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Statistical Behavior of a Turbulent Multicomponent Mixture with First-Order Reactions

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The dilute turbulent concentration fields of a multicomponent mixture with any type isothermal first-order reaction are investigated. For certain given initial conditions, the reacting concentration fields are related to the nonreacting case provided that the diffusivities of all species with respect to the main solution are equal. This enables us to utilize some known results of turbulent mixing to estimate the rate of decay and/or growth of the reacting turbulent concentration fields. For the case of stationary turbulence with first-order reactions and with *nonequal* diffusivities, where the Reynolds number and Péclet number are large, the small-scale structure of the turbulent concentration fields are investigated under the assumption of local isotropy and local homogeneity. A unified concept for spectral transfer at large wave numbers is proposed which, in essence, is a generalization of the Onsager-Corrsin spectral transfer concept. With this unified spectral transfer concept, as well as other concepts, the reacting concentration spectrum functions are deduced for three wave number ranges: 1) the inertial-convective range, 2) the viscous-convective and viscous-diffusive range for large Schmidt numbers, and 3) the inertial-diffusive range for small Schmidt numbers.

1. Introduction

THE complexities of turbulence have long been revealed, but are far from being completely understood. Despite continuous efforts, it still defies a thorough theoretical treatment, and reliable turbulence measurements are tedious and hard to obtain. The difficulties are mainly due to its randomness, nonlinearity, and inherent three-dimensionality. With the added complexity of chemical reaction in turbulent flow, the problem becomes even more intractable. Fortunately, there are some partial theories, well supported by observations and experimental results, which enable us to understand the phenomena of turbulence and turbulent mixing to a certain extent. Based on these, some problems of turbulent mixing with chemical reaction can be investigated. For an exploratory account of the statistical theory of turbulent mixing with chemical reaction, the reader is referred to an article by Corrsin.[1] O'Brien[2] has investigated the statistical behavior of the reactant of a first-order irreversible reaction in isotropic turbulence by using the zero fourth-cumulant approximation. However, the numerical computation shows that the approximation leads to negative concentration spectrum functions.[3] Corrsin[4, 5] has obtained

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Table 1 **Λ_μ for various first-order reactions,[a] $\Theta_\mu(\mathbf{x}, t) = M(\mathbf{x}, t)\Lambda_\mu(t)$**

First-order reactions	Λ_1	Λ_2	Λ_3
Irreversible ($S_1 \xrightarrow{a} S_2$) $\Phi_1 = -\Phi_2 = -a\Theta_1$	e^{-at}	$1 - e^{-at}$	. . .
Reversible ($S_1 \overset{a}{\underset{b}{\rightleftarrows}} S_2$) $\Phi_1 = -\Phi_2 = -a\Theta_1 + b\Theta_2$	$(a + b)^{-1}(b + ae^{-(a+b)t})$	$a(a + b)^{-1}(1 - e^{-(a+b)t})$	. . .
Parallel irreversible ($S_1 \xrightarrow{a} S_2$, $S_1 \xrightarrow{b} S_3$) $\Phi_1 = -(a + b)\Theta_1$, $\Phi_2 = a\Theta_1$, $\Phi_2 = b\Theta_1$	$e^{-(a+b)t}$	$a(a + b)^{-1}(1 - e^{-(a+b)t})$	$b(a + b)^{-1}(1 - e^{-(a+b)t})$
Consecutive irreversible ($S_1 \xrightarrow{a} S_2 \xrightarrow{b} S_3$) $\Phi_1 = -a\Theta_1$, $\Phi_2 = a\Theta_1 - b\Theta_2$, $\Phi_3 = b\Theta_2$	e^{-at}	$a(a - b)^{-1}(e^{-bt} - e^{-at})$	$1 + (a - b)^{-1}(be^{-at} - ae^{-bt})$

[a] Initial conditions: $\Theta_1(\mathbf{x}, 0) = M(\mathbf{x}, 0)$, $\Theta_2(\mathbf{x}, 0) = 0$, $\Theta_3(\mathbf{x}, 0) = 0$.

the stationary concentration spectrum functions of the reactant and the product of a first-order irreversible reaction at large wave numbers.

In this analysis, we are interested in the behavior of the turbulent concentration fields of a multicomponent mixture with first-order reactions. The term "first-order reactions" is used in the broad sense; it includes all types of first-order reactions, such as the reversible, irreversible, parallel, consecutive, and pseudo first-order reactions, etc. Generally speaking, the chemical reactions evolve or absorb heat, change the fluid properties, and affect the fluid motion. The general problem is rather difficult to handle. In order to obtain some idea of the problem of turbulent mixing with chemical reactions, it is idealized to a certain extent. The species present are assumed to be dilute. The heat of reaction is assumed to be negligible, the reaction is then taken to be isothermal. The fluid total density ρ, the kinematic viscosity ν, the molecular diffusivity of species μ with respect to the solution $\mathfrak{D}_\mu$ and the reaction-rate coefficient $c_{\mu\varkappa}$ are taken to be constant. The interspecies diffusion is assumed to be negligible. Under these restrictions, neither the reactants nor the products of reaction can exert any influence on the fluid motion, and they are dynamically passive. The foregoing assumptions may perhaps be realized for dilute reactants in liquid solution.

Under the restrictions given previously, the governing equations are: the Navier-Stokes equations,

$$(\partial/\partial t)\mathbf{U} + (\mathbf{U}\cdot\nabla)\mathbf{U} = -(1/\rho)\nabla p + \nu\nabla^2\mathbf{U} \tag{1.1}$$

the equation of continuity,

$$\nabla\cdot\mathbf{U} = 0 \tag{1.2}$$

and the convective diffusion equations with chemical reaction (in this analysis, symbols with Greek subscripts are not tensors, thus the summation convention is not applicable to Greek subscripts):

$$(\partial\Theta_\mu/\partial t) + \mathbf{U}\cdot\nabla\Theta_\mu = \mathfrak{D}_\mu\nabla^2\Theta_\mu + \Phi_\mu$$
$$\mu = 1, 2, 3, \ldots \zeta \text{ species} \tag{1.3}$$

where $\Theta_\mu(\mathbf{x}, t)$ is the concentration field of species μ, $\mathbf{U}(\mathbf{x}, t)$ is the velocity field, and Φ_μ is the rate of change of Θ_μ due to the chemical reaction. For first-order reactions,

$$\Phi_\mu = \sum_{\varkappa=1}^{\zeta} c_{\mu\varkappa}\Theta_\varkappa = c_{\mu1}\Theta_1 + c_{\mu2}\Theta_2 + \ldots + c_{\mu\zeta}\Theta_\zeta \tag{1.4}$$

Relation (1.3) is a set of partial differential equations mutually coupled by the reaction-rate term Φ_μ. They are also coupled with the Navier-Stokes equation (1.1) and the continuity equation (1.2).

For later convenience, let us define the velocity and concentration fields in the usual way,

$$\mathbf{U}(\mathbf{x}, t) = \langle\mathbf{U}(\mathbf{x}, t)\rangle + \mathbf{u}(\mathbf{x}, t),\ \Theta_\mu(\mathbf{x}, t) = \langle\Theta_\mu(\mathbf{x}, t)\rangle + \theta_\mu(\mathbf{x}, t) \tag{1.5}$$

where the angular brackets indicate ensemble averages, $\langle\mathbf{U}\rangle$ and $\langle\Theta_\mu\rangle$ are the ensemble mean of the velocity and concentration fields, respectively, and $\mathbf{u}$ and θ_μ are the fluctuations about their respective means. Furthermore, let $M(\mathbf{x}, t)$ be the concentration field of a nonreactive species, $M(\mathbf{x}, t) = \langle M(\mathbf{x}, t)\rangle + m(\mathbf{x}, t)$, which obeys the convective diffusion equation,

$$(\partial/\partial t)M + \mathbf{U}\cdot\nabla M = \mathfrak{D}\nabla^2 M \tag{1.6}$$

For simplicity, we shall hereafter refer to the case of turbulent mixing without chemical reaction as the pure mixing case.

In the following sections, we shall investigate 1) the decay and/or growth of the turbulent concentration fields of a multicomponent mixture with first-order reactions and equal diffusivities, and 2) the stationary concentration spectrum functions at large wave numbers (thus small-scales) of a multicomponent mixture with first-order reactions and with *equal* or *nonequal* diffusivities in stationary turbulence.

2. Decay and Growth of the Concentration Fields with First-Order Reactions and Equal Diffusivities

It will be shown in this section that, for certain given initial conditions, the reacting concentration fields $\Theta_\mu(\mathbf{x}, t)$ can be related to the nonreacting concentration field $M(\mathbf{x}, t)$ by certain relations, provided that the reactions are first-order and the diffusivities of all species are equal, i.e., $\mathfrak{D}_1 = \mathfrak{D}_2 \ldots = \mathfrak{D}_\zeta = \mathfrak{D}$.

Given the initial condition, at $t = 0$,

$$\Theta_\mu(\mathbf{x}, 0) = M(\mathbf{x}, 0)\Lambda_\mu(0) \qquad \mu = 1, 2, \ldots \zeta \text{ species} \tag{2.1}$$

This initial condition suggests a possible relation

$$\Theta_\mu(\mathbf{x}, t) = M(\mathbf{x}, t)\Lambda_\mu(t) \qquad \mu = 1, 2, \ldots \zeta \text{ species} \tag{2.2}$$

where $\Lambda_\mu(t)$ is the function to be determined.

If we put (2.2) into (1.3), with some rearrangement, we obtain

$$\frac{\partial M}{\partial t} + \mathbf{U}\cdot\nabla M = \mathfrak{D}\nabla^2 M + \frac{M}{\Lambda_\mu}\left(\sum_{\varkappa=1}^{\zeta} c_{\mu\varkappa}\Lambda_\varkappa - \frac{d\Lambda_\mu}{dt}\right) \tag{2.3}$$

By demanding

$$\sum_{\varkappa=1}^{\zeta} c_{\mu\varkappa}\Lambda_\varkappa - \frac{d\Lambda_\mu}{dt} = 0 \qquad \mu = 1, 2, \ldots, \zeta \text{ species} \tag{2.4}$$

then (2.3) reduces to (1.6). Thus, we have shown that, for the given initial condition (2.1), $\Theta_\mu(\mathbf{x}, t)$ can be related to $M(\mathbf{x}, t)$ by (2.2) for properly chosen Λ_μ. Λ_μ is determined by (2.4), which is a set of simultaneous first-order ordinary differential equations and can be solved. In Table 1, we list the solutions of $\Lambda_\mu(t)$ for 1) first-order irreversible reactions, 2) first-order reversible reactions, 3) parallel first-order irreversible reactions, and 4) consecutive first-order irreversible reactions. Taking ensemble averages of (2.2), we obtain

$$\langle \Theta_\mu(\mathbf{x}, t)\rangle = \langle M(\mathbf{x}, t)\rangle \Lambda_\mu(t) \tag{2.5}$$

Subtracting (2.5) from (2.2), we have

$$\theta_\mu(\mathbf{x}, t) = m(\mathbf{x}, t)\Lambda_\mu(t) \tag{2.6}$$

Consequently,

$$\langle \theta_\mu^2(\mathbf{x}, t)\rangle = \langle m^2(\mathbf{x}, t)\rangle \Lambda_\mu^2(t) \tag{2.7}$$

$$\langle \theta_\mu(\mathbf{x}, t)\theta_\nu(\mathbf{x}', t)\rangle = \langle m(\mathbf{x}, t)m(\mathbf{x}', t)\rangle \Lambda_\mu(t)\Lambda_\nu(t), \text{ etc.} \tag{2.8}$$

Corrsin[1] and O'Brien[2] found the relation between the reactant concentration of a first-order irreversible reaction and that of pure mixing. Corrsin[5] has further found the relation between the product concentration of a first-order irreversible reaction and that of pure mixing by conjecturing that the fluctuating reactant and product concentration fields are perfectly correlated, i.e., $\langle \theta_\mu \theta_\nu \rangle = \langle \theta_\mu^2 \rangle^{1/2} \langle \theta_\nu^2 \rangle^{1/2}$. This conjecture, as can be shown from (2.6–2.8), is indeed a valid one, provided that the diffusivities are equal. The relations obtained by Corrsin and O'Brien are special cases of relations (2.5–2.8).

The approach used previously can be further extended to a more general initial condition, where the Θ_μ field is, initially, a linear combination of M fields, i.e.,

$$\Theta_\mu(\mathbf{x}, 0) = \sum_{I=1}^{J} M_I(\mathbf{x}, 0)\Lambda_{\mu I}(0) \tag{2.9}$$

where $M_1, M_2, \ldots, M_J$ are the nonreacting concentration fields with the same diffusivities, but different initial conditions. Each M_I obeys the convective diffusion equation (1.6). Similarly, the initial condition (2.9) suggests the relation

$$\Theta_\mu(\mathbf{x}, t) = \sum_{I=1}^{J} M_I(\mathbf{x}, t)\Lambda_{\mu I}(t) \tag{2.10}$$

Putting (2.10) into (2.3), we obtain

$$\sum_{I=1}^{J} \Lambda_{\mu I}\left(\frac{\partial M_I}{\partial t} + \mathbf{U}\cdot\nabla M_I - \mathfrak{D}\nabla^2 M_I\right) = \sum_{I=1}^{J} M_I\left(\sum_{\kappa=1}^{\zeta} c_{\mu\kappa}\Lambda_{\kappa I} - \frac{d\Lambda_{\mu I}}{dt}\right) \tag{2.11}$$

Thus, if $\Lambda_{\mu I}$ are so chosen that

$$\sum_{\kappa}^{\zeta} c_{\mu\kappa}\Lambda_{\kappa I} - \frac{d\Lambda_{\mu I}}{dt} = 0 \qquad \mu = 1, 2, 3, \ldots \zeta \text{ species} \qquad I = 1, 2, 3, \ldots J \tag{2.12}$$

Then, with the given initial condition (2.9), (2.10) relates the nonreacting concentration fields $M_1, M_2, \ldots, M_J$ to the reacting concentration field Θ_μ.

Relations (2.2, 2.5–2.8, and 2.10) are most useful for pure initial value problems. They enable us to understand the phenomena of turbulent mixing with first-order reactions through some known results of pure turbulent mixing; we shall discuss two cases.

2.1 Homogeneous Turbulent Mixing with First-Order Reactions and Equal Diffusivities

For very large turbulence Reynolds numbers, $Re = (u\lambda/\nu) \gg 1$, and turbulence Péclet numbers, $P\acute{e} = (u\lambda_s/\mathfrak{D}) \gg 1$, by assuming self-preservation in the "initial period of decay," one obtains[2]

$$\langle m^2 \rangle \sim (t - t_1)^{-3/2} \tag{2.13}$$

where t_1 is the apparent initial time, $u = \langle \mathbf{u}^2 \rangle^{1/2}$, λ is the microscale of turbulence, and λ_s is the microscale of the turbulent scalar field. Measurements of temperature and concentration fluctuations behind a grid[7, 8] give some support to (2.13). Then, from (2.7) and (2.13), the decay or growth of concentration fields with first-order reactions in the "initial period of decay" are

$$\langle \theta_\mu^2 \rangle \sim (t - t_1)^{-3/2}\Lambda_\mu^2(t) \tag{2.14}$$

For very small turbulence Reynolds number and Péclet number, $\langle m^2 \rangle$ varies in the "final period of decay" as[9]

$$\langle m^2 \rangle \sim (t - t^2)^{-3/2} \tag{2.15}$$

where t_2 is an apparent initial time. Then, with first-order reactions,

$$\langle \theta_\mu^2 \rangle \sim (t - t_2)^{-3/2}\Lambda_\mu^2(t) \tag{2.16}$$

where the special case of first-order irreversible reaction was obtained by Corrsin.[1]

2.2 Convective Diffusion of a Small Blob in Isotropic Turbulence with First-Order Reactions and Equal Diffusivities

Townsend[10] investigated the diffusion of a heat spot in isotropic turbulence. He proposed a uniform straining model and the results deduced from it agreed quite well with measurements of heat spots in grid turbulence in the "initial period of decay." Neglecting viscous dissipation, the temperature variation obeys (1.6), where $\mathfrak{D}$ is then the thermal diffusivity. Taking M as the temperature difference from ambient temperature, Townsend obtained

$$\langle M(\mathbf{x}, t)\rangle = M_m(t) \prod_{\rho=1}^{3} \exp\left(-\frac{x_\rho^2}{2l_\rho^2}\right) \tag{2.17}$$

where

$$M_m(t) = A \prod_{\rho=1}^{3} 2^{1/2}(\mathfrak{D}t_0 l_\rho)^{-1} \tag{2.18}$$

and

$$l_\rho^2 = \frac{2\mathfrak{D}t_0}{1 - 2\alpha_\rho t_0}\left[\left(\frac{t}{t_0}\right) - \left(\frac{t}{t_0}\right)^{2\alpha_\rho t_0}\right] \tag{2.19}$$

where $\alpha_\rho = (\alpha_1, \alpha_2, \alpha_3)$ are the turbulent straining rates along the principal axes $x_\rho = (x_1, x_2, x_3)$, respectively. Thus, for a small reacting blob in isotropic turbulence, the concentrations of the reactant and the product of a first-order reaction vary as, from (2.5) and (2.17),

$$\langle \Theta_\mu(\mathbf{x}, t)\rangle = M_m(t)\, \Lambda_\mu(t) \prod_{\rho=1}^{3} \exp\left(-\frac{1}{2}\frac{x_\rho^2}{l_\rho^2}\right) \tag{2.20}$$

provided that all species present have equal diffusivities.

3. Small-Scale Structure of Turbulent Concentration Fields with First-Order Reactions

In the following analysis, we shall investigate the small-scale structure of the turbulent concentration fields with first-order reactions and with either equal or nonequal diffusivities, where the turbulence Reynolds number and Péclet number are large. A unified concept for spectral transfer at large wave numbers will be proposed, which in essence is a generalization of the Onsager[11]-Corrsin[4, 5] spectral transfer concept. Under the assumption of local isotropy and local homogeneity, the reacting concentration spectra at large wave numbers will be deduced with the unified spectral transfer concept as well as other concepts; the results will be compared and discussed.

As we shall extend the concepts established for the pure mixing case to the reacting case, it is advantageous at this point to briefly review some pertinent concepts and results for the pure mixing case.

For large turbulence Reynolds number and Péclet number, Obukhov[12] and Corrsin[13] extended Kolmogorov's universal equilibrium hypothesis[14, 15] to turbulent mixing problems. They obtained the concentration spectrum through dimensional reasoning as

$$F(k) \sim \chi\epsilon^{-1/3}k^{-5/3} \tag{3.1}$$

This applies to the inertial-convective range of wave numbers,

$$L^{-1} \ll k \ll (\epsilon/\nu^3)^{1/4} \text{ for } (\nu/\mathfrak{D}) \gg 1 \tag{3.2}$$

$$L^{-1} \ll k \ll (\epsilon/\mathfrak{D}^3)^{1/4} \text{ for } (\nu/\mathfrak{D}) < 1 \tag{3.3}$$

as clarified by Batchelor.[16] χ is the rate of change of $\langle m^2\rangle$ by diffusion, ϵ is the turbulent energy dissipation rate, and L is the integral length scale of the turbulent concentration field.

For large Schmidt number $(\nu/\mathfrak{D}) \gg 1$, Batchelor[16] points out that there can exist a viscous-convective range

$$(\epsilon/\nu^3)^{1/4} \ll k \ll (\epsilon/\nu\mathfrak{D}^2)^{1/4} \tag{3.4}$$

and a viscous-diffusive range

$$(\epsilon/\nu\mathfrak{D}^2)^{1/4} \ll k \tag{3.5}$$

He further introduced the uniform straining concept for this range, and obtained

$$F(k) \approx -\chi\gamma^{-1}k^{-1}\exp\{\mathfrak{D}\gamma^{-1}k^2\} \tag{3.6}$$

where $\gamma \approx -\frac{1}{2}(\epsilon/\nu)^{1/2}$. Recent measurements[8] of salt concentration fluctuation behind a grid gives partial support to this result. Corrsin[4, 5] extended Batchelor's[16] "Lagrangian analysis" to the irreversible first-order reaction. As will be seen in Sec. 3.2.2, for a reacting multicomponent system, it is simpler to apply Batchelor's[16] "Eulerian analysis," especially for the cases of nonequal diffusivities.

Batchelor, Howells, and Townsend[17] considered the case of small Schmidt number $(\nu/\mathfrak{D}) < 1$ for which there can exist an inertial-diffusive range

$$(\epsilon/\mathfrak{D}^3)^{1/4} \ll k \ll (\epsilon/\nu^3)^{1/4} \tag{3.7}$$

and they obtained

$$F(k) = \tfrac{1}{3}\chi\epsilon^{2/3}\mathfrak{D}^{-3}k^{-17/3} \tag{3.8}$$

The concept introduced by Batchelor, et al.[17] is used by Corrsin[4] to obtain the spectral shape of the reactant of an irreversible first-order reaction. It will be shown in Sec. 3.2.3, with the help of relations (2.6–2.8), that the concept can be applied to any first-order reaction with *equal* diffusivities.

3.1 A Unified Concept for Spectral Transfer at Large Wave Numbers

In the inertial-convective range, the simple dimensional reasoning of the Kolmogorov type does not work for the reacting cases. This is due to the added parameters like the reaction-rate coefficients. To handle the reacting cases, Corrsin[4, 5] extended Onsager's crude spectral transfer concepts for turbulent dynamics to turbulent mixing with or without reaction. The Onsager-Corrsin spectral transfer concept can be summarized as follows[4, 5, 11]: the spectral cascade is visualized as a geometric progression of wave number steps with a factor of two, so that $\Delta k \approx k$. The characteristic time interval $\Delta\tau$ for a step depends on the velocity spectrum $E(k)$; thus, the simplest dimensional possibility is

$$\Delta\tau(k) = k^{-3/2}E^{-1/2} \tag{3.9}$$

Then,

$$\text{spectral flux of } m \text{ across } k \approx Fk/\Delta\tau \tag{3.10}$$

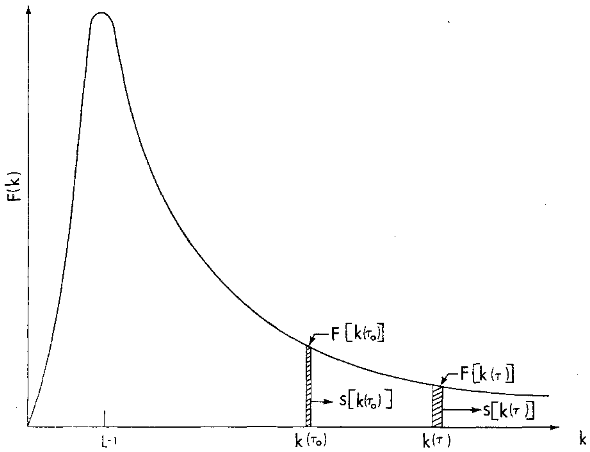


Fig. 1 **Cascading process of a spectral element.**

In the inertial-convective range and the viscous-convective range, the spectral content is conserved for the nonreacting case; thus

$$\frac{d}{dk}\left(\frac{Fk}{\Delta\tau}\right) = 0 \tag{3.11}$$

For the reacting spectrum function $G(k)$, Corrsin[4, 5] further proposed that

$$\frac{d}{dk}\left(\frac{Gk}{\Delta\tau}f\right) = 0 \tag{3.12}$$

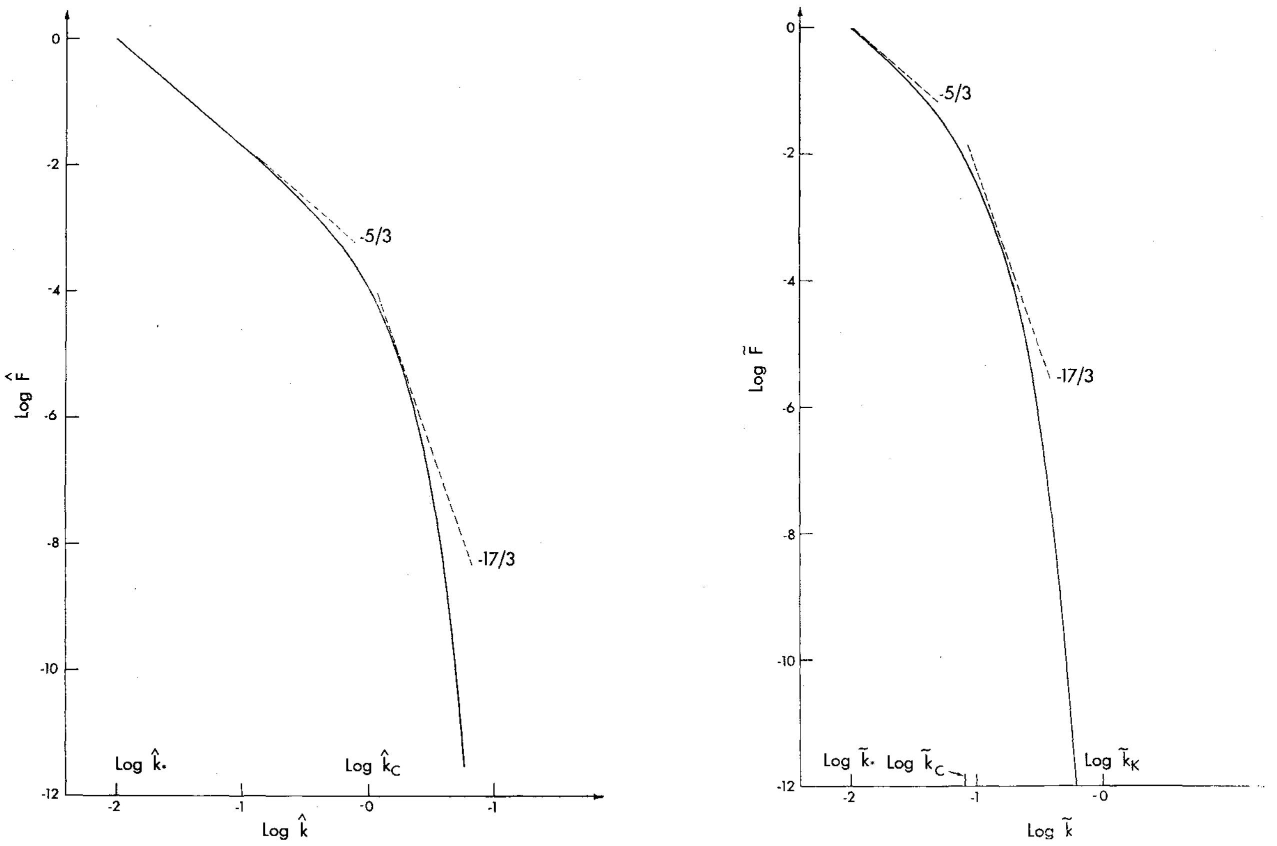
The difficulty of this approach is finding $f(k)$. Using this approach, Corrsin[4, 5] obtained the reactant and the product concentration spectra of an irreversible first-order reaction with equal diffusivities in the inertial-convective range and the viscous-convective range. Pao[18] applied this approach to the case of reversible first-order reactions with equal diffusivities.

In this section, we shall propose a unified concept of spectral transfer at large wave numbers which enables us to deduce the concentration spectrum functions of a nonreacting species as well as a reacting multicomponent mixture in all the large wave number ranges and for the cases of *equal* or *nonequal* diffusivities. This unified spectral transfer concept, in essence, is a generalization of the Onsager-Corrsin[4, 5, 11] concept, but it does not require the idea of geometric progression of wave number steps with a factor of 2. We shall again follow the migration of a spectral element to ever larger wave numbers (Fig. 1). Let the rate that an m-spectral element is transferred across k be $s(k) = dk/d\tau$. Then,

$$\text{spectral flux of } m \text{ across } k = F(k)s(k) \tag{3.13}$$

As one can see, (3.13) can be made equivalent to (3.10) by letting $s(k) = k/\Delta\tau$. The advantage of (3.13) is that it is an exact relation and the argument that leads to (3.13) does not require the concept of geometric progression of wave number steps with a factor of two. In addition to estimating $s(k)$ for the inertial-convective range and the viscous-convective range for large Schmidt numbers, we shall obtain $s(k)$ for the inertial-diffusive range for small Schmidt numbers by physical reasoning. Furthermore, we shall formally incorporate (3.13) into the m-spectral equation, which can readily be extended to the case of a reacting multicomponent mixture with equal or nonequal diffusivities. First, let us write down the covariance equation for the fluctuating concentration field of a nonreactive species $m(\mathbf{x}, t)$,[6]

$$\left[\frac{\partial}{\partial t} - 2\mathfrak{D}\nabla_r{}^2\right]\langle mm'\rangle(r, t) = \langle(\mathbf{u} - \mathbf{u}')\cdot\nabla_r(mm')\rangle(r, t) = Z(r, t) \tag{3.14}$$



a) $\hat{F}(\hat{k})$ vs $\hat{k}$: $[\hat{k} = k/(\epsilon\mathcal{D}^{-3})^{1/4},\ \hat{F}(\hat{k}) = F(\hat{k})/F(\hat{k}_*)]$

b) $\tilde{F}(\tilde{k})$ vs $\tilde{k}$: $(\nu/\mathcal{D}) = 1/26.5$. $[\tilde{k} = k/(\epsilon\nu^{-3})^{1/4},\ \tilde{F}(\tilde{k}) = F(\tilde{k})/F(\tilde{k}_*)]$

Fig. 2 Sample concentration spectrum at large wave numbers of a nonreacting species: small Schmidt number.

where local homogeneity and local isotropy have been assumed (as is appropriate for small $\mathbf{r}$). m' is written for $m(\mathbf{x} + \mathbf{r}, t)$.

The transforms of $\langle mm'\rangle(r, t)$ and $Z(r, t)$ are defined as[6]

$$\left.\begin{aligned} F(k, t) &= \frac{2}{\pi}\int_0^\infty kr\langle mm'\rangle(r, t)\sin kr\, dr \\ T(k, t) &= \frac{2}{\pi}\int_0^\infty kr\, Z(r, t)\sin kr\, dr \end{aligned}\right\} \tag{3.15}$$

$F(k, t)$ is the spectrum function of m. The inverse transforms are[6]

$$\left.\begin{aligned} \langle mm'\rangle(r, t) &= \int_0^\infty F(k, t)\frac{\sin kr}{kr}\, dk \\ Z(r, t) &= \int_0^\infty T(k, t)\frac{\sin kr}{kr}\, dk \end{aligned}\right\} \tag{3.16}$$

Transform (3.14), and then for the stationary spectrum, i.e., $(\partial/\partial t) = 0$, we obtain

$$2\mathcal{D}k^2F(k) = T(k) \tag{3.17}$$

Then

$$\int_k^\infty T(k)dk = \text{the spectral flux of } m \text{ across } k \tag{3.18}$$

Equating (3.18) to (3.13), we have

$$\int_k^\infty T(k)dk = F(k)s(k) \tag{3.19}$$

Thus,

$$T(k) = -(d/dk)(Fs) \tag{3.20}$$

Combining (3.17) and (3.20), we obtain

$$2\mathcal{D}k^2F = -(d/dk)(Fs) \tag{3.21}$$

This is the equation for determining the m spectrum at large wave numbers. $s(k)$ is to be obtained for various wave number ranges by physical reasoning.

In the *inertial-convective range*, the cascading of the spectral element is expected to depend mainly upon the turbulent energy flux ϵ. Dimensional reasoning gives

$$s(k) = l\epsilon^{1/3}k^{5/3} \tag{3.22}$$

where l is a dimensionless constant. Furthermore, the viscous and diffusive effects are negligible in this range, thus (3.21) can be further simplified as

$$(d/dk)(Fs) = 0 \tag{3.23}$$

This can be made identical to (3.11) by letting $s = k/\Delta\tau$. Combining (3.22) and (3.23), one obtains

$$F(k) \sim \epsilon^{-1/3}k^{-5/3} \tag{3.24}$$

which is the same form as obtained by Corrsin[4] and is consistent with (3.1).

In the *viscous-convective range and viscous-diffusive range* for large Schmidt numbers, we use Batchelor's concept[16] that the transfer of spectral content is mainly controlled by the straining motion associated with small eddies. Therefore, $s(k)$ mainly depends on the local least turbulent straining rate γ. Dimensional reasoning gives

$$s(k) = n\gamma k \tag{3.25}$$

where n is a dimensionless constant. Equation (3.25) again is equivalent to Corrsin's proposal[4, 5] that $\Delta\tau \sim -\gamma^{-1}$. Combining (3.25) and (3.21), we obtain

$$F(k) \sim k^{-1}\exp\{(-n\mathcal{D}/\gamma)k^2\} \tag{3.26}$$

which is consistent with (3.6). Equation (3.26) reduces to (3.6) exactly by letting $n = -1$.

In the *inertial-diffusive range* for small Schmidt numbers, the turbulent energy spectrum is still in the inertial-subrange. The cascading process is again dependent on the turbulent energy flux ϵ. Thus,

$$s(k) = l\epsilon^{1/3}k^{5/3} \tag{3.27}$$

is the same as the $s(k)$ for the inertial-convective range (3.22). However, the diffusive term in (3.21) can no longer be neglected in this range. Combining (3.27) and (3.21), we obtain

$$F(k) = Nk^{-5/3}\exp\left\{-\frac{3}{2}l^{-1}\left[\frac{k}{(\epsilon/\mathfrak{D}^3)^{1/4}}\right]^{4/3}\right\} \tag{3.28}$$

where N is a constant. Equation (3.28), in fact, is a unified spectral representation for both the inertial-convective range and the inertial-diffusive range for $(\nu/\mathfrak{D}) < 1$. For $k \ll (\epsilon/\mathfrak{D}^3)^{1/4}$, $l = 0(1)$, then (3.28) reduces to $F(k) \sim k^{-5/3}$. A sample calculation of (3.28) is plotted in Fig. 2. In the inertial-diffusive range, a portion of the curve behaves like $k^{-17/3}$ but decreases much faster for higher wave numbers.

To apply the unified spectral transfer concept to the case of a reacting turbulent multicomponent mixture with *equal* or *nonequal* diffusivities, let us first write down the governing equation of the fluctuating concentration field of species $-\mu$ with first-order reactions $\theta_\mu(\mathbf{x}, t)$:

$$\frac{\partial\theta_\mu}{\partial t} + \mathbf{u}\cdot\nabla\theta_\mu = \mathfrak{D}_\mu\nabla^2\theta_\mu + \varphi_\mu$$

$$\mu = 1, 2, \ldots \zeta \text{ species} \tag{3.29}$$

where local isotropy and local homogeneity have been assumed. φ_μ is the rate of change of θ_μ due to chemical reaction ($\Phi_\mu = \langle\Phi_\mu\rangle + \varphi_\mu$). Thus, for the first-order reactions,

$$\varphi_\mu = \sum_{\varkappa=1}^{\zeta} c_{\mu\varkappa}\theta_\varkappa \tag{3.30}$$

The covariance equations for $\theta_\mu(\mathbf{x}, t)$ and $\theta_\nu'(\mathbf{x}', t)$, with local isotropy and local homogeneity (as is appropriate for small $\mathbf{r}$), are

$$[(\partial/\partial t) - (\mathfrak{D}_\mu + \mathfrak{D}_\nu)\nabla_r^2]\langle\theta_\mu\theta_\nu'\rangle - \langle\phi_\mu\theta_\nu'\rangle - \langle\theta_\mu\phi_\nu'\rangle = \langle(\mathbf{u} - \mathbf{u}')\cdot\nabla_r(\theta_\mu\theta_\nu')\rangle = Z_{\mu\nu}(r, t) \tag{3.31}$$

where

$$\langle\theta_\mu\phi_\nu'\rangle = \sum_{\lambda=1}^{\zeta} c_{\nu\lambda}\langle\theta_\mu\theta_\lambda'\rangle \tag{3.32}$$

$$\langle\phi_\mu\theta_\nu'\rangle = \sum_{\varkappa=1}^{\zeta} c_{\mu\varkappa}\langle\theta_\varkappa\theta_\nu'\rangle \tag{3.33}$$

Defining the transform, as before,

$$G_{\mu\nu}(k, t) = \frac{2}{\pi}\int_0^\infty kr\,\langle\theta_\mu\theta_\nu'\rangle(r, t)\,\sin krdr \tag{3.34}$$

$$T_{\mu\nu}(k, t) = \frac{2}{\pi}\int_0^\infty krZ_{\mu\nu}(r, t)\,\sin krdr \tag{3.35}$$

$G_{\mu\mu}$ is the spectrum function of species $-\mu$. Assuming the spectrum functions are stationary, the transform of (3.31) becomes

$$(\mathfrak{D}_\mu + \mathfrak{D}_\nu)k^2G_{\mu\nu} - \sum_{\varkappa=1}^{\zeta} c_{\mu\varkappa}G_{\varkappa\nu} - \sum_{\lambda=1}^{\zeta} c_{\nu\lambda}G_{\mu\lambda} = T_{\mu\nu} \tag{3.36}$$

where $G_{\varkappa\nu} = G_{\nu\varkappa}$, due to homogeneity and isotropy. With the restriction given previously, all the reacting species under consideration are dynamically passive. Therefore, the spectral transfer mechanism should not be affected by the chemical reaction, and it should be similar to the pure mixing case (3.20). We then have

$$T_{\mu\nu} = -(d/dk)(G_{\mu\nu}s) \tag{3.37}$$

Combining (3.36) and (3.37), we obtain

$$(\mathfrak{D}_\mu + \mathfrak{D}_\nu)k^2G_{\mu\nu} - \sum_{\varkappa=1}^{\zeta} c_{\mu\varkappa}G_{\varkappa\nu} - \sum_{\lambda=1}^{\zeta} c_{\nu\lambda}G_{\mu\lambda} = -\frac{d}{dk}(G_{\mu\nu}s) \tag{3.38}$$

where, from (3.22, 3.25, and 3.27), $s(k) = l\epsilon^{1/3}k^{5/3}$ in the inertial-convective range, and the inertial-diffusive range for $(\nu/\mathfrak{D}_\mu) < 1$, and $s(k) = n\gamma k$ in the viscous-convective and viscous-diffusive ranges for $(\nu/\mathfrak{D}_\mu) \gg 1$.

3.2 Stationary Concentration Spectrum Functions of Species with First-Order Reaction

The solution of (3.38) for various wave number ranges, together with the extension of the more analytical approaches by Batchelor[16] and Batchelor, et al.,[17] will be discussed and compared in this section. Consider the case of a reversible first-order reaction; its stoichiometric equation may be

$$S_1 \underset{b}{\overset{a}{\rightleftarrows}} S_2$$

$$\varphi_1 = c_{11}\theta_1 + c_{12}\theta_2 = -a\theta_1 + b\theta_2 \tag{3.39}$$

$$\varphi_2 = c_{21}\theta_1 + c_{22}\theta_2 = a\theta_1 - b\theta_2 \tag{3.40}$$

Thus

$$-c_{11} = c_{21} = a \qquad c_{12} = -c_{22} = b \tag{3.41}$$

where a and b are the forward and backward reaction-rate coefficients, respectively.

3.2.1 *In the inertial-convective range*

As diffusive effects are negligible in this range, and with the $s(k)$ from (3.22), (3.38) reduces to

$$\sum_{\varkappa=1}^{\zeta} c_{\mu\varkappa}G_{\varkappa\nu} + \sum_{\lambda=1}^{\zeta} c_{\nu\lambda}G_{\mu\lambda} = \frac{d}{dk}(l\epsilon^{1/3}k^{5/3}G_{\mu\nu}) \tag{3.42}$$

For a reversible first-order reaction, (3.42) becomes

$$\left.\begin{aligned} -2aG_{11} + 2bG_{12} &= \frac{d}{dk}(l\epsilon^{1/3}k^{5/3}G_{11}) \\ 2aG_{12} - 2bG_{22} &= \frac{d}{dk}(l\epsilon^{1/3}k^{5/3}G_{22}) \\ aG_{11} + bG_{22} - (a + b)G_{12} &= \frac{d}{dk}(l\epsilon^{1/3}k^{5/3}G_{12}) \end{aligned}\right\} \tag{3.43}$$

Equations (3.43) are a set of determinant, simultaneous, first-order ordinary differential equations. The solutions are:

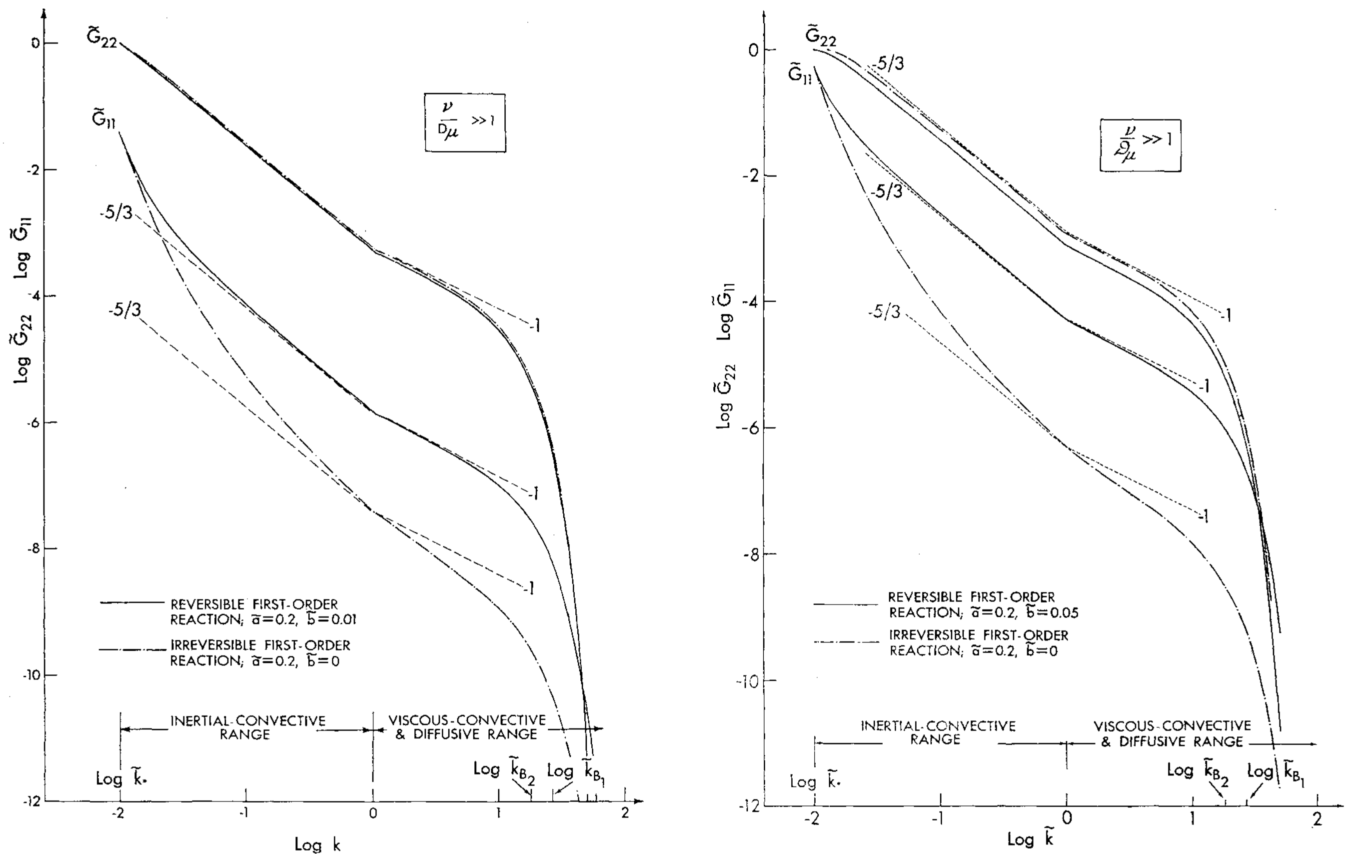
$$G_{11}(k) = k^{-5/3}(a + b)^{-2}[N_1b^2 + N_2b\exp(\tfrac{3}{2}pk^{-2/3}) + N_3\exp(3pk^{-2/3})] \tag{3.44}$$

$$G_{22}(k) = k^{-5/3}(a + b)^{-2}[N_1a^2 - N_2a\exp(\tfrac{3}{2}pk^{-2/3}) + N_3\exp(3pk^{-2/3})] \tag{3.45}$$

where

$$\left.\begin{aligned} p &= l^{-1}\epsilon^{-1/3}(a + b) \\ N_1 &= k_*^{5/3}(G_{11*} + G_{22*} + 2G_{12*}) \\ N_2 &= 2k_*^{5/3}[aG_{11*} - bG_{22*} + (a - b)G_{12*}] \times \exp(-\tfrac{3}{2}pk_*^{-2/3}) \\ N_3 &= k_*^{5/3}[a^2G_{11*} + b^2G_{22*} - 2abG_{12*}] \times \exp(-3pk_*^{-2/3}) \end{aligned}\right\} \tag{3.46}$$

k_* is the wave number marking the beginning of the inertial-



a) $\tilde G_{11}(\tilde k_*) = 0.04$, $\tilde G_{22}(\tilde k_*) = 1.0$, $\tilde G_{12}(\tilde k_*) = 0.1$, $(\nu/\mathfrak{D}_1) = 700$, $(\nu/\mathfrak{D}_2) = 350$

b) $\tilde G_{11}(\tilde k_*) = 0.5$, $\tilde G_{22}(\tilde k_*) = 1.0$, $\tilde G_{12}(\tilde k_*) = 0.6$, $(\nu/\mathfrak{D}_1) = 700$, $(\nu/\mathfrak{D}_2) = 350$

Fig. 3 Sample concentration spectra at large wave numbers of the reactants and the products of first-order reactions: large Schmidt numbers [$\tilde k = k/k_K$, $k_K = (\epsilon/\nu^3)^{1/4}$, $\tilde k_{B\mu} = k_{B\mu}/k_K = (\epsilon\nu^{-1}\mathfrak{D}_\mu^{-2})^{1/4}/k_K = (\nu/\mathfrak{D}_\mu)^{1/2}$, $\tilde G_{11}(\tilde k) = G_{11}(\tilde k)/G_{22}(\tilde k_*)$, $\tilde G_{22}(\tilde k) = G_{22}(\tilde k)/G_{22}(\tilde k_*)$, $\tilde G_{12}(\tilde k) = G_{12}(\tilde k)/G_{22}(\tilde k_*)$, $\tilde a = a/(\epsilon\nu^{-1})^{1/2}$, $\tilde b = b/(\epsilon\nu^{-1})^{1/2}$].

convective range, and G_{11*}, G_{22*}, and G_{12*} are the values of G_{11}, G_{22}, and G_{12} at k_*, respectively.

The preceding results reduce to the results for an irreversible first-order reaction by letting $b = 0$; we then have the reactant concentration spectrum:

$$G_{11}(k) = N_3k^{-5/3}\exp(3pk^{-2/3}) \qquad (3.47)$$

which is identical to Corrsin's result.[4, 5] The product concentration spectrum is

$$G_{22}(k) = k^{-5/3}[N_1 - N_2a^{-1}\exp(\tfrac{3}{2}pk^{-2/3}) + N_3a^{-2}\exp(3pk^{-2/3})] \qquad (3.48)$$

Equation (3.48) reduces to Corrsin's[4, 5] results for the case of equal diffusivities.

Sample computations of (3.44, 3.45, 3.47, and 3.48) are plotted in Fig. 3.

3.2.2 In the viscous-convective and viscous-diffusive range: large Schmidt number $(\nu/\mathfrak{D}) \gg 1$

In this section, before we consider the reacting cases, we shall compare in detail the consequences of the generalized Onsager-Corrsin spectral transfer concept with that of a more analytical approach by Batchelor for the viscous-convective and viscous-diffusive range with $(\nu/\mathfrak{D}) \gg 1$. From the observation that the velocity gradient is approximately uniform over regions with linear dimensions not much smaller than $l_\kappa = (\nu^3/\epsilon)^{1/4}$ and the assumption that the principal axes of rate of strain rotate with the fluid element and that level surfaces of θ are approximately aligned normal to the direction of the least rate of strain, Batchelor deduced a relation for the right-hand side of (3.14) as

$$Z(r, t) = -\gamma r(\partial/\partial r)\,\langle mm'\rangle(r, t) \qquad (3.49)$$

Saffman[19] suggested that experimental evidence does not rule out the possibility of rotation of the principal axes of rate of strain relative to the fluid. With the relative rotation, he considered the requirements for which (3.49) holds for each realization. These are sufficient conditions for (3.49) to hold, but may not be necessary. Saffman thus further suggested that (3.49) is simply a consequence of dimensional analysis and the assumption that the transfer term Z decreases the scale. However, in the following analysis we shall arrive at (3.49) from a different approach. Instead of analyzing the phenomena from each realization, we shall approach it from the point of view of weak statistical dependence. From (3.14), the transfer term is, with local isotropy and local homogeneity,

$$Z(r, t) = \langle(\mathbf{u} - \mathbf{u}')\cdot\nabla_r(mm')\rangle\,(r, t) \qquad (3.50)$$

In the viscous-convective and viscous-diffusive ranges, the smallest characteristic scales of turbulence are much larger than that of the m concentration field; we propose that the statistical connections between the turbulent velocity field and the concentration field are so weak that

$$\langle(\mathbf{u} - \mathbf{u}')\cdot\nabla_r(mm')\rangle\,(r, t) \approx \langle|\mathbf{u} - \mathbf{u}'|^2\rangle^{1/2}(\partial/\partial r)\langle mm'\rangle(r, t) \qquad (3.51)$$

For small separation $\mathbf{r}$, $(|\mathbf{r}| < l_\kappa)$

$$\mathbf{u}'(\mathbf{x} + \mathbf{r}, t) \approx \mathbf{u}(\mathbf{x}, t) + \mathbf{V}\cdot\mathbf{r} \qquad (3.52)$$

where $\mathbf{V}$ is the velocity gradient tensor. Combining (3.51) and (3.52), we obtain

$$Z(r, t) = \langle(\mathbf{u} - \mathbf{u}')\cdot\nabla_r(mm')\rangle(r, t) \approx \langle|\mathbf{V}\cdot\mathbf{r}|^2\rangle^{1/2}(\partial/\partial r)\langle mm'\rangle(r, t) = -\gamma r(\partial/\partial r)\langle mm'\rangle \qquad (3.53)$$

as (3.49). γ is taken as the least turbulent straining rate at $\mathbf{x}$. Thus, we have shown that the relation (3.49) deduced by Batchelor can be considered a consequence of the argument that, in the viscous ranges for $(\nu/\mathfrak{D}) \gg 1$, the statistical connections between the velocity and concentration fields are weak and that the fields are locally isotropic and homogeneous within a small region $|\mathbf{r}| < l_{\varkappa}$. Putting (3.53) in (3.14), and transforming the resulting equation to wave number space with stationarity, one obtains[19]

$$2\mathfrak{D}k^2F = \gamma F + \gamma k(dF/dk) \tag{3.54}$$

which is identical to (3.21) with $s = -\gamma k$. Thus, Batchelor's straining concept is identical to the generalized Onsager-Corrsin concept with $s = -\gamma k$.

Then, for the cases of first-order reactions in the viscous-convective and viscous-diffusive ranges, we have

$$(\mathfrak{D}_\mu + \mathfrak{D}_\nu)k^2G_{\mu\nu} - \sum_{\varkappa=1}^{\zeta} c_{\mu\varkappa}G_{\varkappa\nu} - \sum_{\lambda=1}^{\zeta} c_{\nu\lambda}G_{\mu\lambda} = \gamma G_{\mu\nu} + \gamma k\,\frac{dG_{\mu\nu}}{dk} \tag{3.55}$$

Equation (3.55) can be considered either as the consequence of (3.38) by taking $s = -\gamma k$ (generalized Onsager's spectral transfer concept) or as the extension of Batchelor's uniform straining concepts to the reacting cases.

We shall demonstrate the solutions of (3.55) again with the reversible first-order reaction. Equation (3.55) becomes

$$\left.\begin{aligned} &2\mathfrak{D}_1k^2G_{11} + 2aG_{11} - 2bG_{12} = \gamma G_{11} + \gamma k\,\frac{d}{dk}\,G_{11} \\ &2\mathfrak{D}_2k^2G_{22} - 2aG_{12} + 2bG_{22} = \gamma G_{22} + \gamma k\,\frac{d}{dk}\,G_{22} \\ &(\mathfrak{D}_1 + \mathfrak{D}_2)k^2G_{12} + (a+b)G_{12} - aG_{11} - bG_{22} = \\ &\qquad\qquad \gamma G_{12} + \gamma k\,\frac{d}{dk}\,G_{12} \end{aligned}\right\} \tag{3.56}$$

In the viscous-convective range, the diffusive effects, which are the leading terms in (3.56), are negligible. With the leading terms neglected, the solutions of (3.56) are

$$\left.\begin{aligned} G_{11}(k) &= k^{-1}(a+b)^{-2}(L_1b^2 + L_2bk^{(a+b)/\gamma} + L_3k^{2(a+b)/\gamma}) \\ G_{22}(k) &= k^{-1}(a+b)^{-2}(L_1a^2 - L_2ak^{(a+b)/\gamma} + L_3k^{2(a+b)/\gamma}) \end{aligned}\right\} \tag{3.57}$$

where

$$L_1 = k_\dagger(G_{11\dagger} + G_{22\dagger} + 2G_{12\dagger})$$

$$L_2 = 2k_\dagger(aG_{11\dagger} - bG_{22\dagger} + (a-b)G_{12\dagger})k_\dagger^{-(a+b)/\gamma}$$

$$L_3 = k_\dagger(a^2G_{11\dagger} + b^2G_{22\dagger} - 2abG_{12\dagger})k_\dagger^{-2(a+b)/\gamma}$$

$k_\dagger$ marks the beginning of viscous-convective range and $G_{11\dagger}$, $G_{22\dagger}$, and $G_{12\dagger}$ are the values of G_{11}, G_{22}, and G_{12} at $k_\dagger$, respectively.

Equation (3.57) reduces to the results for an irreversible first-order reaction by letting $b = 0$. Again, for $b = 0$, G_{11} and G_{22} reduce to Corrsin's[4, 5] result for the case of equal diffusivities.

For the viscous-diffusive range with $(\nu/\mathfrak{D}) \gg 1$, where the diffusive effect is important, one has to include the leading diffusive term. For equal diffusivities, the solutions are (3.57) multiplied by $\exp[(\mathfrak{D}/\gamma)k^2]$. For nonequal diffusivities, we are unable to find closed form solutions for (3.56), but (3.56) are solved numerically for two sample cases and plotted in Fig. 3.

3.2.3 *In the inertial-diffusive range: small Schmidt number* $(\nu/\mathfrak{D}) < 1$

Corrsin[4] has applied the concepts introduced by Batchelor, et al.[16] to obtain the concentration spectrum functions for the reactant of a first-order irreversible reaction. In this section, we shall show that the concepts can be applied to obtain the reactant and the product concentration spectrum functions for all types of first-order reactions with equal diffusivities. To illustrate, let us again take the case of a reversible first-order reaction. Let θ_1 and θ_2 be the reactant and product fluctuating concentration fields, respectively. With local homogeneity and isotropy and $\mathfrak{D}_1 = \mathfrak{D}_2 = \mathfrak{D}$, from (3.29, 3.39, and 3.40), we obtain

$$(\partial\theta_1/\partial t) + \mathbf{u}\cdot\nabla\theta_1 = \mathfrak{D}\nabla^2\theta_1 - a\theta_1 + b\theta_2 \tag{3.58}$$

$$(\partial\theta_2/\partial t) + \mathbf{u}\cdot\nabla\theta_2 = \mathfrak{D}\nabla^2\theta_2 + a\theta_1 - b\theta_2 \tag{3.59}$$

Define the generalized Fourier transforms[20]

$$\mathbf{Q}(\mathbf{k}, t) = (2\pi)^{-3}\int_{\mathbf{x}} \mathbf{u}(\mathbf{x}, t)e^{-i\mathbf{k}\cdot\mathbf{x}}\,d\mathbf{x} \tag{3.60}$$

$$P_\mu(\mathbf{k}, t) = (2\pi)^{-3}\int_{\mathbf{x}} \theta_\mu(\mathbf{x}, t)e^{-i\mathbf{k}\cdot\mathbf{x}}\,d\mathbf{x} \tag{3.61}$$

$$\mathrm{A}(\mathbf{k}, t) = (2\pi)^{-3}\int_{\mathbf{x}} m(\mathbf{x}, t)e^{-i\mathbf{k}\cdot\mathbf{x}}\,d\mathbf{x} \tag{3.62}$$

The generalized Fourier transform of (3.58) and (3.59) become

$$(\partial/\partial t)P_1(\mathbf{k}, t) + i\int\mathbf{k}'\cdot\mathbf{Q}(\mathbf{k}-\mathbf{k}', t)P_1(\mathbf{k}', t)d\mathbf{k}' = -\mathfrak{D}k^2P_1(\mathbf{k}, t) - aP_1(\mathbf{k}, t) + bP_2(\mathbf{k}, t) \tag{3.63}$$

$$(\partial/\partial t)P_2(\mathbf{k}, t) + i\int\mathbf{k}'\cdot\mathbf{Q}(\mathbf{k}-\mathbf{k}', t)P_2(\mathbf{k}', t)d\mathbf{k}' = -\mathfrak{D}k^2P_2(\mathbf{k}, t) + aP_1(\mathbf{k}, t) - bP_2(\mathbf{k}, t) \tag{3.64}$$

From (2.6, 3.61, and 3.62) we have

$$P_\mu(\mathbf{k}, t) = A(\mathbf{k}, t)\Lambda_\mu(t) \tag{3.65}$$

Consequently, we have

$$P_\mu(\mathbf{k}, t)P_\nu{}^*(\mathbf{k}, t) = A(\mathbf{k}, t)A^*(\mathbf{k}, t)\Lambda_\mu(t)\Lambda_\nu(t) = P_\nu(\mathbf{k}, t)P_\mu{}^*(\mathbf{k}, t) \tag{3.66}$$

Thus,

$$\left.\begin{aligned} \langle P_\mu P_\nu{}^*\rangle &= \langle P_\nu P_\mu{}^*\rangle \\ \langle P_\mu P_\mu{}^*\rangle\,\langle P_\nu P_\nu{}^*\rangle &= \langle P_\mu P_\nu{}^*\rangle^2 \end{aligned}\right\} \tag{3.67}$$

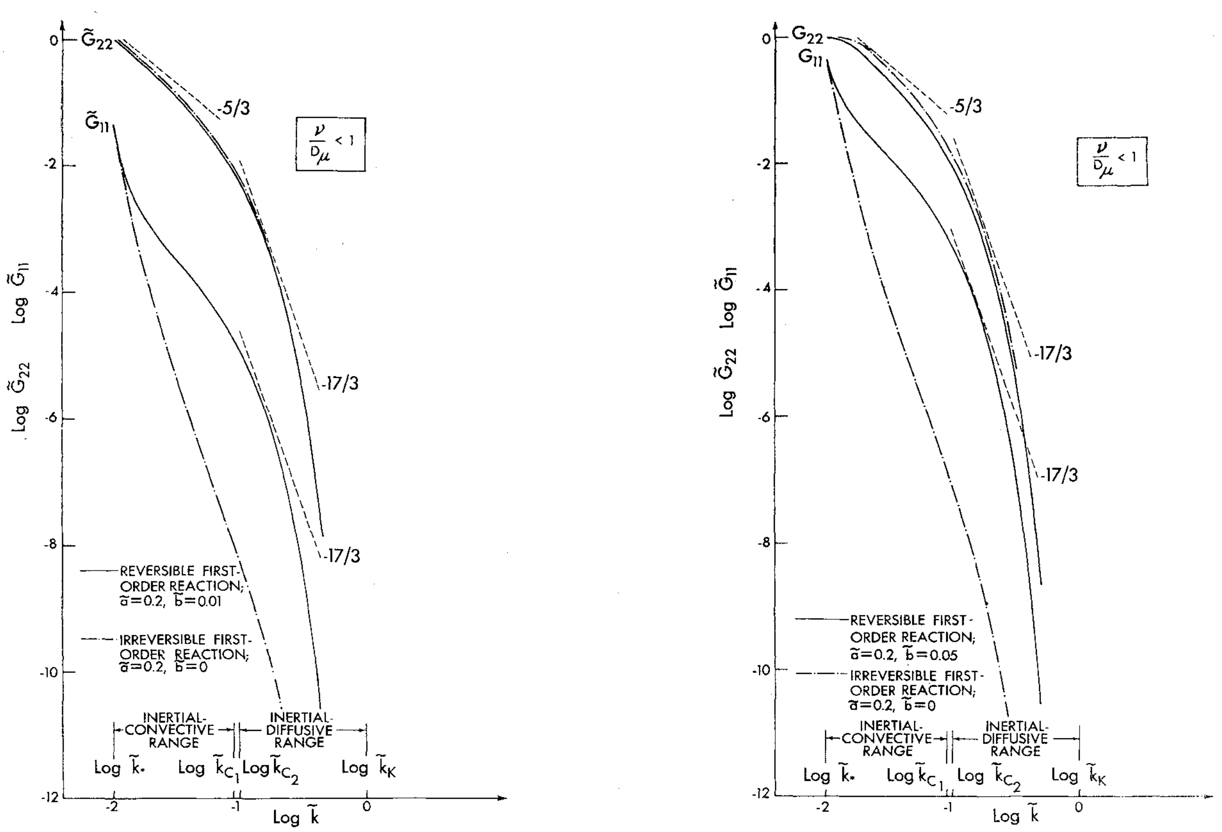
where the superscript * denotes the complex conjugate.

In the inertial-diffusive range, from the argument of Batchelor, et al.,[17] one expects that the $P_\mu(\mathbf{k}')$ will decrease rapidly as k' increases beyond $k_2 = (\epsilon/\mathrm{D}^3)^{1/4}$ because of the diffusive effects, then the contribution to the integrals in (3.63) and (3.64) are mainly from the range $k' < k_c$. But, since the wave number k in the inertial-diffusive range is much greater than k_c,

$$k' \ll |\mathbf{k} - \mathbf{k}'|$$

This enables us to neglect the statistical connection between $\mathbf{Q}(\mathbf{k} - \mathbf{k}')$ and $P_\mu(\mathbf{k}')$. Applying the arguments by Batchelor, et al.[17] to the present problem, the terms $\partial P_1/\partial t$ and $\partial P_2/\partial t$ in (3.63) and (3.64) would cancel the corresponding small contribution to the integrals from values of $\mathbf{k}'$ near $\mathbf{k}$. Then, multiplying the remainder of (3.63) and (3.64) by its own complex conjugate, with isotropy and (3.67), we have

$$\{(\mathfrak{D}k^2 + a)\langle P_1(\mathbf{k})P_1{}^*(\mathbf{k})\rangle^{1/2} - b\langle P_2(\mathbf{k})P_2{}^*(\mathbf{k})\rangle^{1/2}\}^2 \approx \iint \sum_{i=1}^{3}\sum_{j=1}^{3} k_i'k_j''\langle Q_i(\mathbf{k}-\mathbf{k}')Q_j{}^*(\mathbf{k}-\mathbf{k}'') \times P_1(\mathbf{k}')P_1{}^*(\mathbf{k}'')\rangle d\mathbf{k}'d\mathbf{k}'' \approx \left\langle \sum_{i=1}^{3} Q_i(\mathbf{k})Q_i{}^*(\mathbf{k}) \right\rangle \times \int k'^2\langle P_1(\mathbf{k}')P_1{}^*(\mathbf{k}')\rangle d\mathbf{k}' \tag{3.68}$$



a) $\tilde{G}_{11}(\tilde{k}_*) = 0.04$, $\tilde{G}_{22}(\tilde{k}_*) = 1.0$, $\tilde{G}_{12}(\tilde{k}_*) = 0.1$, $(\nu/\mathfrak{D}_1) = 1/26.5$, $(\nu/\mathfrak{D}_2) = \frac{1}{23}$

b) $\tilde{G}_{11}(\tilde{k}_*) = 0.5$, $\tilde{G}_{22}(\tilde{k}_*) = 1.0$, $\tilde{G}_{12}(\tilde{k}_*) = 0.6$, $(\nu/\mathfrak{D}_1) = 1/26.5$, $(\nu/\mathfrak{D}_2) = \frac{1}{23}$

Fig. 4 Sample concentration spectra at large wave numbers of the reactants and the products of first-order reactions: small Schmidt numbers [$\tilde{k} = k/k_K$, $k_K = (\epsilon/\nu^3)^{1/4}$, $\tilde{k}C_\mu = kC_\mu/k_K = (\epsilon\mathfrak{D}_\mu^{-3})^{1/4}/(\epsilon\nu^{-3})^{1/4} = (\nu/\mathfrak{D}_\mu)^{3/4}$, $\tilde{G}_{11}(\tilde{k}) = G_{11}(\tilde{k})/G_{22}(\tilde{k}_*)$, $\tilde{G}_{22}(\tilde{k}) = G_{22}(\tilde{k})/G_{22}(\tilde{k}_*)$, $\tilde{G}_{12}(\tilde{k}) = G_{12}(\tilde{k})/G_{22}(\tilde{k}_*)$, $\tilde{a} = a/(\epsilon\nu^{-1})^{1/2}$, $\tilde{b} = b/(\epsilon\nu^{-1})^{1/2}$].

$$\{(\mathfrak{D}k^2 + b)\langle P_2(\mathbf{k})P_2^*(\mathbf{k})\rangle^{1/2} - a\langle P_1(\mathbf{k})P_1^*(\mathbf{k})\rangle^{1/2}\}^2 \approx \left\langle \sum_{i=1}^{3} Q_i(\mathbf{k})Q_i^*(\mathbf{k}) \right\rangle \int k'^2\langle P_2(\mathbf{k}')P_2^*(\mathbf{k}')\rangle d\mathbf{k}' \quad (3.69)$$

With isotropy,

$$\left.\begin{aligned} \langle P_\mu(\mathbf{k})P_\mu^*(\mathbf{k})\rangle &= \frac{G_{\mu\mu}(k)}{4\pi k^2} \\ \left\langle \sum_{i=1}^{3} Q_i(\mathbf{k})Q_i^*(\mathbf{k}) \right\rangle &= \frac{E(k)}{2\pi k^2} \end{aligned}\right\} \quad (3.70)$$

From (3.68–3.70), and with the turbulent energy spectrum function $E(k) \approx \epsilon^{2/3}k^{-5/3}$ in this range, we obtain

$$G_{11}(k) \approx \frac{1}{3}\,\epsilon^{2/3}\mathfrak{D}^{-3}k^{-17/3}\left\{\frac{(\mathfrak{D}k^2 + b)\chi_{11}^{1/2} + b\chi_{22}^{1/2}}{\mathfrak{D}k^2 + a + b}\right\}^2 \quad (3.71)$$

$$G_{22}(k) \approx \frac{1}{3}\,\epsilon^{2/3}\mathfrak{D}^{-3}k^{-17/3}\left\{\frac{(\mathfrak{D}k^2 + a)\chi_{22}^{1/2} + a\chi_{11}^{1/2}}{\mathfrak{D}k^2 + a + b}\right\}^2 \quad (3.72)$$

where χ_{11} and χ_{22} are the diffusive rates of $\langle\theta_1^2\rangle$ and $\langle\theta_2^2\rangle$, respectively. With $b = 0$, (3.71) reduces to the reactant concentration spectrum of an irreversible first-order reaction as obtained by Corrsin.[4] With $b = 0$, (3.72) reduces to the product concentration spectrum of an irreversible first-order reaction as obtained by Pao.[18] Using relation (3.67), the preceding approach can be applied to other types of first-order reactions with *equal* diffusivities.

For the more general cases of first-order reactions with *nonequal* diffusivities, we cannot find relations similar to (3.67), therefore, the preceding approach will not yield concrete results. The unified spectral transfer concept becomes very useful in this case. For small Schmidt numbers, $s(k) = l\epsilon^{1/3}k^{5/3}$ in both the inertial-convective and inertial-diffusive ranges; then (3.38) becomes

$$(\mathfrak{D}_\mu + \mathfrak{D}_\nu)k^2G_{\mu\nu} - \sum_{\varkappa=1}^{\zeta} c_{\mu\varkappa}G_{\varkappa\nu} - \sum_{\lambda=1}^{\zeta} c_{\nu\lambda}G_{\mu\lambda} = -\frac{d}{dk}\,(l\epsilon^{1/3}k^{5/3}G_{\mu\nu}) \quad (3.73)$$

For a reversible first-order reaction, (3.73) becomes

$$\left.\begin{aligned} 2\mathfrak{D}_1k^2G_{11} + 2aG_{11} - 2bG_{12} &= -\frac{d}{dk}\,(l\epsilon^{1/3}k^{5/3}G_{11}) \\ 2\mathfrak{D}_2k^2G_{22} - 2aG_{12} + 2bG_{22} &= -\frac{d}{dk}\,(l\epsilon^{1/3}k^{5/3}G_{22}) \\ (\mathfrak{D}_1 + \mathfrak{D}_2)k^2G_{12} + (a + b)G_{12} - aG_{11} - bG_{22} &= -\frac{d}{dk}\,(l\epsilon^{1/3}k^{5/3}G_{12}) \end{aligned}\right\} \quad (3.74)$$

Equation (3.74) is also solved numerically. Two sample computations are plotted in Fig. 4.

4. Discussion

For the given initial conditions (2.1), the reacting concentration fields are related to the nonreacting field by (2.2). Relation (2.10) admits the more general initial conditions (2.9). Relations (2.2) and (2.10) are useful for pure-initial value problems. We are so far unsuccessful in the search for similar relations for the mixed initial- and boundary-value problems.

With the concepts of local isotropy and local homogeneity, and by following the migration of a spectral element, a unified spectral transfer concept is deduced. It enables us to predict the concentration spectra of a reacting multicomponent mixture (as well as a nonreacting mixture) for large wave numbers. The consequences of this concept are compared with those of other spectral transfer concepts. Measurements of concentration spectra of reacting or nonreacting species at large wave numbers are anxiously awaited.

As a step toward further understanding of the general problem of turbulent mixing with chemical reaction,[21] the investigation of weak exothermic reactions is under way. We hope to report some results in the near future.

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