.

In particular if $P[X,0]$ is symmetric, as for example when $\Gamma_A(\underset{\sim}{x},o)$ and $\Gamma_B(\underset{\sim}{x},o)$ are identically distributed, then

$$\overline{\Gamma^2}_A(t) = \overline{\Gamma^2}_B(t) = 1/2\ \overline{X^2}$$

We note that the elementary requirements $\overline{\Gamma_A} \geqslant 0$, $\overline{\Gamma_A^2} - \overline{\Gamma_A}^2 \geqslant 0$ are satisfied by these solutions and that they include the particular solution proposed by Toor who assumed a normal distribution for $\Gamma_A - \Gamma_B$.

(B) The Case of Unequal Diffusivities

Consider the functions $X_A(\underset{\sim}{x},t)$, $X_B(\underset{\sim}{x},t)$ defined as solutions of the

$$\frac{\partial X_A}{\partial t} + \underline{u} \cdot \nabla X_A = D_A \nabla^2 X_A \tag{4.4}$$

$$\frac{\partial X_B}{\partial t} + \underline{u} \cdot \nabla X_B = D_B \nabla^2 X_B \tag{4.5}$$

$$X_A(\underline{x},o) = \Gamma_A(\underline{x},o) \tag{4.6}$$

and $$X_B(\underline{x},o) = \Gamma_B(\underline{x},o) \tag{4.7}$$

Now $\Gamma_A(\underset{\sim}{x},t) = X_A(\underset{\sim}{x},t) - L_A(\underset{\sim}{x},t)$ where $L_A(\underset{\sim}{x},t)$ is a representation for the loss of species A due to its reaction with B in the element of fluid that is at position $\underline{x}$ at time t. Similarly we can define an analogous quantity $L_B(\underline{x},t)$ by the relationship

$$\Gamma_B(\underline{x},t) = X_B(\underline{x},t) - L_B(\underline{x},t)$$

Furthermore when $D_A = D_B$ it is easy to show by comparing (2.1)

(2.2) and (4.4) (4.5) that

$$\Gamma_B(\underline{x},t) - \Gamma_A(\underline{x},t) = X_B(\underline{x},t) - X_A(\underline{x},t) \quad t>0 \quad ,$$

if it is true at t=0.

Consequently, when $D_A = D_B$

$$L_A(\underline{x},t) = L_B(\underline{x},t) \tag{4.8}$$

When $D_A \neq D_B$ (4.8) no longer holds although from the laws of mass conservation

$$\overline{L_A(\underline{x},t)} \equiv \overline{L_B(\underline{x},t)} \tag{4.9}$$

The local lack of equality of the loss term for species A and B is caused by the interaction between the reactive decay and the non similar diffusive loss of each species. In the context of single species reactions it has been shown that an accurate approximation can be obtained which ignores the interaction between decay and diffusion. The direct effect of reaction and of diffusion can be taken into account by replacing (4.9) by (4.8) even when $D_A = D_B$. It is this approximation which we propose now as a means of solving (2.1) and (2.2). The details follow closely the method established for the equal diffusivity case.

Let $Y = X_A - X_B$

where $X_A(\underline{x},t)$ and $X_B(\underline{x},t)$ are the solutions of (4.4) and (4.5) respectively and their solutions are assumed known from these pure mixing equations. Therefore, for example, $P[Y,t]$ can be considered known.

Now on applying the approximation (4.8)

$$X_A - X_B = \Gamma_A - \Gamma_B \quad ,$$

which is identically true in the average, we obtain

$$Y = \Gamma_A - \Gamma_B \tag{4.10}$$

By arguments quite analogous to those used in the previous section we obtain

$$P[\Gamma_A, t] = P[Y,t] + k(t)\delta(Y) \qquad Y \geq 0 \qquad (4.11)$$

$$P[\Gamma_B, t] = P[Y,t] + [1-k(t)]\delta(Y) \qquad Y \leq 0 \qquad (4.12)$$

where
$$k(t) = \int_{-\infty}^{0} P[Y,t]dY \quad ,$$

$$\overline{\Gamma_A} = \int_{0}^{\infty} Y\; P[Y,t]dY = \overline{\Gamma_B} \qquad (4.13)$$

$$\overline{\Gamma^2}_A = \int_{0}^{\infty} Y^2 P[Y,t]dY \quad , \qquad (4.14)$$

$$\overline{\Gamma^2_B} = \int_{-\infty}^{0} Y^2 P[Y,t]dY \qquad (4.15)$$

where $Y(\underline{x},t) = X_A(\underline{x},t) - X_B(\underline{x},t)$

and $X_A(\underline{x},t)$, $X_B(\underline{x},t)$ satisfy (4.4) and (4.5) respectively.

When $D_A = D_B$, $P[Y,t]$ is symmetric for all time if it is initially so and we reproduce the results of section 4(A). We also note that the inequalities associated with first and second moments of non negative random functions are preserved for all time by this solution.

To obtain concrete analytical results for the two species reaction it is necessary to have available a pure mixing situation for which analytical results are known. Fortunately in the final period of turbulence pure mixing results are obtainable and it is precisely in that regime that the actual value of the diffusivity is most significant. Final period turbulence is, by definition, that state of mixing in which the role of turbulent convection on the scalar spectrum is less important for most wave numbers than the role of molecular diffusion.

Consider a turbulence in which the distribution of X_A, the concentration of species A in pure mixing, is accurately described by the following normal distribution

$$P[X_A, t] = (2\pi\overline{\mu_A^2}(t))^{-1/2} \exp - \left\{ \frac{(X_A - \overline{X})^2}{2\,\overline{\mu_A^2}(t)} \right\} \quad ,$$

where the mean $\overline{X}(t)$ and the mean square fluctuations $\overline{\mu_A^2}(t)$ are determined by the turbulent field, the initial statistical state and D_A. Since X_A is a non negative random variable this is not a possible distribution in principle but it is a reasonable approximation if the concentration of A exhibits a large mean and a low level of fluctuations. For the purpose of investigating the relative roles of diffusivities it is analytically simple and typical of what one expects in the final period of a non reacting scalar field.

Let the concentration of species B in pure mixing be likewise represented by

$$P[X_B, t] = (2\pi\overline{\mu_B^2(t)})^{-1/2} \exp - \left\{ \frac{(X_B - \overline{X})^2}{2\overline{\mu_B^2(t)}} \right\}$$

then

$$P[Y, t] = P[X_A - X_B, t] = \{2\pi(\mu_A^2(t) + \mu_B^2(t))\}^{-1/2} \exp - \left\{ \frac{Y^2}{2(\overline{\mu_A^2 + \mu_B^2})} \right\}$$

$$\overline{\Gamma_A} = \overline{\Gamma_B} = \frac{1}{2}|\overline{Y}| = (\frac{1}{2\pi}[\overline{\mu_A^2} + \overline{\mu_B^2}])^{1/2}$$

$$\overline{\Gamma_A^2} = \int_0^\infty Y^2 P[Y, t] dY = \frac{1}{2}(\overline{\mu_A^2} + \overline{\mu_B^2}) = \overline{\Gamma_B^2}$$

and consequently $\overline{\gamma_A^2} = \overline{\Gamma_A^2} - \overline{\Gamma_A^2} = \frac{\pi-1}{2\pi}(\overline{\mu_A^2} + \overline{\mu_B^2})$

where in all the above $\overline{\mu_A^2}$ and $\overline{\mu_B^2}$ refer to the variance of concentrations of A and B in the pure mixing mode. In final period turbulent mixing it has been shown that

$$\overline{\mu_A^2} = C_1 [2D_A t]^{-3/2} \quad \text{as} \quad t \to \infty, \quad \text{where} \quad C_1 \quad \text{is a constant}$$

and

$$\overline{\mu_A^2} + \overline{\mu_B^2} = C_1 (2t)^{-3/2} (D_A^{-3/2} + D_B^{-3/2}) \quad , \quad \text{when we have assumed ap-}$$

proximate equalities of the constants in the expression for $\overline{\mu_A^2}$ and $\overline{\mu_B^2}$.

Hence $\overline{\gamma_A^2}(t) = \frac{\pi-1}{2\pi} c_1 (2t)^{-3/2} (D_A^{-3/2} + D_B^{-3/2})$

and an effective diffusivity D can be defined as

$$D^{-3/2} = \frac{\pi-1}{2\pi} (D_A^{-3/2} + D_B^{-3/2})$$

or $\quad D = \dfrac{2D_A D_B}{[D_A^{3/2} + D_B^{3/2}]^{2/3}}$

To within an order of magnitude $D = D_{min}$ where D_{min} is the smaller of D_A and D_B.

It seems reasonable to generalize this result to turbulent situations less crucially dependent on the values of D_A and D_B to predict that when the two diffusivities are widely different very fast stoichiometric reactions in the diffusion controlled limit, decay at a rate determined by the smaller of the two diffusivities. Such a generalization, if it holds up under experimental examination, would make available to diffusion controlled two species reactions the information accumulated in the literature on one species turbulent mixing.

CONCLUSIONS

The statistical description of the reacting fields at the conclusion of the reaction dominated first stage are easily computed in terms of the initial description of the distribution of reactants. For the second, or diffusion controlled stage it has been demonstrated for instantaneous reactions in turbulence that when $D_A = D_B$ the mean square concentrations of species A and B decay at a time scale entirely determined by the time scale of turbulent mixing of a single species whose initial statistical distribution is the same as $\Gamma_A - \Gamma_B$. When the two species have nonequal molecular diffusivities a solution

for the mean square intensities has been proposed which again relates the time scale of decay of each species to time scales entirely associated with turbulent mixing of a single species.

For kinetic reaction rates which are not very rapid, no exact solution appears to be possible. Closure approximation schemes will be necessary similar to those employed in the study of turbulence dynamics[9] except that one must clearly be prepared to confront strongly non-Gaussian and highly skewed concentration probability density functions.

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