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Behavior of the reaction front between initially segregated species in a two-stage reaction

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The large-time asymptotic behavior of a two-stage reaction ($A+B\rightarrow R,\quad B+R\rightarrow S$) with initially segregated reactants is described. The concentration of the reactants is found to be significantly less than the initial concentrations in a depletion zone of width proportional to $t^{1/2}$, where t is time; the reaction takes place in a thinner zone of width proportional to $t^{1/6}$. Similarity solutions for the chemical concentration profiles in the reaction zone are calculated, and are compared with numerical simulations of the full partial differential reaction-diffusion equations. The large-time asymptotic scalings reported here are the same as in the absence of the secondary reaction, but we find that the location of the reaction zone is significantly shifted due to the secondary reaction. The reaction zone may behave in an exotic fashion at large time, moving first one way, then reversing its direction.

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I. INTRODUCTION

The chemical reaction between initially segregated reactants can depend sensitively upon the manner in which the reactants are brought into contact with each other (see, for example, Ref. [1]). As a consequence, the distribution of products from a multistage reaction process can vary widely according to the way in which the reactants are mixed, and this is of particular concern in the chemical process industry, for example. The simplest prototypical problem involving the reaction and diffusion of initially segregated reactants involves their initial separation by a planar interface, with subsequent evolution depending only on the normal coordinate and time. Such a setup, with the simplest two-stage (also called ''series-parallel'' or ''competitive-consecutive'') reaction scheme, $A+B\rightarrow R,\quad B+R\rightarrow S$, is the subject of this paper.

The single reaction $A+B\rightarrow R$, with such initial conditions, has been thoroughly analyzed in both the small- and large-time limits; numerical simulations have confirmed these analyses and extended them to intermediate times, where no asymptotic treatment is possible [2–18]. The initial segregation of the reactants allows one to identify at early times a reaction front, which in general advances into one or other of the reactants. If the diffusivities of the reactants A and B differ, this reaction front may behave in an exotic fashion [6,7,11,14–17], reversing its direction twice before settling to its large-time behavior, traveling with speed proportional to $t^{-1/2}$. Alternatively, the front may initially move in one direction, then come to a halt. Such exotic behavior is supported by experimental evidence [16].

At large time, a reaction zone, in which the chemical reaction takes place, is surrounded by a rather wider depletion zone, in which the concentration of one or other of the reactants differs significantly from its initial value. In general the reaction zone has width proportional to $t^{1/6}$ and moves with a speed proportional to $t^{-1/2}$; the depletion zone has width proportional to $t^{1/2}$. These results were first derived by Gálfi and Rácz [2] in the case where the diffusivities of the two reactants are equal [6,7,12,13], although, as these authors noted, this restriction is not essential, and, indeed, corresponding results have been derived by other authors when the two diffusivities differ [3,8–10]. A rigorous analysis of the large-time behavior of the $A+B\rightarrow 0$ system has also been given [19].

Of course, the single reaction $A+B\rightarrow 0$ is rather a simple case, and other, more sophisticated reaction schemes with initially segregated components have been analyzed. Reversibility of the reaction [20] gives rise to large-time asymptotic scalings that are simpler than in the irreversible case, with all length scales being diffusive, proportional to $t^{1/2}$; if the backwards reaction proceeds only slowly, there is a crossover between small-time irreversible and large-time reversible regimes [21–23]. A ternary reaction $A+2B\rightarrow C$ [24] and extensions to reaction schemes of the form $mA+nB\rightarrow 0$ [4,25] have been analyzed in the large-time limit, where the asymptotic scalings differ from those of the $A+B\rightarrow 0$ reaction scheme of Gálfi and Rácz [2]. The ternary scheme may be thought of as a limit of our two-stage reaction scheme when the secondary reaction is fast. Experiments and numerical simulations with competing reactions [18] are in excellent agreement.

The structure of the paper is as follows. In Sec. II we introduce the two-stage reaction-diffusion problem to be solved. In Sec. III we examine the asymptotic behavior of the reactions at large time, by analytical and numerical means. Here, the asymptotic results are compared with numerical simulation of the full problem. In Sec. IV we show that exotic behavior of the reaction front is possible before it settles to its large-time behavior, which depends on the initial stoichiometry. Finally, in Sec. V we summarize our conclusions.

II. THE REACTION SCHEME

We consider the influence of a secondary reaction on the progress of a primary reaction between reactants A and B, and hence we examine the two-stage reaction

$$A+B\xrightarrow{k_1}R,\quad B+R\xrightarrow{k_2}S, \tag{1}$$

where k_1 and k_2 are the rates of the two reactions. In practice, of course, there may be many side reactions competing with the primary reaction, but such complexity is not considered here.

We assume that the four chemical species *A*, *B*, *R*, and *S* all have equal diffusivity, *D*. We believe that this assumption is not essential in deriving the large-time asymptotic scalings below, but without it we cannot make such a high degree of analytical progress. We make the problem dimensionless by adopting $(k_1C)^{-1}$ as the time scale and $[D/(k_1C)]^{1/2}$ as the length scale, where *C* is a concentration scale to be specified below. Then the governing equations for one-dimensional diffusion and reaction of the four species are

$$\frac{\partial a}{\partial t}=\frac{\partial^2 a}{\partial x^2}-ab, \tag{2a}$$

$$\frac{\partial b}{\partial t}=\frac{\partial^2 b}{\partial x^2}-ab-\epsilon br, \tag{2b}$$

$$\frac{\partial r}{\partial t}=\frac{\partial^2 r}{\partial x^2}+ab-\epsilon br, \tag{2c}$$

$$\frac{\partial s}{\partial t}=\frac{\partial^2 s}{\partial x^2}+\epsilon br, \tag{2d}$$

where

$$\epsilon=\frac{k_2}{k_1}. \tag{3}$$

We shall be concerned with order-one values of ϵ in addition to the limit $\epsilon\to 0^+$. As an initial condition we suppose that *A* and *B* are initially segregated and that the products *R* and *S* are initially absent, so that

$$a(x,0)=\begin{cases}1 & \text{if} \quad x<0,\\ 0 & \text{if} \quad x>0,\end{cases} \tag{4a}$$

$$b(x,0)=\begin{cases}0 & \text{if} \quad x<0,\\ q & \text{if} \quad x>0,\end{cases} \tag{4b}$$

$$r(x,0)=0, \tag{4c}$$

$$s(x,0)=0. \tag{4d}$$

With this choice of initial condition, the concentration scale *C* is thus the initial concentration of *A* in dimensional units, while qC is the initial concentration of *B* in dimensional units. We apply the boundary conditions

$$a(x,t)-1,b(x,t),r(x,t),s(x,t)\to 0 \quad \text{as} \quad x\to-\infty, \tag{5a}$$

$$a(x,t),b(x,t)-q,r(x,t),s(x,t)\to 0 \quad \text{as} \quad x\to+\infty. \tag{5b}$$

To solve the system (2), (4), and (5), we note that the quantities

$$u(x,t)=2a-b+r, \tag{6a}$$

$$v(x,t)=a+b+2r+3s \tag{6b}$$

satisfy, respectively, the linear diffusion equations

$$\frac{\partial u}{\partial t}=\frac{\partial^2 u}{\partial x^2},$$

$$\frac{\partial v}{\partial t}=\frac{\partial^2 v}{\partial x^2},$$

subject to the initial conditions

$$u(x,0)=\begin{cases}2 & \text{if} \quad x<0,\\ -q & \text{if} \quad x>0,\end{cases}$$

$$v(x,0)=\begin{cases}1 & \text{if} \quad x<0,\\ q & \text{if} \quad x>0.\end{cases}$$

It follows that

$$u=\frac{2-q}{2}-\frac{2+q}{2}\operatorname{erf}\eta, \quad v=\frac{1+q}{2}-\frac{1-q}{2}\operatorname{erf}\eta, \tag{7}$$

where $\eta=xt^{-1/2}/2$. The problem may now be reduced to solving a pair of reaction-diffusion equations,

$$\frac{\partial a}{\partial t}=\frac{\partial^2 a}{\partial x^2}-ab, \tag{8}$$

$$\frac{\partial b}{\partial t}=\frac{\partial^2 b}{\partial x^2}+(2\epsilon-1)ab-\epsilon bu-\epsilon b^2, \tag{9}$$

for *a* and *b* [together with the initial and boundary conditions for these quantities given, respectively, in Eqs. (4) and (5)], with *r* and *s* then being reconstructed from Eq. (6). Note that the single-reaction scheme $A+B\to R$ may be obtained as a special case of the two-stage reaction scheme by setting $\epsilon=0$. The small-time asymptotic solution to this initial-boundary-value problem has been given elsewhere [5], and we now turn to its large-time asymptotic behavior.

III. LARGE-TIME ASYMPTOTIC SOLUTION IN THE REACTION ZONE

Guided by numerical experimentation with the system (2), (4), and (5), and by experience with the simpler single-reaction system of Gálfi and Rácz [2], we suppose that at large times the reaction takes place in a reaction zone centered around $x=x_f$, where

$$x_f=\mu t^{1/2} \tag{10}$$

and μ is a constant to be determined. We seek reactant concentration profiles in the reaction zone of similarity form, with

$$a(x,t)=t^{-\alpha}A(z),\quad b(x,t)=t^{-\beta}B(z),\quad z=(x-x_f)t^{-\gamma}. \tag{11}$$

The exponents α, β, and γ are determined by balancing leading-order terms in the governing equations (8) and (9). Their values can be found by considering (9), which becomes

$$\begin{aligned}-t^{\alpha-1}[\beta B+(\gamma z+\tfrac{1}{2}\mu t^{1/2-\gamma})B']&\\ =t^{\alpha-2\gamma}B''+(2\epsilon-1)AB-u_0\epsilon t^{\alpha}B&\\ +u_1\epsilon z t^{\alpha+\gamma-1/2}B-\epsilon t^{\alpha-\beta}B^2,&\end{aligned} \tag{12}$$

where

$$u_0=\frac{2-q}{2}-\frac{2+q}{2}\operatorname{erf}\tfrac{1}{2}\mu$$

and

$$u_1=\frac{(2+q)\ e^{-\mu^2/4}}{2\pi^{1/2}}$$

are determined by expanding

$$u(x,t)=\frac{2-q}{2}-\frac{2+q}{2}\operatorname{erf}\tfrac{1}{2}(\mu+zt^{\gamma-1/2})$$

in the reaction zone for $|zt^{\gamma-1/2}|\ll 1$. If we are to retain in Eq. (12) the terms representing diffusion, consumption of A and B in the primary reaction, and production of R and S, then we are forced to take

$$\alpha-2\gamma=0=\alpha+\gamma-1/2=\alpha-\beta,$$

and hence

$$\alpha=\beta=2\gamma=\tfrac{1}{3}. \tag{13}$$

This is the same scaling as obtained by Gálfi and Rácz [2] for the single-stage reaction $A+B\rightarrow R$. All terms on the left-hand side of Eq. (12) are then negligible compared with those on the right-hand side. At large times, the term $u_0\epsilon t^{\alpha}B(z)$ dominates all others unless $u_0=0$. Thus we require $u_0=0$; this fixes the value of μ to be given by

$$\operatorname{erf}\tfrac{1}{2}\mu=\frac{2-q}{2+q}, \tag{14}$$

and hence determines the location of the reaction zone, through Eq. (10). It follows that if $q>2$, there is an excess of B and the reaction zone advances *leftwards* into the reservoir of A; conversely, if $q<2$ there is a deficit of B and the reaction zone instead advances *rightwards* into the reservoir of B. The threshold value $q=2$ corresponds to the stoichiometry required for all R to convert to S [5].

With the scaling given by Eq. (13), the leading-order equations to be satisfied by the concentration profile functions A and B are thus

$$A''=AB, \tag{15}$$

$$B''=(1-2\epsilon)AB-u_1\epsilon zB+\epsilon B^2. \tag{16}$$

The choice of correct boundary conditions to apply to this system of equations requires careful consideration. First, it is clear that the concentrations of B and A tend to zero to the left and right of the reaction zone, respectively, so that

$$B\rightarrow 0\quad\text{as}\quad z\rightarrow-\infty,\qquad A\rightarrow 0\quad\text{as}\quad z\rightarrow+\infty. \tag{17}$$

At the right-hand side of the reaction zone, the product R is consumed in the secondary reaction with B, and hence

$$R\rightarrow 0\quad\text{as}\quad z\rightarrow+\infty. \tag{18}$$

In contrast, at the left-hand side of the reaction zone, B is virtually absent and so the secondary reaction does not significantly deplete the concentration of R. Neither does the primary reaction generate significant amounts of R. Thus R is subject to diffusion only: since the diffusion length scale for R is much greater than the width of the reaction zone, it follows that the appropriate boundary condition is

$$R'\rightarrow 0\quad\text{as}\quad z\rightarrow-\infty. \tag{19}$$

We have found supporting evidence for the appropriateness of these boundary conditions by careful analysis of numerical simulations of the full system (2), (4), and (5). Of course, in order to apply the boundary conditions (18) and (19) to the system (15) and (16), we must translate them into boundary conditions on A and B. We do this by applying Eq. (6) and by expanding u around the point $x=x_f$, from which it follows that in the reaction zone $-u_1z\sim 2A-B+R$, and hence Eqs. (18) and (19) are to be replaced by

$$A'\sim-\tfrac{1}{2}u_1\quad\text{as}\quad z\rightarrow-\infty,\qquad B\sim u_1z\quad\text{as}\quad z\rightarrow+\infty. \tag{20}$$

A. The special case $\epsilon=1/2$

Although it seems to have no particular physical significance, the special case $\epsilon=1/2$ simplifies the system to be solved by removing A from the equation for B''. In view of its relative analytical simplicity, we therefore begin by tackling this case. The problem is further simplified by a rescaling with

$$\zeta=\left(\frac{u_1}{2}\right)^{1/3}z$$

and

$$N(\zeta)=\frac{B(z)}{(2u_1^2)^{1/3}},$$

which yields the following boundary-value problem for $N(\zeta)$:

$$N''=N^2-\zeta N,\qquad \begin{cases} N\to 0 & \text{as} \quad \zeta\to-\infty,\\ N\sim\zeta & \text{as} \quad \zeta\to+\infty. \end{cases} \tag{21}$$

The substitution $P(\zeta)=N(\zeta)-\zeta/2$ then makes the problem symmetrical about $\zeta=0$, yielding the boundary-value problem

$$P''=P^2-\tfrac{1}{4}\zeta^2,\qquad \begin{cases} P\sim-\tfrac{1}{2}\zeta & \text{as} \quad \zeta\to-\infty,\\ P\sim\tfrac{1}{2}\zeta & \text{as} \quad \zeta\to+\infty. \end{cases} \tag{22}$$

This problem is readily solved numerically by shooting with the single parameter $P(0)$, since an even solution (as suggested by the boundary conditions) requires $P'(0)=0$. We calculate $P(0)\approx 0.545\,350\,9$.

Remarkably, the same boundary-value problem–Eq. (21) or, equivalently, Eq. (22)–arises in the single-reaction problem ($\epsilon=0$), and has been solved by Gálfi and Rácz [2], whose results are consistent with ours. The value we find for $P(0)$ is also consistent with a rigorous analytical treatment of Eq. (22), which demonstrates that this value lies between 0.53 and 0.57 [19]. Further analytical results relating to the existence and uniqueness of the solution to this boundary-value problem are given by Hastings and McLeod [26] and Holmes [27].

The profile for A remains to be determined. With the rescaling

$$M(\zeta)=\left(\frac{2}{u_1}\right)^{2/3}A(z),$$

we are left to solve

$$M''=2MN,\qquad \begin{cases} M'\sim-1 & \text{as} \quad \zeta\to-\infty,\\ M\to 0 & \text{as} \quad \zeta\to+\infty. \end{cases} \tag{23}$$

This problem is linear in M, a fact that we exploit in finding a numerical solution to Eq. (23) by shooting with just one parameter, despite the second-order nature of the equation. We first compute a solution $M=M_*(\zeta)$ to the equation in (23), choosing $M_*(0)=1$; the parameter $M_*'(0)$ is varied until the asymptotic behavior $M_*\to 0$ as $\zeta\to+\infty$ is achieved. The function M_* automatically acquires a constant slope as $\zeta\to-\infty$ because $N\to 0$ and hence $M''\to 0$ in this limit. This slope does not take the desired value of -1: we can, however, simply scale M_* by a constant factor, so that $M=-M_*/\lim_{\zeta\to-\infty}M_*'$ does satisfy Eq. (23).

B. The general case

In solving numerically the system (15)–(17) and (20) for the special case $\epsilon=1/2$, we were able to exploit special properties of the problem to transform the fourth-order system into two one-parameter shooting problems, both of which involved shooting from the center of the domain. For general values of $\epsilon>0$, however, shooting is not the most appropriate method since the full fourth-order boundary-value problem given by Eqs. (15)–(17) and Eq. (20) must be solved and the most straightforward schemes involve shooting from one edge or other of the domain. The rapid decay of A and B to their large-$|\zeta|$ behaviors makes numerical shooting impractical. Instead, for general values of ϵ we employ a finite-difference approach.

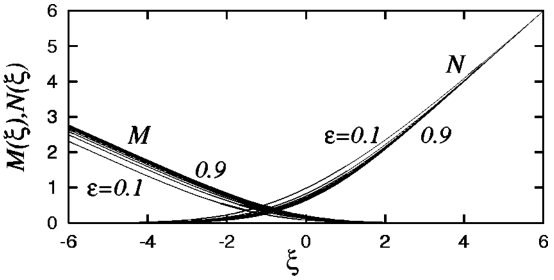

FIG. 1. Scaled profiles for A and B in the reaction zone, for values of ϵ from 0.1 to 0.9 in steps of 0.1, according to Eqs. (25) and (26). All quantities are dimensionless.

As for the case $\epsilon=1/2$ treated above, we find it convenient to rescale the problem to remove the explicit appearance of the constant u_1, so that

$$M(\xi)=u_1^{-2/3}A(z), \tag{24a}$$

$$N(\xi)=u_1^{-2/3}B(z), \tag{24b}$$

$$\xi=u_1^{1/3}z. \tag{24c}$$

(Note that this rescaling differs from that of the previous section.) Then $M(\xi)$ and $N(\xi)$ satisfy

$$M''=MN, \tag{25a}$$

$$N''=(1-2\epsilon)MN-\epsilon\xi N+\epsilon N^2, \tag{25b}$$

subject to the boundary conditions

$$M'(\xi)+\tfrac{1}{2},N(\xi)\to 0 \quad \text{as} \quad \xi\to-\infty, \tag{26a}$$

$$M(\xi),N(\xi)-\xi\to 0 \quad \text{as} \quad \xi\to+\infty. \tag{26b}$$

The resulting profiles are shown in Fig. 1 for values of ϵ between 0.1 and 0.9. As the secondary reaction becomes more rapid (i.e., as ϵ increases), the profiles for A and B in the reaction zone shift to the right (i.e., towards the reservoir of B).

In Fig. 2 we show the excellent agreement between the asymptotic reactant profiles calculated above and direct numerical simulations of Eqs. (2)–(5) at large time ($t=1000$). The parameter values are $\epsilon=0.2$ and $q=1.5$, which correspond to $\mu\approx 0.2546$, and hence the reaction zone is centered about the point $x=x_f$, where $x_f=\mu t^{1/2}\approx 8.05$.

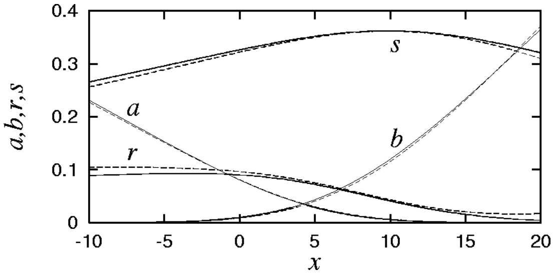

FIG. 2. Comparison between asymptotic and numerical profiles (broken and solid lines, respectively) for *A*, *B*, *R*, and *S* in the reaction zone, with $\epsilon=0.2$ and $q=1.5$, at $t=1000$. The asymptotic profiles are computed from Eqs. (24)–(26) and the numerical profiles from Eqs. (2)–(5). All quantities are dimensionless.

IV. BEHAVIOR OF THE REACTION ZONE

The analysis of Sec. III provides an analytical description of the reaction zone at large times. In this section we discuss the implications of our results, in particular focusing on the differences engendered by the secondary reaction.

For the no-waste reaction scheme of Gálfi and Rácz [2] (i.e., the case $\epsilon=0$), with equal diffusivities of the reactants, the center of the reaction zone $x=x_{\mathrm{GR}}(t)$ is conveniently defined as the point at which $a(x_{\mathrm{GR}},t)=b(x_{\mathrm{GR}},t)$. The *exact* location of the center can be shown to be given by [2]

$$x_{\mathrm{GR}}=\mu_{\mathrm{GR}}t^{1/2}, \tag{27}$$

where

$$\mathrm{erf}\,\tfrac{1}{2}\mu_{\mathrm{GR}}=\frac{1-q}{1+q}. \tag{28}$$

This expression applies for all time and shows that the reaction zone moves monotonically left or right according to whether q is greater than or less than unity.

Two significant results of the analysis of Sec. III are that when a secondary reaction is present (so that $\epsilon>0$) the reaction zone is found at a different location, and, furthermore, that its direction of motion can change with time.

A. Location of the reaction zone in the presence of a secondary reaction

In contrast to the calculation of Gálfi and Rácz [2], our calculation of the reaction zone location for the two-stage reaction is *not* exact, but applies only for asymptotically large times; we find for $\epsilon>0$ that the reaction zone is located at $x_f=\mu t^{1/2}$, where μ is given in (14). Thus at large times the reaction zone moves to the left or right according to the sign of $q-2$. Since

$$\mathrm{erf}\,\tfrac{1}{2}\mu-\mathrm{erf}\,\tfrac{1}{2}\mu_{\mathrm{GR}}=\frac{2q}{(2+q)(1+q)}>0, \tag{29}$$

$\mu>\mu_{\mathrm{GR}}$ and hence the secondary reaction shifts the reaction zone to the right, towards the reservoir of *B*. This is reasonable since the secondary reaction removes *B* from the system, and if the primary reaction is to proceed it must move nearer to the region in which *B* is relatively rich.

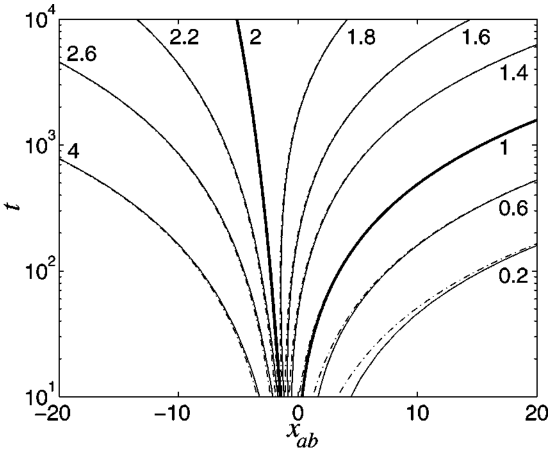

FIG. 3. Large-time motion of the point $x_{ab}(t)$, where $a(x_{ab},t)=b(x_{ab},t)$, for selected values of the parameter *q*. Solid lines show evolution of x_{ab} according to the full problem (2), (4), and (5), for the fixed secondary reaction rate $\epsilon=0.2$; the values of q are marked beside each curve. Dashed lines show our large-time asymptotic estimates for x_{ab}, given in Eq. (30). All quantities are dimensionless.

The equations that determine the location of the reaction zone are Eqs. (27) and (28) for $\epsilon=0$, and Eqs. (10) and (14) for $\epsilon>0$; they demonstrate that the large-time location of the reaction zone with $\epsilon=0$ differs from that with $\epsilon>0$ by an amount of $O(t^{1/2})$, and this difference is independent of the size of ϵ.

To illustrate in more detail the behavior of the reaction zone, we follow Gálfi and Rácz [2], and study the motion of the point $x_{ab}(t)$, where $a(x_{ab},t)=b(x_{ab},t)$; although this point has no particular analytical significance when $\epsilon>0$, it provides a common point of reference inside the reaction zone for various parameter values. It follows from Eqs. (10), (11), (13), and (24) that

$$x_{ab}\sim x_f+u_1^{-1/3}t^{1/6}\xi_{ab}, \tag{30}$$

where ξ_{ab} is defined as the point for which $M(\xi_{ab})=N(\xi_{ab})$ (see Fig. 1). In Fig. 3 we demonstrate the agreement between our calculation of $x_{ab}(t)$ obtained by solving Eqs. (2), (4), and (5) numerically and that derived from Eq. (30).

B. ''Exotic'' behavior of the reaction zone in the presence of a secondary reaction

In deriving the large-time behavior of the reaction zone we have assumed that $t\gg\epsilon^{-3}$; for smaller times than this, the secondary reaction has not proceeded very far, and our analysis does not apply. Indeed, initially the reaction zone for $\epsilon>0$ lies close to its location for $\epsilon=0$ [2], with the perturbation due to the presence of a secondary reaction growing as time advances; in particular, the reaction zone initially moves to the left or right according to the sign of $q-1$. In Fig. 4, we demonstrate the agreement between the

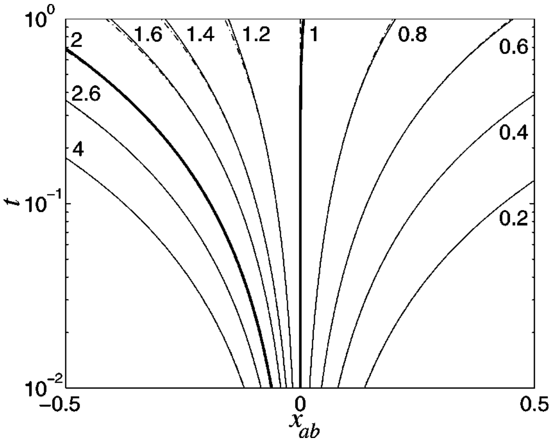

FIG. 4. Small-time motion of the point $x_{ab}(t)$, where $a(x_{ab},t) = b(x_{ab},t)$, for selected values of the parameter q. Solid lines show evolution of x_{ab} according to the full problem (2), (4), and (5), for the fixed secondary reaction rate $\epsilon = 0.2$; the values of q are marked beside each curve. Dashed lines show the exact location of x_{ab} in the corresponding cases, where $\epsilon = 0$ [2]. The secondary reaction causes x_{ab} to be increasingly perturbed to the right of the dashed lines as time increases. All quantities are dimensionless.

small-time behavior of $x_{ab}(t)$ computed numerically from Eqs. (2), (4), and (5) and the analytical behavior computed for $\epsilon = 0$, using Eqs. (27) and (28).

For $\epsilon > 0$, the small-time and large-time asymptotic behaviors of the reaction front do not match, and consequently there is a transition region for $t = O(\epsilon^{-3})$, which we have not analyzed in any detail. The behavior of the reaction zone during this changeover depends on the initial stoichiometry, characterized by the parameter q. Since the quantities $(1-q)/(1+q)$ and $(2-q)/(2+q)$ take different signs when $1 < q < 2$, it follows that in this case (at least for small values of ϵ) the reaction zone initially moves to the left, but then reverses direction to settle into its large-time behavior moving rightwards. For $q < 1$ or $q > 2$, the reaction zone moves monotonically to the right or left, respectively.

This behavior is illustrated in Fig. 5, where numerical simulations of Eqs. (2), (4), and (5), with $\epsilon = 0.2$, show the change of direction of the reaction front to occur at $t \approx 100$ $(\approx \epsilon^{-3} = 125)$, at least for values of q not close to 1 or 2. The reversal in direction of the reaction front at large time is reminiscent of the ''exotic'' *small*-time behavior of the reaction front observed [11,14–17] in a single-stage reaction when the diffusivities of the reactants are not equal.

For the special case $q = 2$, corresponding to the stoichiometry required for the well-mixed reaction to go to completion, the front comes to a halt at asymptotically large times (beyond those displayed in Fig. 3).

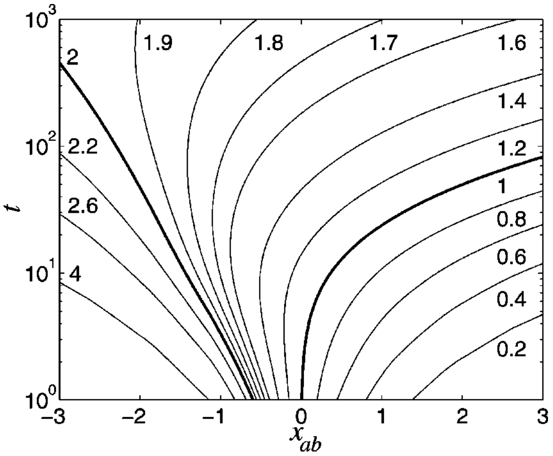

FIG. 5. Transition of $x_{ab}(t)$ between small- and large-time asymptotic behavior for $\epsilon = 0.2$. The point $x_{ab}(t)$, and the reaction zone within which it lies, can exhibit three distinct types of behavior according to the value of the parameter q. For $q < 1$, x_{ab} moves forever to the right, while for $q > 2$ it moves forever leftwards. If q lies between 1 and 2 the point x_{ab} moves intially to the left and then changes direction to move rightwards. All quantities are dimensionless.

V. CONCLUSIONS

We have calculated the large-time asymptotic behavior of the reaction zone for initially segregated chemical species undergoing a two-stage reaction. The location of the reaction zone is significantly altered by the presence of the secondary reaction, regardless of the relative rates of the two reactions. Furthermore the reaction zone may move in different directions at early and late times, with an intermediate transition phase.

Our analysis has been greatly facilitated by the assumption that all the participating chemical species diffuse at the same rate. If this assumption were dropped, we expect that the same large-time scalings would apply, but that there would be the potential for even more exotic behavior of the reaction zone, with more than one change of direction (cf. Refs. [11,14–17]).

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