

Competing reactions with initially separated components in the asymptotic time region

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Two competing irreversible reactions with initially separated components and with essentially different reaction constants are theoretically studied in the asymptotic time region. The description of the two simultaneous reactions is reduced to the consideration of two reactions separated in space. It is shown that the reaction rate profile can have two maxima and their ratio is independent of time. The location and relative value of the maxima are functions of the reaction constants and initial concentrations.

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The irreversible reaction $A+B\rightarrow C$ of two initially separated components A and B is concentrated in a dynamical zone known as the reaction front [1,2]. It was shown, both experimentally [3–7] and theoretically [8–37], that the zone can be characterized by a cupola-shaped profile of the reaction rate $R(x,t)$. To explain the reaction rate profile with two maxima observed in the experiments, the theoretical model of two irreversible reactions $A_1+B\rightarrow C_1$ and $A_2+B\rightarrow C_2$ has been proposed in Refs. [38,39]. Using this model, the authors simulated the behavior of the reactions in small and medium time regions and well explained the experimental results.

In this Brief Report we investigate the long-time asymptotic behavior of two irreversible reactions using the same mathematical model [38] and recently developed the quasistatic approach [40].

The approach is based on the consideration of the quasistatic equations describing two irreversible reactions $A_1+B\rightarrow C_1$ and $A_2+B\rightarrow C_2$ are [40]

$$Dd^2a_1/dx^2 - k_1a_1b = 0, \quad (1)$$

$$Dd^2a_2/dx^2 - k_2a_2b = 0, \quad (2)$$

$$Dd^2b/dx^2 - k_1a_1b - k_2a_2b = 0, \quad (3)$$

with the boundary conditions

$$Dda_1/dx \rightarrow J_1, \quad Dda_2/dx \rightarrow J_2, \quad (4)$$

$$b \rightarrow 0 \quad (\text{for } x \rightarrow +\infty),$$

$$a_1 \rightarrow 0, \quad a_2 \rightarrow 0, \quad Ddb/dx \rightarrow -J \quad (\text{for } x \rightarrow -\infty), \quad (5)$$

where D is the diffusivity of the components that are assumed to be the same; a_1 , a_2 , and b are concentrations of the components A_1 , A_2 , and B , respectively; k_1 and k_2 are the constants of the first and second reactions, respectively. Here we assume that the fluxes of the components A_1 , A_2 are directed from the right to the left and J_1 , J_2 are their fluxes at $x \rightarrow +\infty$; the flux of component B is in the opposite direction and has the value $-J$ at $x \rightarrow -\infty$.

Equations (1)–(3) and boundary conditions (4) and (5) can be rewritten in the following dimensionless form:

$$d^2\alpha_1/d\xi^2 - \alpha_1\beta = 0, \quad (6)$$

$$\varepsilon d^2\alpha_2/d\xi^2 - \alpha_2\beta = 0, \quad (7)$$

$$d^2\beta/d\xi^2 - \alpha_1\beta - \alpha_2\beta/\varepsilon = 0, \quad (8)$$

$$d\alpha_1/d\xi \rightarrow j_1, \quad d\alpha_2/d\xi \rightarrow j_2, \quad \beta \rightarrow 0 \quad (\text{for } \xi \rightarrow +\infty), \quad (9)$$

$$\alpha_1 \rightarrow 0, \quad \alpha_2 \rightarrow 0, \quad d\beta/d\xi \rightarrow -1 \quad (\text{for } \xi \rightarrow -\infty), \quad (10)$$

where $a_1 = (Jw_1/D)\alpha_1$, $a_2 = (Jw_1/D)\alpha_2$, $b = (Jw_1/D)\beta$, $x = w_1\xi$, $w_1 = (D^2/k_1J)^{1/3}$ is the characteristic width of the zone of the first reaction, $j_1 = J_1/J$, $j_2 = J_2/J$, and $\varepsilon = k_1/k_2$.

From systems (6)–(8), the following equation can be obtained:

$$d^2\alpha_1/d\xi^2 + d^2\alpha_2/d\xi^2 - d^2\beta/d\xi^2 = 0. \quad (11)$$

Taking into account boundary conditions (9) and (10) and assuming that $\beta = \alpha_1 + \alpha_2$ at $\xi = 0$, the solution of Eq. (11) can be presented in the form

$$\beta = \alpha_1 + \alpha_2 - \xi, \quad (12)$$

and

$$j_1 + j_2 = 1. \quad (13)$$

The system containing three differential equations of second order [Eqs. (6)–(8)] is reduced to the equation system (6), (7), and (12), where the linear relation (12) replaces one of the differential equations.

Let us assume that $\varepsilon \ll 1$ and consider the solution of Eqs. (6), (7), and (12) in a first approximation ($\varepsilon = 0$). Equation (7) is reduced to $\alpha_2\beta = 0$. Taking into account the boundary conditions, we obtain two regions that are assumed to be

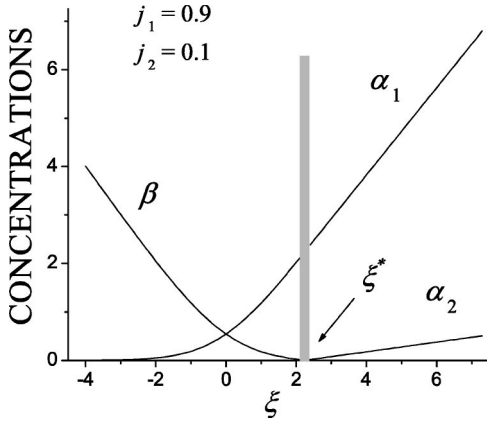


FIG. 1. Profiles of the components given by solution (14) and numerical solution of Eqs. (6) and (15). The zone of the second reaction is marked by a cross-hatch gray region.

separated by some point ξ^* : at $\xi > \xi^*$ $\beta = 0$ and at $\xi < \xi^*$ $\alpha_2 = 0$. The solution for $\xi > \xi^*$ is obtained in the analytical form:

$$\alpha_1 = \xi^* + j_1(\xi - \xi^*), \quad \alpha_2 = j_2(\xi - \xi^*), \quad \beta = 0. \quad (14)$$

At $\xi < \xi^*$ the distribution of the components A_1 and B are determined from the system containing Eq. (6) and

$$d^2\beta/d\xi^2 - \alpha_1\beta = 0, \quad (15)$$

with boundary conditions (10) at $\xi \rightarrow -\infty$. At $\xi = \xi^*$ the boundary conditions are obtained from the continuity of α_1 , β , and $d\alpha_1/d\xi$ at this point:

$$d\alpha_1/d\xi \rightarrow j_1, \quad \beta \rightarrow 0, \quad \alpha_1 \rightarrow \xi^*. \quad (16)$$

The presence of five boundary conditions allows one to find the boundary coordinate ξ^* . The obtained boundary conditions (16) differ from the conditions usually used for the analysis of a single irreversible reaction of the type $A + B \rightarrow C$ [13,16].

Figure 1 shows the numerical solution of Eqs. (6) and (15). The dependence of the coordinate ξ^* on the flux j_2 of the component A_2 is given in Fig. 2. In the framework of the approximation $\varepsilon \ll 1$, the components A_2 and B react in a very narrow region near the point ξ^* (Fig. 1). The influence of the second reaction of A_2 and B components on the first reaction is come to change of the boundary conditions for Eqs. (6) and (15) in the comparison with the case of a single reaction. The first reaction $A_1 + B \rightarrow C_1$ is occurring in the range of $\xi < \xi^*$ only, where the second reaction is absent.

To study the reactions in a narrow zone near $\xi = \xi^*$, we introduce the following variables: $\zeta = (\xi - \xi^*)(j_2/\varepsilon)^{1/3}$; $\alpha_1 = \xi^* + (j_2^2\varepsilon)^{1/3}\mu_1$; $\alpha_2 = (j_2^2\varepsilon)^{1/3}\mu_2$; $\beta = (j_2^2\varepsilon)^{1/3}\eta$ and Eqs. (6)–(8) are rewritten as

$$d^2\mu_1/d\zeta^2 - \xi^*(\varepsilon/j_2)^{2/3}\eta - \varepsilon\mu_1\eta = 0, \quad (17)$$

$$d^2\mu_2/d\zeta^2 - \mu_2\eta = 0, \quad (18)$$

$$d^2\eta/d\zeta^2 - \xi^*(\varepsilon/j_2)^{2/3}\eta - \varepsilon\mu_1\eta - \mu_2\eta = 0. \quad (19)$$

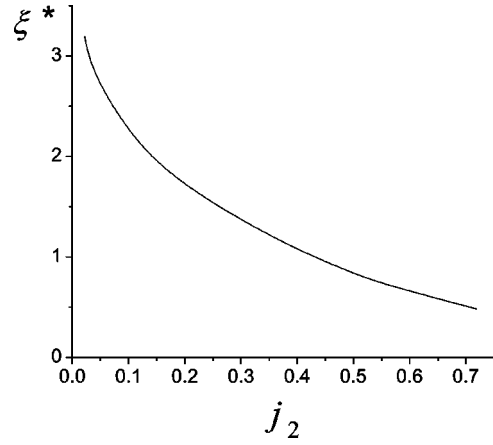


FIG. 2. Dependence of the dimensionless coordinate ξ^* on j_2 .

Systems (17)–(19) contain two dimensionless parameters ε and $\chi = \xi^*(\varepsilon/j_2)^{2/3}$. When $\varepsilon \ll 1$ and $\chi \ll 1$, from Eqs. (17)–(19) we obtain $d^2\mu_1/d\zeta^2 = 0$, i.e., the first reaction $A_1 + B \rightarrow C_1$ can be neglected about the point ξ^* : $\mu_1 = (j_1/j_2)\zeta$. The distribution of the components A_2 and B is given by the solution of the equation system containing Eq. (18) and

$$d^2\eta/d\zeta^2 - \mu_2\eta = 0, \quad (20)$$

obtained from Eq. (19). The boundary conditions can be obtained as the limit of the large scale solution near a point ξ^* :

$$d\mu_2/d\zeta \rightarrow 1, \quad \eta \rightarrow 0 \quad (\text{for } \zeta \rightarrow +\infty), \quad (21)$$

$$\mu_2 \rightarrow 0, \quad d\eta/d\zeta \rightarrow -1 \quad (\text{for } \zeta \rightarrow -\infty). \quad (22)$$

Thus, regarding the considered problem, the second reaction of components A_2 and B occurs in a narrow zone located to the right of the first reaction zone. The first reaction of components A_1 and B can be neglected in the zone of the second one. For the analysis of the second reaction, we can use the well-known dependences obtained for a single reaction in the approximation of an infinite region [13,16]. The separate consideration of the second reaction is possible when both parameters ε and χ are very small simultaneously. As distinct from the parameter ε , the second parameter $\chi = \xi^*(k_1J_1/k_2J_2)^{2/3}$ is determined not only by the ratio of the reaction constants k_1 and k_2 but also by the ratio of the fluxes, J_1 and J_2 , as well as by the coordinate ξ^* .

If $j_2 \ll 1$, the problem of $A_1 + B \rightarrow C_1$ reaction is also reduced to a single reaction in an infinite region. The parameter ξ^* can be determined from the “infinite” solution for $A_1 + B \rightarrow C_1$ reaction at a point where $d\beta/d\xi = -j_2$. The ratio of the maxima of the reaction rates is

$$R_{2max}/R_{1max} \approx (J_2w_1/Jw_2) = j_2^{4/3}/\varepsilon^{1/3}, \quad (23)$$

since the maximum rate of a single reaction is proportional to a component flux and inversely proportional to a characteristic width of the reaction zone [13,16]: $R_{1max} \sim J/w_1$, $R_{2max} \sim J_2/w_2$, and $w_2 = (D^2/k_2J_2)^{1/3}$ is the characteristic width of the zone of the second reaction $A_2 + B \rightarrow C_2$. It has

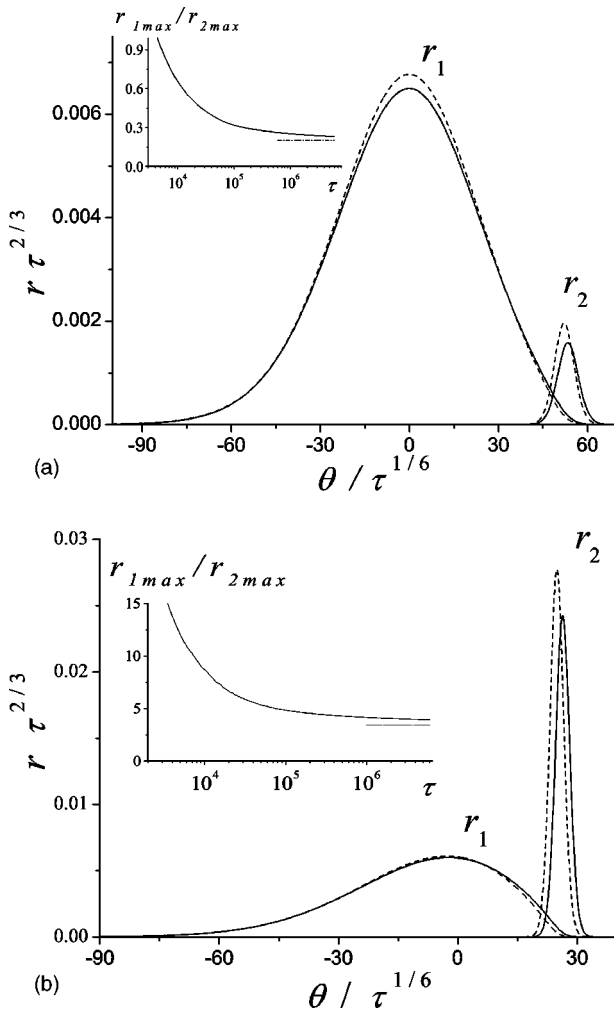


FIG. 3. Reaction rate profiles of r_1 and r_2 given by numerical solution of the dimensionless reaction-diffusion equations for reaction constants $k_1 = 10^{-4}$, $k_2 = 1$, and initial concentration components: (a) $a_{10}/b_0 = 0.97$, $a_{20}/b_0 = 0.03$; and (b) $a_{10}/b_0 = 0.75$, $a_{20}/b_0 = 0.25$. Dashed lines correspond to $\tau = 2 \times 10^5$ and solid curves to $\tau = 2 \times 10^6$. [In the long-time asymptotic the component fluxes used in boundary conditions (4) and (5) are proportional to the initial component concentrations [40].]

been shown that in long-time asymptotic region the component fluxes have the same temporal dependence [1,40] and ratio (23) is independent of time.

Figure 3 presents the results of a numerical solution of the system of the reaction-diffusion equations at long times. The

insets at the left show the temporal dependence of the ratio of the maxima of the reaction rates and illustrate approaching of this ratio to its asymptotic. The dash-dotted lines on these insets mark the asymptotic values obtained from Eq. (23). The reaction-diffusion equations were solved using dimensionless variables: $\theta = x\sqrt{k_2 b_0/D}$, $\tau = tb_0 k_2$, $r_1 = R_1/(k_2 b_0^2)$, and $r_2 = R_1/(k_2 b_0^2)$, and the concentrations were normalized by b_0 . The discrete schematics and algorithm of the calculation are described in Refs. [2,34,35,40]. It is known [40] that the reaction rate is proportional to $\sim \tau^{-2/3}$ and the reaction width is $\sim \tau^{1/6}$ in the long-time asymptotic. Therefore in the coordinates chosen for Fig. 3 the reaction rates and widths should be independent of time. The presented cases show two possible relations between maxima: in the first case the second maximum is lower than the first one, in the second case the relation between the values of the maxima is inverse. In the case presented in Fig. 3(a) the reaction parameters were chosen the same as in Refs. [38,39]. The case presented in Fig. 3(b) differs only by the relation of the initial concentrations. In both cases the results of the numerical calculations and expression (23) give close asymptotic values.

We analyzed the cases of $k_2 \gg k_1$ and obtained two reaction maxima. In another limit, if $k_2 = k_1$, the problem is reduced to the analysis of a single reaction and the reaction rate profile has one maximum at any concentrations of the initial components. One may suppose that there is a critical value of k_2/k_1 separating the regions of existence of single and two maxima. However, it is possible that there is no critical value but there is just a slow crossover between the two reaction-zone regimes. Note that a single maximum can be also observed if the distance between the reaction maxima is small (Fig. 2) and the maxima are not resolvable.

The obtained results can be expanded for the analysis of the reaction processes when the components have various diffusivities. The problem is reduced to Eqs. (1)–(3) using new variables equal to the products of the component concentrations and the diffusivities [13].

In summary, our analysis of two competing irreversible reactions showed that in the asymptotic time region the reaction rate profile could have two maxima and their ratio is independent of time, and what is more important, the second maximum can be higher than the first one. The location and relative value of the second maximum are the functions of the reaction constants k_1 , k_2 and initial concentrations.

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