

Two reaction zones in a competing reactions system with initially separated components

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The long-time properties of a system with initially separated components and two competing reactions, reversible $A_1 + B \leftrightarrow C_1$ and irreversible $A_2 + B \rightarrow C_2$, are studied. It is assumed that the backward constant g_1 of the reversible reaction $A_1 + B \leftrightarrow C_1$ is small. The dynamics of the system is described by means of a crossover from an “irreversible” regime (for times $t \ll g_1^{-1}$) to a “reversible” regime (for times $t \gg g_1^{-1}$). It is shown that in contrast to the “irreversible” regime, where both reactions occur in one reaction zone, the “reversible” regime is characterized by two distinctive reaction zones. These are the $A_1 + B \leftrightarrow C_1$ reversible reaction zone and the $A_2 + C_1 \rightarrow A_1 + C_2$ irreversible reaction zone. Numerical computations of the mean-field kinetic equations confirm these asymptotic results.

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The reaction-diffusion systems with initially separated reactants have recently attracted much attention [1–10]. A series of reactions, both irreversible and reversible, have been studied in the framework of the one reaction zone approach.

The bimolecular irreversible reaction $A + B \rightarrow C$ with initially separated reactants leads to the formation of a distinctive reaction zone [1]. The long-time properties of this reaction zone scale as $x_f \sim t^{1/2}$, $w \sim t^{1/6}$, $R(x_f, t) \sim t^{-2/3}$, and $R(t) \sim t^{-1/2}$, where x_f and w are the center coordinate and the width of the reaction zone, respectively, $R(x_f, t)$ and $R(t) \equiv \int R(x, t) dx$ are the local and the global reaction rates, respectively.

The two competing irreversible reactions $A_1 + B \rightarrow C_1$ and $A_2 + B \rightarrow C_2$ have been used in [5,6] to explain the rich spatio-temporal reaction zone pattern observed in experiment. Recently it was found [10] that the long-time limit of this system is characterized by one reaction zone with a width $\sim t^{1/6}$, where both reactions occur.

The system with a set of two irreversible reactions $A + B \rightarrow R$ and $R + B \rightarrow S$ has been discussed in [7,9] by the numeric method and with simplifying assumptions. In particular, the one reaction zone description was proposed for the long-time limit too [9].

The reversible $A + B \leftrightarrow C$ reaction with initially separated reactants has been considered in [4,8]. The dynamics of the single reaction zone for long times $t \rightarrow \infty$ and the small backward reaction constant $g \rightarrow 0$ is presented as a crossover from the “irreversible” regime at times $t \ll g^{-1}$ to the “reversible” regime at times $t \gg g^{-1}$ [4]. By means of a refined definition of the reaction rate, $R_r(x, t)$ [8], the reversible regime zone properties are characterized by the scale relations $x_f \sim t^{1/2}$, $w \sim t^{1/2}$, $R_r(x_f, t) \sim t^{-1}$, and $R_r(t) \sim t^{-1/2}$. It was also established that the component distributions of the irreversible and the reversible regimes on scale $\sim (Dt)^{1/2}$ are identical.

In this Rapid Communication we study a further degree of complexity of a set of two competing reactions. We assume that one of these reactions is reversible, say $A_1 + B \leftrightarrow C_1$, and we study the long-time asymptotic behavior of this system. It is assumed that the backward reactions constant g_1 of the reversible reaction is small, i.e., $g_1 \rightarrow 0$. The main question is, how does the reversibility of one of the competing reactions change the results for a set of irreversible reactions?

The following is shown: (a) The long-time dynamics of the considered system can be presented as a crossover from the “irreversible” regime $t \ll g_1^{-1}$ to the “reversible” regime $t \gg g_1^{-1}$, similarly to the single reaction case. (b) The irreversible regime $t \ll g_1^{-1}$ coincides with a long-time asymptotic solution for two irreversible competing reactions; both irreversible reactions occur in one reaction zone $\sim t^{1/6}$. (c) The macroscopic pattern of the reversible regime of the considered system drastically changes relative to the irreversible regime. Two new reaction zones, a reversible and an irreversible, separated by the distance $\sim (Dt)^{1/2}$, appear. The reversible zone is the single reversible $A_1 + B \leftrightarrow C_1$ reaction zone. The reaction in the irreversible zone is the total irreversible reaction $A_2 + C_1 \rightarrow A_1 + C_2$. (d) The condition that the front-to-front distance is essentially larger than the reaction zone widths is an outcome of quantitative limitations on the values of time and g_1 in the reversible regime: $g_1 \ll g_{1crit}$ and $t \gg t_{crit}$, where the values g_{1crit} and t_{crit} are functions of the system parameters. (e) Thus, in contrast with the single reaction case of $A + B \leftrightarrow C$, the macroscopic pattern of the system changes through the crossover from an irreversible to a reversible regime. In this way the property of the conservation of the macroscopic quantities is related to only a specific single reaction and does not relate to the multiple reactions case.

The two competing reactions, the reversible and the irreversible with initially separated reactants (A_1, A_2 from the right side and B from the left side) are the following:



The initial concentrations of A_1, A_2 , and B are a_{10}, a_{20} , and b_0 , respectively. The system is described by the following equations:

$$\partial a_1 / \partial t = D \partial^2 a_1 / \partial x^2 - R_1 + g_1 c_1, \quad (3)$$

$$\partial c_1 / \partial t = D \partial^2 c_1 / \partial x^2 + R_1 - g_1 c_1, \quad (4)$$

$$\partial a_2 / \partial t = D \partial^2 a_2 / \partial x^2 - R_2, \quad (5)$$

$$\partial c_2 / \partial t = D \partial^2 c_2 / \partial x^2 + R_2, \quad (6)$$

$$\partial b / \partial t = D \partial^2 b / \partial x^2 - R_1 - R_2 + g_1 c_1, \quad (7)$$

with the initial conditions $a_1(x,0) = a_{10}H(x)$, $a_2(x,0) = a_{20}H(x)$, $b(x,0) = b_0[1 - H(x)]$, and $c_1(x,0) = c_2(x,0) = 0$. Here a_1 , a_2 , b , c_1 , and c_2 are concentrations of A_1 , A_2 , B , C_1 , and C_2 , respectively, and $H(x)$ is the Heaviside function, i.e., $H(x) = 0$, if $x \leq 0$ and $H(x) = 1$, if $x > 0$. In the mean-field approximation we have $R_1 = k_1 a_1 b$, $R_2 = k_2 a_2 b$, where k_1 and k_2 are forward kinetics constants for reactions (1) and (2), respectively.

For simplicity, the same D is assumed for all components. Since the sums $a_1 + c_1$, $a_2 + c_2$, and $b + c_1 + c_2$ are given as

$$a_1 + c_1 = 0.5 a_{10} [1 + \text{erf}(z)] \equiv F_1(z), \quad (8)$$

$$a_2 + c_2 = 0.5 a_{20} [1 + \text{erf}(z)] \equiv F_2(z), \quad (9)$$

$$b + c_1 + c_2 = 0.5 b_0 [1 - \text{erf}(z)] \equiv F_3(z), \quad (10)$$

where $z \equiv x / \sqrt{4Dt}$, $\text{erf}(z) = (2/\sqrt{\pi}) \int_0^z \exp(-u^2) du$.

In the long-time limit $t \rightarrow \infty$, when $t \ll g_1^{-1}$, i.e., in the irreversible regime, the backward term $g_1 c_1$ is canceled, and both reactions become irreversible. The solution on the $\sim (Dt)^{1/2}$ scale is given by [10] for $z < z_0$,

$$\begin{aligned} a_1 = 0, a_2 = 0, \quad b = F_1(z) - F_2(z) - F_3(z), \\ c_1 = F_1(z), \quad c_2 = F_2(z); \end{aligned} \quad (11)$$

for $z > z_0$,

$$a_1 = (F_1 + F_2 - F_3) a_{10} / (a_{10} + a_{20}),$$

$$a_2 = (F_1 + F_2 - F_3) a_{20} / (a_{10} + a_{20}),$$

$$b = 0, \quad c_1 = F_3 a_{10} / (a_{10} + a_{20}), \quad c_2 = F_3 a_{20} / (a_{10} + a_{20}). \quad (12)$$

Here z_0 is defined by the Eq.

$$a_1 + a_2 - b = F_1(z_0) + F_2(z_0) - F_3(z_0) = 0. \quad (13)$$

The component distributions inside region $z \approx z_0$ are described by the quasistatic equations.

For the long-time reversible regime $t \rightarrow \infty$ and $t \gg g_1^{-1}$ the equilibrium relation

$$k_1 a_1 b = g_1 c_1 \quad (14)$$

is true, due to the reversible character of the reaction $A_1 + B \leftrightarrow C_1$. As for the single reversible reaction [8] it is assumed that $g_1 \rightarrow 0$. In this case there is an excess of B or A_1 outside the zone, where the reaction occurs. Assume that the long-time asymptotic solution may be presented on two scales, namely, on the diffusion length scale $\sim (Dt)^{1/2}$ and on the reactions width scale $w \ll (Dt)^{1/2}$. Further, suppose that the long-time behavior of the system is determined by values $a_1 + c_1$, $a_2 + c_2$, and $b + c_1 + c_2$ and the relations between them. The relation between the A_1 and A_2 components and

the B component are determined by the quantity $a_1 + a_2 - b = F_1(z) + F_2(z) - F_3(z)$. Depending on the sign of this expression three regions of the z axis may be considered: (1) $a_1 + a_2 - b < 0$ ($z < z_0$); (2) $a_1 + a_2 - b > 0$; ($z > z_0$); and (3) $a_1 + a_2 - b \approx 0$ ($z \approx z_0$).

In the first region $z < z_0$ an excess of B exists in the long-time limit and no A_1 and A_2 are present at all. So from Eqs. (8)–(10) we obtain the profiles, which are consistent with Eqs. (11).

In the second region $z > z_0$ we have $b \approx 0$ in the long-time limit. Therefore the profiles of the components are described by Eqs. (8), (9), and (14), and also by Eq. (15), which follows from Eq. (10)

$$c_1 + c_2 = F_3(z). \quad (15)$$

An additional equation is required since we have five unknown variables. For convenience Eq. (5) was chosen. Let us substitute Eq. (14) into Eq. (5). The reaction rate R_2 is expressed as $R_2 = (k_2 g_1 a_2 c_1) / (k_1 a_1)$. Assume the value of a_1 in region 2 is not small, which will be confirmed later. Therefore, the expression $R_2 \sim a_2 c_1$ describes an irreversible reaction between A_2 and C_1 inside some reaction zone. Indeed, from Eqs. (14) and (15)

$$\begin{aligned} R_2 &= \partial c_2 / \partial t - D \partial^2 c_2 / \partial x^2 \\ &= -\partial c_1 / \partial t + D \partial^2 c_1 / \partial x^2 \\ &= -R_1 + g_1 c_1 \\ &= -R_{1r}. \end{aligned} \quad (16)$$

This means that the reaction rate of the reversible reaction R_{1r} is negative and equal in magnitude to R_2 in region 2. It follows that the reaction $A_1 + B \leftrightarrow C_1$ sharply deviates to the left and the sum of the reactions $C_1 \leftrightarrow A_1 + B$ and $A_2 + B \rightarrow C_2$, i.e., the total reaction of $A_2 + C_1 \rightarrow A_1 + C_2$, occurs inside the irreversible reaction zone. The coordinate z_1 of this reaction zone, just as for the single irreversible reaction case, is determined by the condition

$$a_2 - c_1 = F_2(z_1) - F_3(z_1) = 0. \quad (17)$$

It may be shown that $z_1 > z_0$.

Taking into account the boundary conditions, it can be shown that $a_2 \approx 0$ to the left and $c_1 \approx 0$ to the right of the irreversible reaction zone. On a macroscopic scale $\sim (Dt)^{1/2}$, i.e., excluding regions $z \approx z_0$ and $z \approx z_1$, we have from Eqs. (8), (9), (14), and (15) expressions (18) and (19) for component profiles. For $z > z_1$,

$$a_1 = F_1(z), \quad a_2 = F_2(z) - F_3(z), \quad c_1 = 0, \quad c_2 = F_3(z); \quad (18)$$

for $z_0 < z < z_1$,

$$\begin{aligned} a_1 &= F_1(z) + F_2(z) - F_3(z), \quad a_2 = 0, \\ c_1 &= F_3(z) - F_2(z), \quad c_2 = F_2(z). \end{aligned} \quad (19)$$

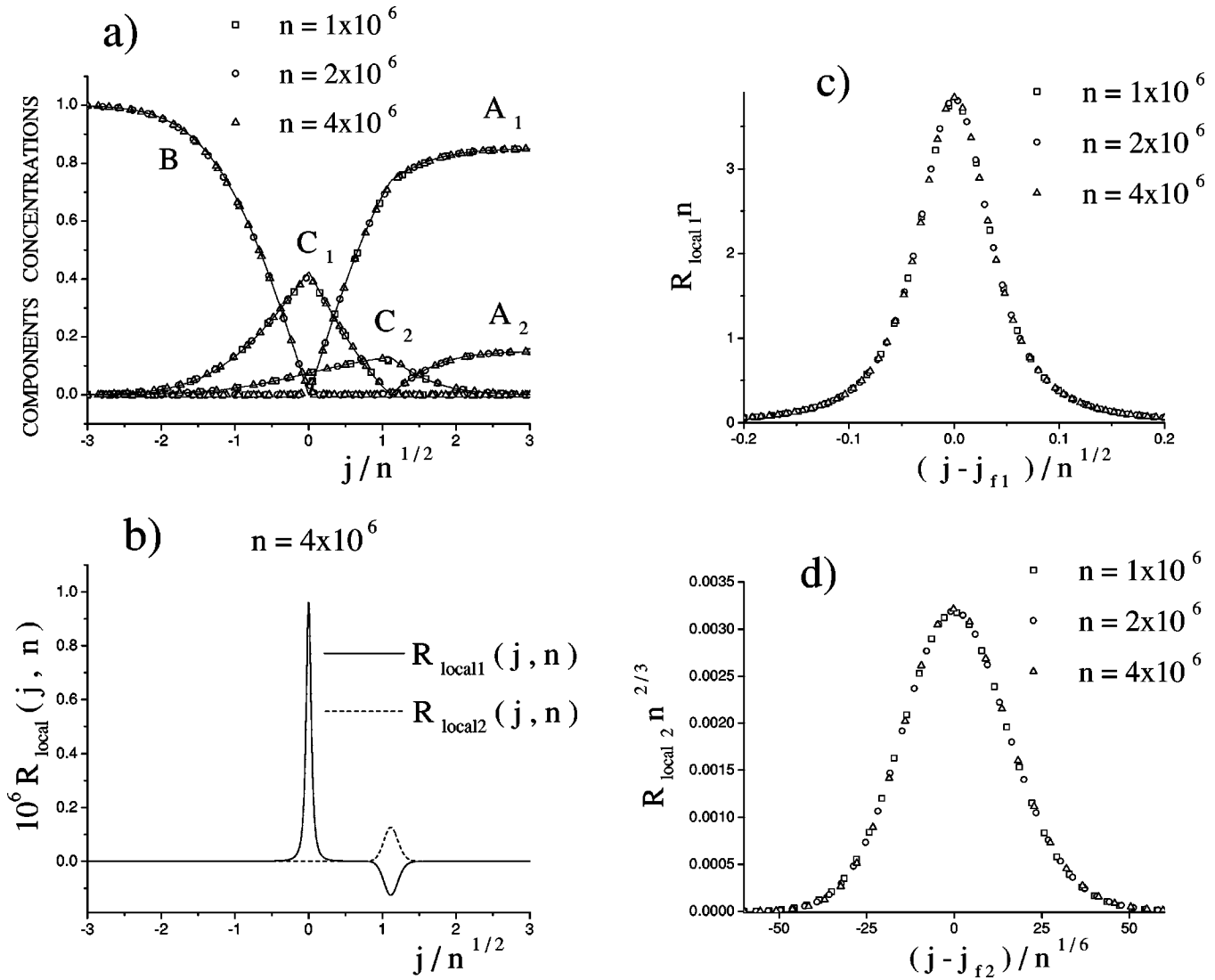


FIG. 1. (a) The A_1 , A_2 , B , C_1 , C_2 profiles, and (b)–(d) the local rate $R_{1l}(j, n)$, and $R_2(j, n)$ profiles calculated by simulation of Eqs. (3)–(7) for the reversible regime $g_1 t \gg 1$ ($k_1 = 1.0$, $k_2 = 1.0$, $g_1 = 10^{-3}$) at times $n = 1 \times 10^6$, 2×10^6 , and 4×10^6 are shown. Asymptotical profiles of the components calculated on the basis of Eqs. (11), (18), and (19) are presented for comparison too (continuous lines). All component concentrations are expressed in units of b_0 . The values of $a_{10}/b_0 = 0.85$ and $a_{20}/b_0 = 0.15$ are used in calculations.

Here z_0 may be interpreted as the coordinate of the $A_1 + B \leftrightarrow C_1$ reaction front. This follows from the components distributions (11), (18), and (19) and the necessity to contact this front with region 1, where there is an excess of the B .

The components profiles inside the reaction zones are described by quasistatic equations and by corresponding boundary conditions, like in Refs. [1,8]. The same form of the quasistatic equations and the boundary conditions determines the same long-time scaling behavior of the reversible reaction front $w_1 \sim t^{1/2}$, $R_{f1}(x_{f1}, t) \sim t^{-1}$, $R_{f1}(t) \sim t^{-1/2}$ [8] and the irreversible reaction front $w_2 \sim t^{1/6}$, $R_2(x_{f2}, t) \sim t^{-2/3}$, $R_2(t) \sim t^{-1/2}$ [1]. Thus, the zone with two reactions ($A_1 + B \rightarrow C_1$ and $A_2 + B \rightarrow C_2$) in the irreversible regime split into two different reaction zones: the $A_1 + B \leftrightarrow C_1$ reversible zone and the $A_2 + C_1 \rightarrow A_1 + C_2$ irreversible zone in the reversible regime.

Note that the reaction front “coordinates” z_0 and z_1 depend on the initial concentrations a_{10} , a_{20} , and b_0 only [see

Eqs. (13) and (17)]. Assuming that $a_{10} + a_{20} \sim b_0$, it can be seen that the magnitude of the front-to-front distance $z_1 - z_0$ relates to the initial concentrations a_{10} , a_{20} as $z_1 - z_0 \sim 1$ if $a_{10} \sim a_{20}$, $z_1 - z_0 \gg 1$ if $a_{10} \gg a_{20}$ and $z_1 - z_0 \ll 1$ if $a_{10} \ll a_{20}$. The value of the distance $z_1 - z_0$ substantially affects time and g_1 for which the reversible description becomes true. Indeed, the magnitudes of the width of the reaction zones $A_1 + B \leftrightarrow C_1$ and $A_2 + C_1 \rightarrow A_1 + C_2$ are determined by the values of time and g_1 . These widths should be small compared to the distance between them: $w_1/(Dt)^{1/2}, w_2/(Dt)^{1/2} \ll z_1 - z_0$. With the evaluations $w_1 \sim (g_1 c_{10} Dt / k_1 a_{10}^2)^{1/2}$ [1] and $w_2 \sim t^{+1/6} D^{1/2} (k_1 a_{11} / g_1 k_2 a_{20})^{1/3}$ [8], the limitations on the time and g_1 values can be written in the form $g_1 \ll g_{1\text{crit}}$ and $t \gg t_{\text{crit}}$, here $g_{1\text{crit}} \sim (z_1 - z_0)^2 k_1 a_{10}^2 / c_{10}$, $t_{\text{crit}} \sim (k_1 a_{11} / g_1 k_2 a_{20}) / (z_1 - z_0)^3$; c_{10} and a_{11} are the C_1 and A_1 concentrations near the reversible and irreversible reaction zones, respectively. From these evaluations it can be shown that the

most convenient condition for observing the two reaction zones in the reversible regime is $z_1 - z_0 \sim 1$.

The validity of the reversible regime description was tested by solving numerically the Eqs. (3)–(7). The exact enumeration method [2,3,8] was used. At first the diffusion step is calculated and then only the reactions are taken into account. The equations describing the reaction step were obtained on the basis of the following approximation without considering the diffusion terms: $a_1(j, n+1) = a_1(j, n) + R_{local}(j)$, where j is the discrete spatial point. The time step is equal to one [2].

A wide range of reaction constants and initial concentrations have been examined. The results of the simulations confirmed the validity of the conditions $z_1 - z_0 \sim 1$, $g_1 \ll g_{1crit}$ and $t \gg t_{crit}$ for the appearance of the two reaction zones in the reversible regime. The simulations of the irreversible regime $g_1 n = 0.1 \ll 1$ confirm the single reaction zone picture described by Eqs. (11) and (12) of Ref. [10] and it is not presented here. The example of the simulations of the reversible regime $g_1 n \gg 1$ is shown in Figs. 1(a)–1(d). The initial concentrations are $a_{10}/b_0 = 0.85$ and $a_{20}/b_0 = 0.15$, such that $z_1 - z_0 = 0.80$. For simplicity the same constants are used, $k_1 = k_2 = 1.0$. (If the constants are different, the time for achieving the reversible regime changes. It can be evaluated by multiplying the simulated time of equal constants by the factor k_1/k_2 . Thus, if we take the experimental value $k_1/k_2 = 250$ [6], for example, then very long simulation time is required for achieving the reversible regime $\sim 250 \times 6 \times 10^4 = 1.5 \times 10^7$. The decrease of this time can be realized in practice by increasing the initial concentration values of the components.) The critical value of the backward reaction constant can be evaluated as $g_{1crit} \sim k_1 a_{10} \sim 1$. It is assumed $g_1 = 10^{-3} \ll g_{1crit}$. All component concentrations and reaction constants are expressed in units of b_0 .

In Fig. 1(a) the calculated profiles of the components are presented in special coordinates of $j/n^{1/2}$ for some periods of times n . It can be seen that the profiles for different time are very close together and to the profiles by Eqs. (11), (18), and

(19). Figure 1(b) illustrates reaction rates distributions at time $n = 4 \times 10^6$. The two distinctive reaction zones can be clearly seen. Notice, the $A_1 + B \leftrightarrow C_1$ reaction rate R_{1r} is equal in magnitude but opposite in sign to the $A_2 + B \rightarrow C_2$ reaction rate R_2 in the irreversible reaction zone in concordance with Eq. (16). In Figs. 1(c) and 1(d) the simulated data of the reaction rates are presented in the appropriate special coordinates $(j - j_{f1})/n^{1/2}$ and $(j - j_{f2})/n^{1/6}$ for some periods of time. The coincidence of the calculated profiles for different times confirms the asymptotic solutions. The following time dependencies are obtained from an analysis of the temporal behavior of the system at times $n \leq 4 \times 10^6$: $w_1 \sim n^{+0.48}$, $w_2 \sim n^{+0.171}$, $R_{rlocal1}(x_{f1}, n) \sim n^{-0.99}$, $R_{local2}(x_{f2}, n) \sim n^{-0.674}$, $(x_{f1} - x_{f2}) \sim n^{+0.51}$, and $R_{rglobal1} \sim R_{global2} \sim n^{-0.50}$. The calculated time exponents are close to the asymptotic solution values.

Note that the time scaling inside the reversible zone $R_{1r}(x_{f1}, t) \sim t^{-1}$ and inside the irreversible reaction zone $R_2(x_{f2}, t) \sim t^{-2/3}$ are essentially different in the reversible regime $g_1 t \gg 1$, while the dependencies of the global reaction rates on time are the same: $R_{r1}(t) \sim t^{-1/2}$ and $R_2(t) \sim t^{-1/2}$. So, we have the relations $R_{r2}(x_{f2}, t)/R_1(x_{f1}, t) \sim t^{-1/3}$ and $R_{r2}(t)/R_1(t) \sim 1$. These relations can be used for comparison of the results of our analysis with an experiment.

Thus, a system with initially separated components and two competing reactions, one a reversible $A_1 + B \leftrightarrow C_1$ and an irreversible $A_2 + B \rightarrow C_2$ are studied. Long-time asymptotic behavior $t \rightarrow \infty$ of the system assuming small $g_1 \rightarrow 0$ is analyzed. The dynamics of the system is presented as a crossover from the irreversible $g_1 t \ll 1$ to the reversible $g_1 t \gg 1$ regime. A heuristic analysis of reaction-diffusion equations confirmed by numerical simulation shows that the system can be described as a two reactions zone pattern in the reversible regime. Thus, the introduction of the reversibility for one of the two competing irreversible reactions results in the appearance of a new reaction zone.

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- [1] L. Gálfi and Z. Rácz, Phys. Rev. A **38**, 3151 (1988).
 [2] H. Taitelbaum, S. Havlin, J.E. Kiefer, B. Trus, and G.H. Weiss, J. Stat. Phys. **65**, 873 (1991).
 [3] H. Larralde, M. Araujo, S. Havlin, and H.E. Stanley, Phys. Rev. A **46**, 855 (1992); **46**, R6121 (1992).
 [4] B. Chopard, M. Droz, T. Karapiperis, and Z. Rácz, Phys. Rev. E **47**, R40 (1993).
 [5] H. Taitelbaum *et al.*, Phys. Rev. Lett. **77**, 1640 (1996).
 [6] A. Yen, A. Lin, Y.E. Koo, B. Vilensky, H. Taitelbaum, and R. Kopelman, J. Phys. Chem. A **101**, 2819 (1997).
 [7] S.M. Cox, M.J. Clifford, and E.P.L. Roberts, Physica A **256**, 65 (1998).
 [8] M. Sinder and J. Pelleg, Phys. Rev. E **60**, R6259 (1999); **61**, 4935 (2000).
 [9] S.M. Cox and M.D. Finn, Phys. Rev. E **63**, 051102 (2001).
 [10] M. Sinder, H. Taitelbaum, and J. Pelleg, Nuclear Instum Methods Phys. Res. B (to be published).