VERY RAPID, ISOTHERMAL, TWO SPECIES REACTIONS IN FINAL PERIOD TURBULENCE

by

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Abstract

Asymptotic decay rates for mean concentration and root mean square fluctuations in concentration are derived for a decaying second order, isothermal two species reaction in final period turbulence. The relative intensity of each species approaches $(\pi-1)$ for stoichiometric reactions and it becomes unbounded for the under represented species when the proportions of reactants are not stoichiometric.

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In a previous paper[1] it was pointed out that for single species, second order, isothermal reactions in a final period turbulence the asymptotic behavior of mean square fluctuations of concentration $\overline{\gamma^2}(t)$, is as $t^{-11/2}$, where t is the time from some virtual origin. In that situation the mean concentration field (t) decays as t^{-1} asymptotically[2] so that the relative intensity $\overline{\gamma^2}\,\overline{\Gamma}^{-2} \sim 0(t^{-7/2})$, as $t \to \infty$. It is the purpose of this note to indicate a quite different situation when the second order reaction is very rapid and involves two species having equal molecular diffusivities. We will show that for stoichiometrically distributed reactants both the mean and the root mean square fluctuations of a species concentration decay as $t^{-3/4}$ asymptotically and that the relative intensity of each species approaches a constant value of $\pi - 1$. We will also determine for nonstoichiometric distributions the mean concentrations and root mean square fluctuations of each species. In particular the mean concentration of the under represented species decays as $t^{-9/4} \exp\{-Ct^{3/2}\}$ asymptotically, where C is a constant.

We consider the irreversible isothermal reaction

$$\Gamma_A + n\,\Gamma_B \to \text{product},$$

where n is the stoichiometric parameter, imbedded in a final period homogeneous turbulence in which the convective action of the turbulence for a fixed Fourier mode of the concentration field is negligible compared to the direct role of molecular diffusion.[3] Consequently a second order isothermal reaction of two species in such a turbulence[4] can be described by the following equations which are valid after some virtual time origin.

$$\frac{\partial \Gamma_A}{\partial t} = D\nabla^2\Gamma_A - C\Gamma_A\Gamma_B \qquad (1)$$

$$\frac{\partial \Gamma_B}{\partial t} = D\nabla^2\Gamma_B - Cn\Gamma_A\Gamma_B \qquad (2)$$

where $\Gamma_A(x,t)$ is the concentration of species A, $\Gamma_B(x,t)$ is the concentration of species B, D is the molecular diffusivity of each species assumed constant and identical and C is a reaction rate also assumed constant.

If we replace $n\Gamma_A$ by Γ_A^* and then drop the asterisk for the remainder of the paper, equations (1) and (2) can be written without the explicit appearance of n

$$\frac{\partial \Gamma_A}{\partial t} = D\nabla^2\Gamma_A - C\Gamma_A\Gamma_B \qquad (3)$$

$$\frac{\partial \Gamma_B}{\partial t} = D\nabla^2\Gamma_B - C\Gamma_A\Gamma_B \qquad (4)$$

It is useful[5] to define a random variable $\chi(x,t) = \Gamma_A(x,t) - \Gamma_B(x,t)$, where from (3) and (4)

$$\frac{\partial \chi}{\partial t} = D\nabla^2\chi \qquad (5)$$

and by homogeneity $\overline{\chi}$ is a constant in both space and time. Here as elsewhere the bar indicates an ensemble average.

When the proportion of A and B are nonstoichiometric we will assume that B is under represented and we can identify $\overline{\chi}$ in the following way:

$$\lim_{t\to\infty} \overline{\Gamma}_A(x,t) = \overline{\chi} \qquad (6)$$

$$\lim_{t\to\infty} \overline{\Gamma}_B(x,t) = 0 \qquad (7)$$

Thus $\overline{\chi}$ is the excess of species A and, when the proportions are stoichiometric, $\overline{\chi} \equiv 0$.

Reasoning similar to that adopted for the central limit theorem suggests[6] that χ will be normally distributed in the limit as $t \to \infty$ for a final period turbulence. Hence we adopt the probability density of χ described by

$$P\,[\chi,t] = [2\pi\sigma^2(t)]^{-\frac{1}{2}} \exp\{-\frac{(\chi-\overline{\chi})^2}{2\sigma^2}\} \tag{8}$$

where from the theory of simple mixing in final period turbulence[3] we have

$$\sigma^2(t) \sim 0\,(t^{-3/2}), \text{ as } t \to \infty$$

For a diffusion controlled reaction characterized by segregation of species A and B and reaction zones of molecular dimensions[4]

$$\Gamma_A(x,t) = \begin{cases} \chi(x,t) &, \chi > 0 \\ 0 &, \chi \leq 0 \end{cases}$$

$$\Gamma_B(x,t) = \begin{cases} 0 &, \chi > 0 \\ -\chi(x,t) &, \chi \leq 0 \end{cases}$$

and hence

$$\overline{\Gamma}_A(x,t) = \int_0^\infty \chi\, P[\chi,t]\, d\chi \tag{9}$$

By definition

$$\overline{\Gamma}_B(t) = \overline{\Gamma}_A(t) - \overline{\chi} \tag{10}$$

also

$$\overline{\Gamma^2}_A(t) = \int_0^\infty \chi^2\, P[\chi,t] d\chi \tag{11}$$

and, since $\overline{\Gamma_A \Gamma_B} = 0$ for the very rapid reaction

$$\overline{\Gamma_B^2}(t) = \overline{\chi^2}(t) - \overline{\Gamma_A^2}(t) \tag{12}$$

where

$$\overline{\chi^2}(t) = \int_{\infty}^{\infty} \chi^2 P[\chi,t]\, d\chi = \bar{\chi}^2 + \sigma^2(t) .$$

Also $$\overline{\gamma_A \gamma_B} = - \bar{\Gamma}_A \bar{\Gamma}_B$$

Substitution of (8) into (9) (10) (11) (12) yields the following asymptotic results.

Case I Reactants are Stoichiometrically Distributed, $\bar{\chi} = 0$ as $t \to \infty$, $\bar{\Gamma}(t) = (\frac{\sigma^2(t)}{2\pi})^{\frac{1}{2}} \sim 0(t^{-3/4})$; $\overline{\Gamma^2} = \frac{\sigma^2(t)}{2} \sim 0(t^{-3/2})$; $\overline{\gamma^2}\, \bar{\Gamma}^{-2} = \pi - 1$; and $\overline{\gamma_A \gamma_B} = - \bar{\Gamma}_A \bar{\Gamma}_B = - \frac{\sigma^2(t)}{2\pi} \sim - 0(t^{-3/2})$ where, since $\overline{\Gamma_A^m} = \overline{\Gamma_B^m}$ for all m, the subscript A and B have been deleted wherever possible.

Case II Reactants are not stoichiometrically Distributed, $\bar{\chi} \neq 0$.

We find as $t \to \infty$

$$\bar{\Gamma}_A(t) = \bar{\chi} + \frac{(2\sigma^2)^{3/2}}{4\bar{\chi}^2 \pi^{\frac{1}{2}}} \exp\{-\frac{\bar{\chi}^2}{2\sigma^2}\} - 0\,(\sigma^5 \exp\{-\frac{\bar{\chi}^2}{2\sigma^2}\})$$

$$\bar{\Gamma}_B(t) = \frac{(2\sigma^2)^{3/2}}{4\bar{\chi}^2 \pi^{\frac{1}{2}}} \exp\{-\frac{\bar{\chi}^2}{2\sigma^2}\} - 0\,(\sigma^5 \exp\{-\frac{\bar{\chi}^2}{2\sigma^2}\}$$

$$\overline{\Gamma_A^2}(t) = \bar{\chi}^2 + \sigma^2 - \frac{(2\sigma^2)^{5/2}}{\pi^{\frac{1}{2}}\, \bar{\chi}^3} \exp\{-\frac{\bar{\chi}^2}{2\sigma^2}\} + 0\,(\sigma^7 \exp\{-\frac{\bar{\chi}^2}{2\sigma^2}\})$$

$$\overline{\Gamma_B^2}(t) = \frac{(2\sigma^2)^{5/2}}{\pi^{\frac{1}{2}}\, \bar{\chi}^3} \exp\{-\frac{\bar{\chi}^2}{2\sigma^2}\} - 0\,(\sigma^7 \exp\{-\frac{\bar{\chi}^2}{2\sigma^2}\})$$

In terms of t these asymptotic results for cases in which $\bar{\chi} \neq 0$ can be expressed as

$$\overline{\Gamma}_A = \overline{\chi} + 0\ (t^{-9/4} \exp\{-Ct^{3/2}\})$$

$$\overline{\Gamma}_B = 0\ (t^{-9/4} \exp\{-Ct^{3/2}\})$$

$$\overline{\Gamma_A{}^2} = \bar{\chi}^2 + \sigma^2 - 0\ (t^{-15/4} \exp\{-\ Ct^{3/2}\})$$

$$\overline{\Gamma_B{}^2} = 0\ (t^{-15/4} \exp\{-Ct^{3/2}\})\ .$$

Construction of the relative intensities of each species then shows, as $t \to \infty$,

$$\frac{\overline{\gamma_A^2}}{\bar{\Gamma}_A{}^2} = \frac{\overline{\Gamma_A{}^2}}{\bar{\Gamma}^2} - 1 = \frac{\sigma^2}{\bar{\chi}^2} = 0\ (t^{-3/2}),$$

$$\frac{\overline{\gamma_B{}^2}}{\bar{\Gamma}_B{}^2} = \frac{0(t^{-15/4} \exp\{-Ct^{3/2}\})}{0(t^{-18/4} \exp\{-2Ct^{3/2}\})} - 1$$

Hence

$$\frac{\overline{\gamma_B{}^2}}{\bar{\Gamma}_B{}^2} \to \infty \text{ as } t \to \infty.$$

Also

$$\overline{\gamma_A \gamma_B} = -\ \overline{\Gamma}_A \overline{\Gamma}_B = -\ 0(t^{-9/4} \exp\{-Ct^{3/2}\}) \text{ as } t \to \infty$$

It is evident from the above results that one consequence of diffusion controlled reactions is to deplete the mean concentration field of each species more rapidly than the fluctuation field with the result that relative intensities of order unity and higher will be common. This implies that approximation theories capable of handling positive random variables of high relative intensity must be invoked in dealing with fully turbulent fast multi-species reactions. Another consequence of these results is that even stoichiometric turbulent reaction fields of this kind can be expected to exhibit pronounced spottiness or intermittency where local nonstoichiometry produces marked depletion of one species and excess of the other.

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