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Effects of bias on the kinetics of $A+B\rightarrow C$ with initially separated reactants

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The effects of a constant field on the early-time kinetic behavior of the $A+B\rightarrow C$ reaction-diffusion system with initially separated reactants are analyzed. This is in order to account for the pressure effect resulting from the injection of the reactants on both sides of the experimental capillary. The kinetics at early times depends on the magnitude of the field relative to the reaction rate constant, in a suitable set of units. An approximate solution is given for the case in which the effect of the reaction is smaller than that of the bias. We show that the production rate of C is initially proportional to $t^{1/2}$ with a crossover to proportionality to t, a behavior which has been experimentally observed. The converse case, in which the effect of the bias is smaller than that of the reaction, has been studied numerically, and exhibits effects of bias only in the long-time limit. [S1063-651X(96)01411-0]

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I. INTRODUCTION

A considerable literature has developed within the last 15 years on the kinetics of chemical reactions in restricted geometries. Interest in this class of problems is generated by the fact that restricting the geometry can lead to kinetic equations differing substantially from those in general use. Initial theoretical contributions in this area were made by Ovchinnikov and Zeldovich [1] and by Toussaint and Wilczek [2]. A review of recent research directions in this area is to be found in [3]. Much of the literature devoted to the subject assumes an initially uniform mixture of reactant species, a condition which would be difficult to implement in the laboratory. Some time ago Gálfi and Rácz considered the kinetics at long times of a one-dimensional reaction-diffusion system for the reaction $A+B\rightarrow C$ in which the A and B species are initially separated in space rather than being uniformly mixed [4]. This system has been implemented in the capillary experiments of Koo and Kopelman [5]. The experiments were based on optical absorbance profile measurements along the capillary, using a moving system of light source, filters, slit unit, and a photomultiplier tube as a detector (see Fig. 1). Subsequently the theoretical study of this system was extended so as to examine the dynamical behavior of several chemically interesting parameters at short times [6].

Thus far theoretical investigations of the system have mainly been based on a mean-field diffusion-reaction model in which the rate of production of the product C has the form

$$R(x,t)=ka(x,t)b(x,t). \tag{1}$$

In this relation $a(x,t)$ is the local concentration of species A at position x at time t, $b(x,t)$ is the analogous concentration of species B, and k is taken to be a constant. In this framework the equations that govern the reaction kinetics are

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

$$\frac{\partial b}{\partial t}=D_B\frac{\partial^2 b}{\partial x^2}-kab,$$

where D_A and D_B are diffusion constants for species A and B, respectively. The supposition that the species are separated at $t=0$ is built into the initial conditions, which are

$$a(x,0)=a_0H(x), \quad b(x,0)=b_0[1-H(x)]. \tag{3}$$

Here $H(x)$ is the Heaviside step function and a_0 and b_0 are the initial (uniform) concentrations of species A and B, respectively. This mean-field description has been argued by Cornell *et al.* [7] to be valid above an upper critical dimension $d_{\mathrm{up}}=2$, and thus is suitable for experimental systems. Results for systems below this critical dimension, in particular in one dimension, have been obtained by Cornell *et al.* [7] and Araujo *et al.* [8].

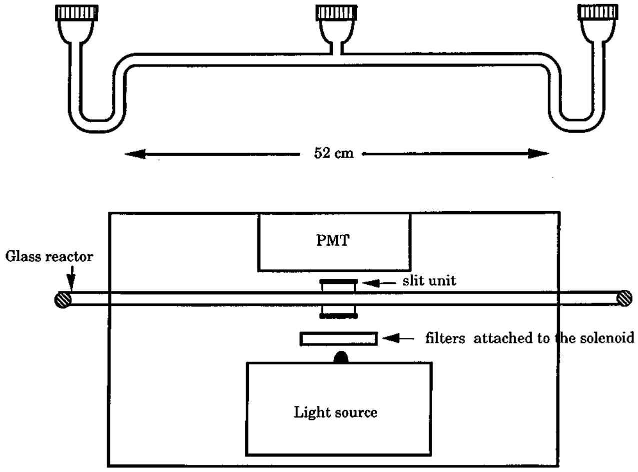

FIG. 1. A view of the experimental system of Koo and Kopelman [5]. The top of the figure is a side view of the glass reactor and the bottom is a top view of the experimental setup.

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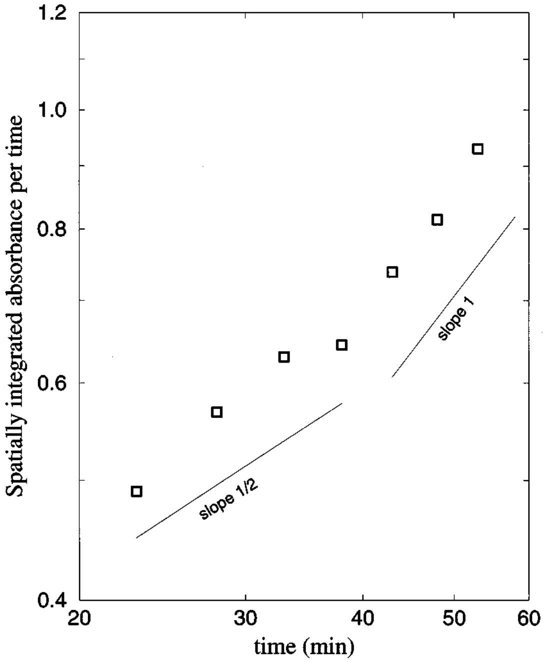

FIG. 2. Experimental results (log-log plot) of the spatially integrated absorbance per time, which is proportional to the global reaction rate $R(t)$. The crossover from $t^{1/2}$ to t behavior is indicated by the two slopes.

Other quantities which can be derived in terms of $R(x,t)$ include the global production rate of C defined by $R(t)=\int_{-\infty}^{+\infty} R(x,t)dx$, the location of the center of the reaction front, $x_f(t)$, i.e., the position at which the local reaction rate is a maximum, and the width of the peak around $x_f(t)$, a quantity to be denoted by $w(t)$. This function, essentially a variance, is defined by

$$w^2(t)=\frac{\int_{-\infty}^{+\infty}[x-x_f(t)]^2R(x,t)dx}{\int_{-\infty}^{+\infty}R(x,t)dx}. \tag{4}$$

The analysis in [6] indicated that at short times (or, equivalently, small k) both $R(t)$ and $w(t)$ are approximately proportional to $t^{1/2}$. Gálfi and Rácz analyzed the behavior of these quantities in the asymptotic regime, finding that $R(t)$ and $w(t)$ fell off at a rate proportional to $t^{-1/2}$ and $t^{1/6}$, respectively.

Some of the predicted dependences on time have been confirmed experimentally [5]. In particular, the possibly surprising nonmonotonic behavior of $x_f(t)$ has been observed for a theoretically predicted set of parameters [9]. However, the initial increase in the global reaction rate has not been clearly obtained. In Fig. 2 we show experimental data for the reaction $\mathrm{Cr}^{3+}+$ Xylenol Orange → product. These reactants have been used in a few experimental studies of the short-time behavior [9,10], due to the noninstantaneous reaction (finite reaction constant k) in this case. In the particular data shown, the initial concentrations are 5×10^{-5} M for Cr^{3+} and 7.5×10^{-4} M for Xylenol Orange. Product formation with time is measured via optical absorption measurements, using the system described in detail in Ref. [5] (see Fig. 1). In Fig. 2 we plot the spatially integrated absorbance per time of the product which is proportional to the global production rate $R(t)$. It can be seen that the initial increase of this quantity consists of two parts, the first is a $t^{1/2}$ behavior, followed by a sharper slope which tends towards a proportionality to t. In the present paper we explore a possible effect for interpreting these experimental data.

In the capillary experiments as schematized in Fig. 1 the two chemical species are injected at the two ends of the tube and pushed towards the center, at which point the reaction-diffusion process begins. Earlier theoretical analyses of this experiment are based on the assumption that the movement of the reacting species is purely diffusive, which is equivalent to there being no residual effects of the initial injection process. The present analysis is based on an assumption that the initial pressure plays a continuing role in determining kinetic behavior. This effect will be modeled in terms of convective terms added to both of the equations in Eq. (2), which leads to the set of equations to be analyzed:

$$\begin{aligned}\frac{\partial a}{\partial t}&=D_A\frac{\partial^2 a}{\partial x^2}+v_A\frac{\partial a}{\partial x}-kab,\\ \frac{\partial b}{\partial t}&=D_B\frac{\partial^2 b}{\partial x^2}-v_B\frac{\partial b}{\partial x}-kab,\end{aligned} \tag{5}$$

in which $v_A\geqslant0$ and $v_B\geqslant0$ are the (constant) velocities caused by the uniform pressures. The initial conditions for this set of equations are just those shown in Eq. (3).

Any type of analysis of the reaction-diffusion equations in Eq. (5) will depend on the magnitudes of v_A and v_B relative to k. We follow our earlier work in deriving an approximate solution to Eq. (5) using a perturbation analysis [6] for systems in which $k<v_A,v_B$. This is equivalent to studying the short-time behavior of the system. The case in which the inequality is reversed proved analytically intractable since the zeroth order equation is nonlinear. One expects that at very long times the global reaction rate should primarily be determined by field effects. However, at very early times the influence of v_A, for example, will only begin to play a role in determining kinetic behavior at a time of the order of $(v_A\sqrt{a_0b_0})^{-1}$. This time would be within the short-time region only for $k<v_A,v_B$. Hence in the following exposition we present an analysis of lowest order effects for this case, and numerical results for the converse case $k>v_A,v_B$.

II. ANALYSIS

The first step in the perturbation analysis is to convert Eq. (5) to dimensionless variables. It will be assumed that D_A and D_B are approximately of the same order of magnitude, as are the pairs (a_0,b_0) and (v_A,v_B). The variables a and b in Eq. (5) will be replaced by dimensionless variables α and β defined by the transformations $a=a_0\alpha$ and $b=b_0\beta$. The two dependent variables, the time t and the spatial variable x, will be replaced by a dimensionless time τ, and a dimensionless distance y which are, respectively, defined by

$$t=\frac{1}{a_0b_0\sqrt{D_AD_B}}\tau,\quad x=\frac{1}{\sqrt{a_0b_0}}y. \tag{6}$$

Finally, we define the dimensionless parameters

$$D=\sqrt{\frac{D_A}{D_B}},\quad v=\frac{v_A}{\sqrt{a_0 b_0 D_A D_B}},\quad \varepsilon=\frac{k}{\sqrt{a_0 b_0 D_A D_B}} \tag{7}$$

and the ratios

$$\theta=\frac{v_B}{v_A},\quad r=\sqrt{\frac{a_0}{b_0}}. \tag{8}$$

The perturbation expansion is based on the assumption that $\varepsilon \ll 1$.

Equation (5) can then be rewritten in terms of these variables as

$$\begin{aligned}\frac{\partial \alpha}{\partial \tau}&=D\frac{\partial^2 \alpha}{\partial y^2}+v\frac{\partial \alpha}{\partial y}-\frac{\varepsilon}{r}\alpha\beta,\\ \frac{\partial \beta}{\partial \tau}&=\frac{1}{D}\frac{\partial^2 \beta}{\partial y^2}-\theta v\frac{\partial \beta}{\partial y}-r\varepsilon\alpha\beta,\end{aligned} \tag{9}$$

which are to be solved subject to the initial conditions $\alpha(y,0)=H(y)$ and $\beta(y,0)=1-H(y)$. The functions $\alpha(y,\tau)$ and $\beta(y,\tau)$ will next be expanded in terms of powers of ε as

$$\alpha(y,\tau)=\sum_{n=0}^{\infty}\alpha_n(y,\tau)\varepsilon^n,\quad \beta(y,\tau)=\sum_{n=0}^{\infty}\beta_n(y,\tau)\varepsilon^n. \tag{10}$$

We consider only the zeroth order functions α_0 and β_0 to see the dominant effects.

It is readily verified that these can be expressed in terms of the normal probability integral

$$\Phi(x)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{x}e^{-u^2/2}du \tag{11}$$

as

$$\begin{aligned}\alpha_0(y,\tau)&=\Phi\left(\frac{y+v\tau}{\sqrt{2D\tau}}\right),\\ \beta_0(y,\tau)&=\Phi\left((\theta v\tau-y)\sqrt{\frac{D}{2\tau}}\right)\end{aligned} \tag{12}$$

so that the lowest order approximation to the global production rate is

$$R_0(\tau)=\frac{\varepsilon}{r}\int_{-\infty}^{+\infty}\Phi\left(\frac{y+v\tau}{\sqrt{2D\tau}}\right)\Phi\left((\theta v\tau-y)\sqrt{\frac{D}{2\tau}}\right)dy. \tag{13}$$

When τ is fixed $\alpha_0(y,\tau)$ increases as a function of y and $\beta_0(y,\tau)$ decreases as a function of y. Hence Eq. (13) can be put into a slightly more transparent form by noting that the maximum value of the integrand occurs at a point to be denoted by y_f. We next transform the variable of integration in Eq. (13) by writing $y=y_f+\rho\sqrt{2\tau}$, which converts Eq. (13) to

$$R_0(\tau)=\frac{\varepsilon}{r}\sqrt{2\tau}\int_{-\infty}^{+\infty}\Phi\left(bv\sqrt{\tau}+\frac{\rho}{\sqrt{D}}\right)\Phi(bv\sqrt{\tau}-\rho\sqrt{D})d\rho, \tag{14}$$

in which

$$b=\frac{\sqrt{D}(1+\theta)}{\sqrt{2}(D+1)}. \tag{15}$$

Hence at very small values of the dimensionless time τ one finds

$$R_0(\tau)\sim\frac{\varepsilon}{r}\sqrt{2\tau}\int_{-\infty}^{+\infty}\Phi\left(\frac{\rho}{\sqrt{D}}\right)\Phi(-\rho\sqrt{D})d\rho, \tag{16}$$

which means that at these times the global reaction rate increases as $\tau^{1/2}$ exactly as in the field-free case treated in [6]. This is to be expected since the bias does not begin to be felt until times of the order of $1/v$.

At longer times when the bias begins to be important [i.e., when $v\tau=O(1)$] we can approximate to the integrand in Eq. (14) by making the crude assumption that it is equal to 1 in the interval $(-bv\sqrt{D\tau},\ bv\sqrt{\tau/D})$ and equal to zero otherwise. The end points of the interval are chosen as the points at which the arguments of the functions in Eq. (12) are equal to zero. This simplification leads to the result that $R_0(\tau)$ increases approximately linearly in time when $v\tau=O(1)$, having the form

$$R_0(\tau)\sim\varepsilon(1+\theta)v\tau, \tag{17}$$

where the coefficient of $v\tau$ is a consequence of our analysis. This linear increase in time of $R_0(\tau)$ is not surprising since the effect of the field must dominate the effect of diffusion in feeding fresh particles of one of the species into the complementary region. Because of the dominating effect of the field only the velocity appears in Eq. (17) while D does not, at least in the lowest order terms.

A comparison of Eqs. (16) and (17) indicates that the crossover time between the diffusive and convective regimes occurs approximately at a time

$$\tau=O(1/v^2). \tag{18}$$

Hence, for chemical systems characterized by $\varepsilon \ll v \ll 1$, i.e., when the field is small but dominant, we expect to see a crossover between Eqs. (16) and (17) at time of the order of v^{-2} as illustrated by the curves in Fig. 3. However, it is obvious that when $v=O(1)\gg\varepsilon$ the diffusive regime will be almost unobservable.

The crossover of the production rate from $t^{1/2}$ to t explains very well the experimental data of Fig. 2 which exhibit the same behavior. This permits a better understanding of the early-time behavior in the capillary experiments. Moreover, Eq. (18) enables one to extract an estimate for the bias strength from the crossover time.

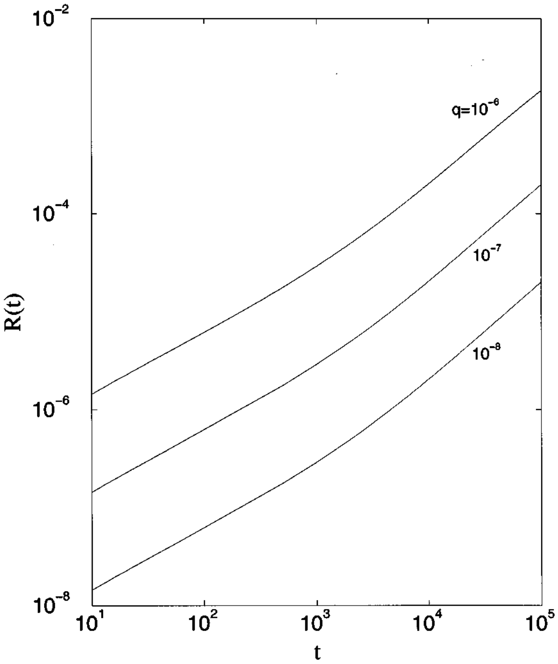

FIG. 3. Curves of the global reaction rate $R(t)$ generated using the split-step algorithm described in [6] for the case $\varepsilon \ll v \ll 1$. The values of the parameters E_A, E_B, q (which are discrete surrogates for v_A, v_B, k) are $E_A = E_B = 10^{-2}$ (fixed) and various $q = 10^{-6}, 10^{-7}, 10^{-8}$. The slope is seen to change from being proportional to $t^{1/2}$ to being proportional to t at times that are the order of E_A^{-2}.

The curves in Fig. 3 were generated by numerically solving a discretized version of the partial differential equations using the split-step algorithm [6]. The numerical algorithm replaces the rates and velocities by event probabilities for the purpose of deriving a numerical solution. Thus the biasing field in the continuum picture is modeled in terms of different probabilities for moving in the positive or negative directions. These are denoted by E_A and E_B, while the reaction rate is replaced by a finite probability of reaction on contact, q.

Using the same algorithm, we find that when $v_A, v_B < k$, the short-time behavior resembles diffusion while the times at which the velocity terms become important are greater than $1/\varepsilon$ so that the bias is significant only at long times. At these times the production rates and the width of the front become independent of time. This behavior is shown in Fig. 4 for the global reaction rate. As can be seen from the upper curve for $E_A = E_B = 10^{-2}$, the crossover due to the bias starts at times of order v^{-1}, and the rate becomes constant at times of order v^{-2}.

III. FIRST CORRECTION TERMS

One can develop approximations to α_1 and β_1 in the same spirit. For simplicity of notation we define the function

$$\begin{aligned} g_0(y,\tau) &= \alpha_0(y,\tau)\beta_0(y,\tau) \\ &= \Phi\left(\frac{y+v\tau}{\sqrt{2D\tau}}\right)\Phi\left((\theta v\tau - y)\sqrt{\frac{D}{2\tau}}\right). \qquad (19) \end{aligned}$$

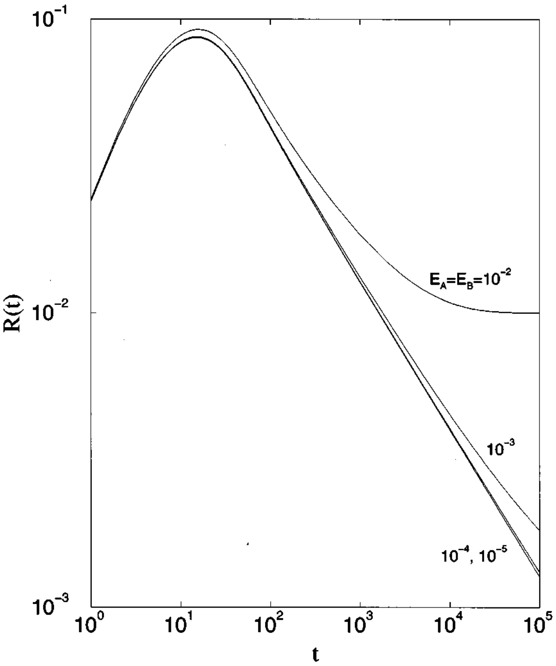

FIG. 4. Curves of the global reaction rate $R(t)$ in the case $v \ll \varepsilon \ll 1$ for $q = 0.1$ (fixed) and various $E_A = E_B = 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}$. As can be seen, at short times the behavior is mainly diffusive and independent of the values of E_A and E_B. The asymptotic behavior tends towards a constant.

The equation satisfied by α_1 is then found from Eq. (9) to be

$$\frac{\partial \alpha_1}{\partial \tau} = D\frac{\partial^2 \alpha_1}{\partial y^2} + v\frac{\partial \alpha_1}{\partial y} - g_0(y,\tau) = L\alpha_1 - g_0(y,\tau), \qquad (20)$$

where L is the indicated diffusion operator. Equation (20) is to be solved subject to the initial condition $\alpha_1(y,0) = 0$. On introducing the Green's function associated with L one finds that $\alpha_1(y,\tau)$ can be expressed as

$$\begin{aligned} \alpha_1(y,\tau) = -\frac{1}{\sqrt{4\pi D}}\int_0^{\tau}\frac{d\tau'}{\sqrt{\tau'}}\int_{-\infty}^{+\infty} g_0(y-\xi,\tau-\tau') \\ \times \exp\left\{-\frac{(\xi + v\tau')^2}{4D\tau'}\right\}d\xi, \qquad (21) \end{aligned}$$

with an analogous formula for $\beta_1(y,\tau)$ except that D is to be replaced by D^{-1}.

An approximation to $\alpha_1(y,\tau)$ based on the small value of τ is also readily calculated. The starting point in the calculation is that at short times the exponential term in Eq. (21) can be approximated by

$$\frac{1}{\sqrt{4\pi D\tau'}}\exp\left\{-\frac{(\xi + v\tau')^2}{4D\tau'}\right\} \sim \delta(\xi + v\tau'). \qquad (22)$$

In this approximation Eq. (21) is replaced by

$$\alpha_1(y,\tau) \sim \int_0^{\tau} g_0(y + v\tau',\ \tau - \tau')d\tau'. \qquad (23)$$

As a second step, in order to get a reasonably compact result we make the further approximation

$$g_0(\rho,\Delta)=\begin{cases}1, & -v\Delta\leqslant\rho\leqslant\theta v\Delta\\ 0, & \text{otherwise}\end{cases}\tag{24}$$

which is equivalent to the approximation utilized in finding the result in Eq. (17). This allows us to evaluate the integral in Eq. (23) exactly,

$$\begin{aligned}\alpha_1(y,\tau)&\sim\min\left\{\frac{\theta v\tau-y}{(1+\theta)v}H(\theta v\tau-y),\tau\right\}\\&=\frac{\theta v\tau-y}{(1+\theta)v}H(\theta v\tau-y),\end{aligned}\tag{25}$$

with a similar result holding for $\beta_1(y,\tau)$. In this equation $H(z)$ is the Heaviside step function. Hence, when y is fixed the time-dependent parts of both $\alpha_1(y,\tau)$ and $\beta_1(y,\tau)$ are essentially proportional to τ. The correction term in the expansion of the global reaction rate,

$$R(\tau)=R_0(\tau)+\varepsilon R_1(\tau)+\cdots,\tag{26}$$

is therefore

$$R_1(\tau)=\int_{-\infty}^{+\infty}[\alpha_0(\xi,\tau)\beta_1(\xi,\tau)+\alpha_1(\xi,\tau)\beta_0(\xi,\tau)]d\xi.\tag{27}$$

On again making use of the approximation $\alpha_0(\xi,\tau)\sim H(y+v\tau)$ we find that $R_1(\tau)\propto\tau^2$ for very small values of τ. This should be contrasted with the result obtained in [6] which does not include a field. In that case we found that $R_1(\tau)\propto\tau^{3/2}$ for small τ. It would therefore appear that the field is the dominant factor in determining the short-time behavior of the global reaction rate.

Similarly the reaction front center, i.e., the position at which the reaction rate is a maximum, is also determined by the field, at least in the zeroth order approximation. To see this we need to maximize the function $g_0(y,\tau)$ defined in Eq. (19) as a function of y. The maximum is seen to occur at $y_f\propto\tau$ which contrasts with the behavior $y_f\propto\tau^{1/2}$ which is the result in the absence of the field.

The final parameter to be considered is the width of the reaction front $w(t)$ as defined in Eq. (4). An approximation to the width is readily calculated taking only the contribution from $R_0(\xi,\tau)$ into account. The calculation closely follows that used to find the global reaction rate $R_0(\tau)$, so we confine ourselves to reporting the results. At short times $w(t)\propto\sqrt{t}$ and at longer times, i.e., at times of order v^{-2}, the field dominates and one finds $w(t)\propto t$. An illustration of this behavior is shown in Fig. 5. As can be seen, the width is independent of the reaction rate constant in times which are smaller than the order of k^{-1}.

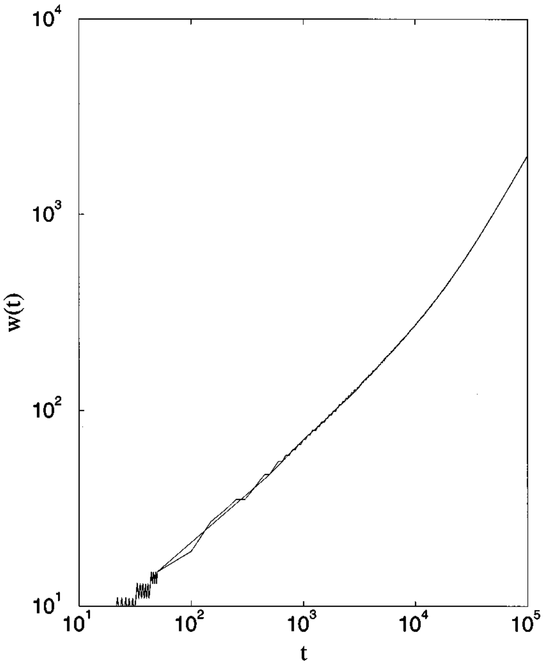

FIG. 5. An illustration of the crossover in the behavior of the width of the reaction front $w(t)$ from being proportional to $t^{1/2}$ to being proportional to t for $\varepsilon\ll v\ll 1$. The parameters are those used to generate Fig. 3, i.e., $E_A=E_B=10^{-2}$ and $q=10^{-6},10^{-7},10^{-8}$. The crossover occurs at time of order E_A^{-2}, and the three curves for various q are indistinguishable at times less than q^{-1}.

IV. DISCUSSION

The results presented in this paper provide a direction to interpret experimental results which do not exhibit pure diffusive kinetic behavior in the system with initially separated reactants. The crossovers in macroscopic dynamic quantities, in particular the global production rate, have already been shown to help in determining the microscopic reaction constant. In this work we have shown how crossovers induced by small bias fields can indicate the existence of such fields and their magnitude relative to the reaction. In the same spirit one can try to control such external fields through the pressure imposed on the reactants on both sides of the capillary. In future work we plan to extend the experimental tests of the theoretical predictions of this paper, as well as to examine the possible case in which the small field effect is not continuous, but rather terminates after some short time.

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