

# Higher-order large-time asymptotics for a reaction of the form $nA+mB\rightarrow C$

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This study examines the large time asymptotic behavior for the family of reactions of the form  $nA+mB\rightarrow C$  when the reactants  $A$  and  $B$  are initially separated. Once the reactants are brought into contact they are assumed to react with a kinetic rate proportional to  $A^n B^m$ . A planar reaction front forms and usually moves away from its initial position to invade one of the reactant solutions. The position of the reaction front relative to the initial position where the reactants were put in contact  $x_f$  for large times  $t$ , is found theoretically to satisfy the expansion  $x_f=2\sqrt{t}[\alpha+\alpha_2 t^{-2\sigma}+\alpha_3 t^{-3\sigma}+O(t^{-4\sigma})]$ , where  $\sigma=1/(n+m+1)$  and  $\alpha$ ,  $\alpha_2$ , and  $\alpha_3$  are constants. This expansion is valid provided that  $n$  and  $m$  are positive constants less than or equal to 3. The implication of this is that when  $n+m\neq 3$ ,  $x_f$  either tends to zero or infinity, while if  $n+m=3$  then there exists the possibility of  $x_f$  tending to a finite nonzero constant. For fractional order kinetics,  $n$  and  $m$  are arbitrary positive constants, however, for simple reactions  $n$  and  $m$  are positive integers. Hence, the reaction  $A+2B\rightarrow C$  is the only reaction of the form  $nA+mB\rightarrow C$  with  $n$  and  $m$  being positive integers less than 4 in an infinite domain that can lead to a reaction front approaching at a finite but nonzero distance from the position at which the two liquids first met.

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## I. INTRODUCTION

The diffusion limited case of the reaction  $A+B\rightarrow C$  was theoretically examined for large times  $t$  by Gálfi and Rácz [1] who found that the position of the reaction front  $x_f$  scaled with  $\sqrt{t}$  and the reaction front width scaled with  $t^{1/6}$ , when the two reactants diffused at the same rate. Both of these results were experimentally verified by Koo and Kopelman [2] in a gel. Recently, similar results have been obtained experimentally using a microfluid reactor [3]. Theoretically, Cornell *et al.* [4,5] went further and examined the family of reactions  $nA+mB\rightarrow C$  to show that the reaction front still moved similar to  $t^{1/2}$  but the reaction front width scaled as  $t^{1/2-\sigma}$ , where  $\sigma=1/(1+n+m)$ . Interestingly, Polanowski and Koza [6] recently examined the case when the diffusion coefficients are functions of the concentrations which is an important first step in modelling the case when the solutions are highly concentrated or when two miscible solutions are employed with each solute diffusing at different rates in each solvent.

In this study the same family of reactions is examined for large times, with the analysis taken beyond leading order to obtain the higher order corrections. The reaction is extended to include fractional order kinetics by allowing each species to have its own kinetic constant. In Sec. II, an outer solution where one of the reactants has been exhausted is asymptotically matched to an inner solution where the reaction takes place. The first order correction to the outer solution is found to be zero and hence the second order correction is the first contributing term. In Sec. III, the solutions obtained in Sec. II are used to obtain the asymptotic position of the front. A special set of solutions are found in which the reaction front position scales with  $t^{1/2-2\sigma}$ . In Sec. IV numerical solutions are compared with the large time analytical asymptotic limits.

## II. MODEL

A liquid contains a reactant  $A$  at concentration  $A_0$  and another liquid contains a reactant  $B$  at concentration  $B_0$ . At time  $t=0$  the two liquids are placed next to each other with the contact surface being planar. The reactants are assumed to react at rates proportional to  $A^n B^m$ . The liquids are assumed to have the same physical properties. By assuming that the liquids remain at rest this reaction is stable to transverse instabilities and hence the problem can be examined in one dimension with the initial position of the reaction front at  $x=0$ . For  $t>0$ , the reaction-diffusion scalings, yield the following dimensionless equations:

$$a_t = a_{xx} - a^n b^m, \quad (1a)$$

$$b_t = \frac{b_{xx}}{r^2} - \psi a^n b^m, \quad (1b)$$

$$c_t = \frac{c_{xx}}{s^2} + \xi a^n b^m, \quad (1c)$$

where  $a$ ,  $b$ , and  $c$  denote the concentration of the species  $A$ ,  $B$ , and  $C$ , respectively, with  $n$ ,  $m$ ,  $r$ ,  $s$ ,  $\psi$ , and  $\xi$  being fixed constants. In dimensional quantities, the molecular diffusion rates  $D_a$ ,  $D_b$ , and  $D_c$  of the species  $A$ ,  $B$ , and  $C$ , respectively, are present through the parameters  $r=\sqrt{D_a/D_b}$  and  $s=\sqrt{D_a/D_c}$ , the kinetic constants for the consumption of  $A$  and  $B$  and production of  $C$  are  $k_a$ ,  $k_b$ , and  $k_c$ , respectively, and are present through the parameters  $\psi=k_b/k_a$  and  $\xi=k_c/k_a$ . The model employed here is a simplified version of that given by Trevelyan *et al.* [7] who examined this problem using immiscible liquids.

For simple reactions,  $n$  and  $m$  are integers and so when the reaction is of the form  $nA+mB \rightarrow C$  then  $\psi \equiv m/n$  and  $\xi \equiv 1/n$ . For fractional order kinetics these simplifying assumptions are not valid and so in general  $\psi$  and  $\xi$  are independent of  $n$  and  $m$ .

The dimensionless initial conditions are

$$a = 1, \quad b = 0, \quad c = 0 \text{ for } x < 0,$$

$$a = 0, \quad b = \phi, \quad c = 0 \text{ for } x > 0$$

with  $\phi = B_0/A_0$  being the ratio of the initial concentrations and  $x=0$  is the location where the two liquids meet at  $t=0$ .

### A. Outer solution

For large times the position of the reaction front is assumed to be located at  $x_f = 2\alpha\sqrt{t}$  where  $\alpha$  is an unknown constant. Outside the reaction zone one of the reactants is exhausted with either  $a$  or  $b$  being zero so that the term  $a^n b^m$  can be neglected. However, a study by Van Baalen *et al.* [8] on these kinds of reactions when  $n=m$  for stationary reaction fronts with equal diffusion coefficients found that the reaction rate  $a^n b^m$  cannot be neglected outside of the reaction front when  $n > 3$ . Further, physically most chemical reactions involve a small number of species and so although the analysis included in this study will extend to say the reaction  $3A+3B \rightarrow C$  the results may be difficult to apply to a realistic reaction. Hence, here we assume that both  $n$  and  $m$  are less than or equal to 3.

Using  $\eta = x/\sqrt{4t}$  the equations in Eq. (2) become

$$-ta_t + \frac{\eta}{2}a_\eta + \frac{a_{\eta\eta}}{4} = 0, \tag{2a}$$

$$-tb_t + \frac{\eta}{2}b_\eta + \frac{b_{\eta\eta}}{4r^2} = 0, \tag{2b}$$

$$-tc_t + \frac{\eta}{2}c_\eta + \frac{c_{\eta\eta}}{4s^2} = 0. \tag{2c}$$

The solution to these equations is sought using large time expansions of  $a$ ,  $b$ , and  $c$  in the form

$$a = a_0(\eta) + \frac{a_1(\eta)}{t^{\mu_1}} + \frac{a_2(\eta)}{t^{\mu_2}} + \frac{a_3(\eta)}{t^{\mu_3}} + O(t^{-\mu_4}), \tag{3a}$$

$$b = b_0(\eta) + \frac{b_1(\eta)}{t^{\mu_1}} + \frac{b_2(\eta)}{t^{\mu_2}} + \frac{b_3(\eta)}{t^{\mu_3}} + O(t^{-\mu_4}), \tag{3b}$$

$$c = c_0(\eta) + \frac{c_1(\eta)}{t^{\mu_1}} + \frac{c_2(\eta)}{t^{\mu_2}} + \frac{c_3(\eta)}{t^{\mu_3}} + O(t^{-\mu_4}), \tag{3c}$$

where  $0 < \mu_1 < \mu_2 < \mu_3 < \mu_4$ . Substituting these expansions into Eq. (2) and retaining terms up to  $O(t^{-\mu_2})$  yields

$$\begin{aligned} & \frac{u_1 a_1}{t^{\mu_1}} + \frac{u_2 a_2}{t^{\mu_2}} + \frac{\eta}{2} \left( a_{0,\eta} + \frac{a_{1,\eta}}{t^{\mu_1}} + \frac{a_{2,\eta}}{t^{\mu_2}} \right) + \frac{1}{4} \left( a_{0,\eta\eta} + \frac{a_{1,\eta\eta}}{t^{\mu_1}} + \frac{a_{2,\eta\eta}}{t^{\mu_2}} \right) \\ & = 0, \end{aligned}$$

$$\begin{aligned} & \frac{u_1 b_1}{t^{\mu_1}} + \frac{u_2 b_2}{t^{\mu_2}} + \frac{\eta}{2} \left( b_{0,\eta} + \frac{b_{1,\eta}}{t^{\mu_1}} + \frac{b_{2,\eta}}{t^{\mu_2}} \right) \\ & + \frac{1}{4r^2} \left( b_{0,\eta\eta} + \frac{b_{1,\eta\eta}}{t^{\mu_1}} + \frac{b_{2,\eta\eta}}{t^{\mu_2}} \right) = 0, \end{aligned}$$

$$\begin{aligned} & \frac{u_1 c_1}{t^{\mu_1}} + \frac{u_2 c_2}{t^{\mu_2}} + \frac{\eta}{2} \left( c_{0,\eta} + \frac{c_{1,\eta}}{t^{\mu_1}} + \frac{c_{2,\eta}}{t^{\mu_2}} \right) \\ & + \frac{1}{4s^2} \left( c_{0,\eta\eta} + \frac{c_{1,\eta\eta}}{t^{\mu_1}} + \frac{c_{2,\eta\eta}}{t^{\mu_2}} \right) = 0. \end{aligned}$$

Collecting terms in powers of  $t$  yields the following sequence of equations:

$$a_{0,\eta\eta} + 2\eta a_{0,\eta} = 0, \quad a_{1,\eta\eta} + 2\eta a_{1,\eta} + 4u_1 a_1 = 0, \tag{4a}$$

$$a_{2,\eta\eta} + 2\eta a_{2,\eta} + 4u_2 a_2 = 0, \tag{4b}$$

$$b_{0,\eta\eta} + 2r^2 \eta b_{0,\eta} = 0, \quad b_{1,\eta\eta} + 2r^2 \eta b_{1,\eta} + 4r^2 u_1 b_1 = 0, \tag{4c}$$

$$b_{2,\eta\eta} + 2r^2 \eta b_{2,\eta} + 4r^2 u_2 b_2 = 0, \tag{4d}$$

$$c_{0,\eta\eta} + 2s^2 \eta c_{0,\eta} = 0, \quad c_{1,\eta\eta} + 2s^2 \eta c_{1,\eta} + 4s^2 u_1 c_1 = 0, \tag{4e}$$

$$c_{2,\eta\eta} + 2s^2 \eta c_{2,\eta} + 4s^2 u_2 c_2 = 0. \tag{4f}$$

Along with  $a=0$  for  $\eta > \alpha$  and  $b=0$  for  $\eta < \alpha$ , the far field boundary conditions are

$$[a_0, a_1, a_2] \rightarrow [1, 0, 0] \text{ as } \eta \rightarrow -\infty, \tag{5a}$$

$$[b_0, b_1, b_2] \rightarrow [\phi, 0, 0] \text{ as } \eta \rightarrow \infty, \tag{5b}$$

$$[c_0, c_1, c_2] \rightarrow [0, 0, 0] \text{ as } |\eta| \rightarrow \infty. \tag{5c}$$

At  $\eta = \alpha$  we impose  $a_0 = b_0 = 0$  and  $c_0$  is continuous to obtain the zeroth order outer solutions

$$a_0 = 1 - \frac{\text{erfc}(-\eta)}{\text{erfc}(-\alpha)}, \quad c_0^L = h \frac{\text{erfc}(-s\eta)}{\text{erfc}(-s\alpha)} \text{ for } \eta < \alpha, \tag{6a}$$

$$\frac{b_0}{\phi} = 1 - \frac{\text{erfc}(r\eta)}{\text{erfc}(r\alpha)}, \quad c_0^R = h \frac{\text{erfc}(s\eta)}{\text{erfc}(s\alpha)} \text{ for } \eta > \alpha \tag{6b}$$

with  $a_0 = 0$  for  $\eta > \alpha$ ,  $b_0 = 0$  for  $\eta < \alpha$ , where  $h$  is an unknown constant and the superscripts  $L$  and  $R$  have been introduced to denote the left and right hand solutions of  $c$ , respectively. These are the same outer solutions given by Koza [9] and Sinder and Pelleg [10]. The first order corrections are given by

$$a_1 = f_1 W_{u_1}(-\eta), \quad c_1^L = h_1 W_{u_1}(-s\eta) \text{ for } \eta < \alpha, \tag{7a}$$

$$b_1 = g_1 W_{u_1}(r\eta), \quad c_1^R = h_2 W_{u_1}(s\eta) \text{ for } \eta > \alpha \tag{7b}$$

with  $a_1 = 0$  for  $\eta > \alpha$ ,  $b_1 = 0$  for  $\eta < \alpha$  and the second order corrections are given by

$$a_2 = f_2 W_{u_2}(-\eta), \quad c_2^L = h_3 W_{u_2}(-s\eta) \text{ for } \eta < \alpha, \quad (8a)$$

$$b_2 = g_2 W_{u_2}(r\eta), \quad c_2^R = h_4 W_{u_2}(s\eta) \text{ for } \eta > \alpha \quad (8b)$$

with  $a_2=0$  for  $\eta > \alpha$ ,  $b_2=0$  for  $\eta < \alpha$ , where  $f_1, g_1, f_2, g_2, h_1, h_2, h_3$ , and  $h_4$  are unknown constants and the function  $W_q$  is a solution of the equation

$$(W_q)_{\eta\eta} + 2\eta(W_q)_\eta + 4qW_q = 0 \quad (9)$$

and  $W_q$  must tend to zero as  $\eta \rightarrow \infty$ . This can easily be solved numerically, for a given  $q$ , to yield a smooth continuous function that decays at both infinities. Known representations of the solution involve confluent hypergeometric functions, see Abramowitz and Stegun [11], however, such representations can have problems at  $\eta=0$ , hence using the Whittaker function in Eqs. (13.1.32) and (13.1.33), in Ref. [11], we can write

$$W_q = \frac{e^{-\eta^2/2}}{\sqrt{\eta}} W_{q-1/4, 1/4}(\eta^2) \text{ for } \eta > 0,$$

$$W_q = \frac{4\sqrt{\pi}}{\Gamma\left(\frac{1}{2}-q\right)} \frac{e^{-\eta^2/2}}{\sqrt{-\eta}} M_{q-1/4, 1/4}(\eta^2)$$

$$+ \frac{e^{-\eta^2/2}}{\sqrt{-\eta}} W_{q-1/4, 1/4}(\eta^2) \text{ for } \eta < 0$$

so that as  $\eta \rightarrow \infty$ ,  $W_q$  decays as  $e^{-\eta^2} \eta^{2q-1}$  and decays proportionally to  $(-\eta)^{-2q}$  as  $\eta \rightarrow -\infty$ . At  $\eta=0$  we have  $W_q = \sqrt{\pi}/\Gamma(1-q)$  and  $(W_q)_\eta = -2\sqrt{\pi}/\Gamma(\frac{1}{2}-q)$ .

### B. Inner solution

The solutions within the reaction zone are established using the inner coordinate  $Z=(\eta-\alpha)t^\sigma$ , where  $\sigma > 0$  so that as  $t$  tends to infinity the term  $Z/t^\sigma$  tends to zero corresponding to  $\eta$  tending to  $\alpha$ . The reaction zone solutions  $(a_l, b_l, c_l)$  are now sought after in a form that can match the outer solution by writing

$$a_l = \frac{A(Z, t)}{t^\gamma}, \quad b_l = \frac{B(Z, t)}{t^\gamma}, \quad c_l = h + \frac{C(Z, t)}{t^\gamma} \quad (10)$$

so that for large times the inner solutions for  $a$  and  $b$  tend to zero whilst  $c$  tends to a finite value,  $h$ . Using Eq. (10), the equations in Eq. (1) become

$$\frac{\gamma A}{t^{2\sigma}} - \frac{tA_t}{t^{2\sigma}} + \left[ \alpha + \frac{1-2\sigma}{t^\sigma} Z \right] \frac{A_Z}{2t^\sigma} + \frac{A_{ZZ}}{4} = \frac{A^n B^m}{t^p}, \quad (11a)$$

$$\frac{\gamma B}{t^{2\sigma}} - \frac{tB_t}{t^{2\sigma}} + \left[ \alpha + \frac{1-2\sigma}{t^\sigma} Z \right] \frac{B_Z}{2t^\sigma} + \frac{B_{ZZ}}{4r^2} = \frac{\psi A^n B^m}{t^p}, \quad (11b)$$

$$\frac{\gamma C}{t^{2\sigma}} - \frac{tC_t}{t^{2\sigma}} + \left[ \alpha + \frac{1-2\sigma}{t^\sigma} Z \right] \frac{C_Z}{2t^\sigma} + \frac{C_{ZZ}}{4s^2} = -\frac{\xi A^n B^m}{t^p}, \quad (11c)$$

where  $p=2\sigma+\gamma(n+m-1)-1$ . We then expand  $A$ ,  $B$ , and  $C$  in the form

$$A = A_0(Z) + \frac{A_1(Z)}{t^{s_1}} + \frac{A_2(Z)}{t^{s_2}} + O(t^{-s_3}), \quad (12a)$$

$$B = B_0(Z) + \frac{B_1(Z)}{t^{s_1}} + \frac{B_2(Z)}{t^{s_2}} + O(t^{-s_3}), \quad (12b)$$

$$C = C_0(Z) + \frac{C_1(Z)}{t^{s_1}} + \frac{C_2(Z)}{t^{s_2}} + O(t^{-s_3}), \quad (12c)$$

where  $0 < s_1 < s_2 < s_3$ . Substituting these expansions into Eq. (11) and retaining terms up to  $O(t^{-2\sigma}, t^{-\sigma-s_1}, t^{-s_2})$  yields

$$\frac{\gamma A_0}{t^{2\sigma}} + (1-2\sigma) \frac{ZA_{0Z}}{2t^{2\sigma}} + \frac{\alpha A_{0Z}}{2t^\sigma} + \frac{\alpha A_{1Z}}{2t^{\sigma+s_1}} + \frac{A_{0ZZ}}{4} + \frac{A_{1ZZ}}{4t^{s_1}}$$

$$+ \frac{A_{2ZZ}}{4t^{s_2}} = \frac{\mathcal{N}}{t^p},$$

$$\frac{\gamma B_0}{t^{2\sigma}} + (1-2\sigma) \frac{ZB_{0Z}}{2t^{2\sigma}} + \frac{\alpha B_{0Z}}{2t^\sigma} + \frac{\alpha B_{1Z}}{2t^{\sigma+s_1}} + \frac{B_{0ZZ}}{4r^2} + \frac{B_{1ZZ}}{4r^2 t^{s_1}}$$

$$+ \frac{B_{2ZZ}}{4r^2 t^{s_2}} = \frac{\psi \mathcal{N}}{t^p},$$

$$\frac{\gamma C_0}{t^{2\sigma}} + (1-2\sigma) \frac{ZC_{0Z}}{2t^{2\sigma}} + \frac{\alpha C_{0Z}}{2t^\sigma} + \frac{\alpha C_{1Z}}{2t^{\sigma+s_1}} + \frac{C_{0ZZ}}{4s^2} + \frac{C_{1ZZ}}{4s^2 t^{s_1}} + \frac{C_{2ZZ}}{4s^2 t^{s_2}}$$

$$= -\frac{\xi \mathcal{N}}{t^p},$$

where  $\mathcal{N}$  is the nonlinear term representing the expansion of  $A^n B^m$ . The expansion for  $\mathcal{N}$  is of the form  $\mathcal{N}_0 + \mathcal{N}_1 t^{-s_1} + \mathcal{N}_{2a} t^{-s_2} + \mathcal{N}_{2b} t^{-2s_1}$ . We notice that the powers of  $t$  present in the equations are  $-2\sigma, -\sigma, -\sigma-s_1, -s_2, -s_1, 0$ , and  $1-2\sigma-\gamma(n+m-1)$ . As  $s_1, s_2$ , and  $\sigma > 0$ , only the leading order kinetic term  $\mathcal{N}_0$  can balance the zeroth order diffusion term, hence  $1=2\sigma+\gamma(n+m-1)$ . Further, as there is only one term of  $O(t^{-\sigma})$ , we require  $s_1=\sigma$ . Similarly the terms of  $O(t^{-2\sigma})$  requires that  $s_2=2\sigma$ . Thus the expansion for  $\mathcal{N}$ , namely,

$$\mathcal{N} = A_0^n B_0^m \left( 1 + \left[ n \frac{A_1}{A_0} + m \frac{B_1}{B_0} \right] t^{-\sigma} + \left[ n \frac{A_2}{A_0} + m \frac{B_2}{B_0} \right] t^{-2\sigma} \right)$$

$$+ A_0^n B_0^m \left[ \frac{n(n-1)}{2} \frac{A_1^2}{A_0^2} + nm \frac{A_1 B_1}{A_0 B_0} + \frac{m(m-1)}{2} \frac{B_1^2}{B_0^2} \right] t^{-2\sigma}$$

will, for convenience, be written as  $\mathcal{N}_0 + \mathcal{N}_1 t^{-\sigma} + \mathcal{N}_2 t^{-2\sigma}$ . Then collecting the terms in powers of  $t$  yields

$$A_{0ZZ} = 4\mathcal{N}_0, \quad A_{1ZZ} + 2\alpha A_{0Z} = 4\mathcal{N}_1, \quad (13a)$$

$$A_{2ZZ} + 2\alpha A_{1Z} + (2-4\sigma)ZA_{0Z} + 4\gamma A_0 = 4\mathcal{N}_2, \quad (13b)$$

$$\frac{\mathcal{B}_{0ZZ}}{r^2} = 4\psi\mathcal{N}_0, \quad \frac{\mathcal{B}_{1ZZ}}{r^2} + 2\alpha\mathcal{B}_{0Z} = 4\psi\mathcal{N}_1, \quad (13c)$$

$$\frac{\mathcal{B}_{2ZZ}}{r^2} + 2\alpha\mathcal{B}_{1Z} + (2-4\sigma)Z\mathcal{B}_{0Z} + 4\gamma\mathcal{B}_0 = 4\psi\mathcal{N}_2, \quad (13d)$$

$$\frac{\mathcal{C}_{0ZZ}}{s^2} = -4\xi\mathcal{N}_0, \quad \frac{\mathcal{C}_{1ZZ}}{s^2} + 2\alpha\mathcal{C}_{0Z} = -4\xi\mathcal{N}_1, \quad (13e)$$

$$\frac{\mathcal{C}_{2ZZ}}{s^2} + 2\alpha\mathcal{C}_{1Z} + (2-4\sigma)Z\mathcal{C}_{0Z} + 4\gamma\mathcal{C}_0 = -4\xi\mathcal{N}_2. \quad (13f)$$

As these equations are nonlinear, analytical solutions are unlikely to be found.

### C. Matching

The inner solution must satisfy their nonlinear equations along with the appropriate matching conditions. The inner solution for  $a$ , given by Eqs. (10) and (12) is

$$a_I = \frac{\mathcal{A}_0}{t^\gamma} + \frac{\mathcal{A}_1}{t^{\gamma+\sigma}} + \frac{\mathcal{A}_2}{t^{\gamma+2\sigma}}. \quad (14)$$

By expanding the outer solution (3) around the reaction front  $\eta=\alpha$  and retaining terms up to  $O(t^{-u_3}, t^{-u_2-\sigma}, t^{-u_1-2\sigma}, t^{-3\sigma})$  yields

$$a = \frac{\bar{a}_1}{t^{u_1}} + \frac{Z\bar{a}_{0\eta}}{t^\sigma} + \frac{\bar{a}_2}{t^{u_2}} + \frac{Z\bar{a}_{1\eta}}{t^{\sigma+u_1}} + \frac{Z^2\bar{a}_{0\eta\eta}}{2t^{2\sigma}} + \frac{\bar{a}_3}{t^{u_3}} + \frac{Z\bar{a}_{2\eta}}{t^{\sigma+u_2}} + \frac{Z^2\bar{a}_{1\eta\eta}}{2t^{2\sigma+u_1}} + \frac{Z^3\bar{a}_{0\eta\eta\eta}}{6t^{3\sigma}}, \quad (15)$$

where the overbar is used to denote that a function is evaluated at  $\eta=\alpha$  and the result  $\bar{a}_0=0$  has been utilized. By comparing powers of  $t$  in the inner solution (14) and the expanded outer solution (15) it is appropriate to choose  $\sigma=\gamma=u_1$ ,  $u_2=2\sigma$ , and  $u_3=3\sigma$ . Hence, equating coefficients in powers  $t$  leads to the following matching conditions as  $Z \rightarrow -\infty$ :

$$\mathcal{A}_0 \rightarrow \bar{a}_1 + Z\bar{a}_{0\eta}, \quad \mathcal{A}_1 \rightarrow \bar{a}_2 + Z\bar{a}_{1\eta} + \frac{Z^2}{2}\bar{a}_{0\eta\eta}, \quad (16a)$$

$$\mathcal{A}_2 \rightarrow \bar{a}_3 + Z\bar{a}_{2\eta} + \frac{Z^2}{2}\bar{a}_{1\eta\eta} + \frac{Z^3}{6}\bar{a}_{0\eta\eta\eta}, \quad (16b)$$

$$\mathcal{C}_0 \rightarrow \bar{c}_1^L + Z\bar{c}_{0\eta}^L, \quad \mathcal{C}_1 \rightarrow \bar{c}_2^L + Z\bar{c}_{1\eta}^L + \frac{Z^2}{2}\bar{c}_{0\eta\eta}^L, \quad (16c)$$

$$\mathcal{C}_2 \rightarrow \bar{c}_3^L + Z\bar{c}_{2\eta}^L + \frac{Z^2}{2}\bar{c}_{1\eta\eta}^L + \frac{Z^3}{6}\bar{c}_{0\eta\eta\eta}^L, \quad (16d)$$

with  $\mathcal{B}_0 \rightarrow 0, \mathcal{B}_1 \rightarrow 0$ , and  $\mathcal{B}_2 \rightarrow 0$ . Similarly, the matching conditions as  $Z \rightarrow \infty$  are

$$\mathcal{B}_0 \rightarrow \bar{b}_1 + Z\bar{b}_{0\eta}, \quad \mathcal{B}_1 \rightarrow \bar{b}_2 + Z\bar{b}_{1\eta} + \frac{Z^2}{2}\bar{b}_{0\eta\eta}, \quad (17a)$$

$$\mathcal{B}_2 \rightarrow \bar{b}_3 + Z\bar{b}_{2\eta} + \frac{Z^2}{2}\bar{b}_{1\eta\eta} + \frac{Z^3}{6}\bar{b}_{0\eta\eta\eta}, \quad (17b)$$

$$\mathcal{C}_0 \rightarrow \bar{c}_1^R + Z\bar{c}_{0\eta}^R, \quad \mathcal{C}_1 \rightarrow \bar{c}_2^R + Z\bar{c}_{1\eta}^R + \frac{Z^2}{2}\bar{c}_{0\eta\eta}^R, \quad (17c)$$

$$\mathcal{C}_2 \rightarrow \bar{c}_3^R + Z\bar{c}_{2\eta}^R + \frac{Z^2}{2}\bar{c}_{1\eta\eta}^R + \frac{Z^3}{6}\bar{c}_{0\eta\eta\eta}^R, \quad (17d)$$

with  $\mathcal{A}_0 \rightarrow 0, \mathcal{A}_1 \rightarrow 0$ , and  $\mathcal{A}_2 \rightarrow 0$ .

### 1. Zeroth order

Now, the leading order inner equations in Eq. (13) can be written as

$$4\mathcal{N}_0 = \mathcal{A}_{0ZZ} = \frac{\mathcal{B}_{0ZZ}}{\psi r^2} = -\frac{\mathcal{C}_{0ZZ}}{\xi s^2}.$$

Two of these equations are linear allowing them to be directly integrated twice, then using the conditions as  $Z \rightarrow -\infty$  from Eq. (16) yields

$$\mathcal{A}_0 - \bar{a}_1 - Z\bar{a}_{0\eta} = \frac{\mathcal{B}_0}{\psi r^2} = \frac{\bar{c}_1^L + Z\bar{c}_{0\eta}^L - \mathcal{C}_0}{\xi s^2}. \quad (18)$$

Then using the conditions as  $Z \rightarrow \infty$  from Eq. (17) in Eq. (18) yields the conditions

$$-\bar{a}_{0\eta} = \frac{\bar{b}_{0\eta}}{\psi r^2} = \frac{\bar{c}_{0\eta}^L - \bar{c}_{0\eta}^R}{\xi s^2}, \quad -\bar{a}_1 = \frac{\bar{b}_1}{\psi r^2} = \frac{\bar{c}_1^L - \bar{c}_1^R}{\xi s^2}. \quad (19)$$

Using Eq. (6) the first two equations become

$$\frac{e^{\alpha^2 r^2} \operatorname{erfc}(r\alpha)}{e^{\alpha^2} \operatorname{erfc}(-\alpha)} = \frac{\phi}{\psi r}, \quad h = \frac{\xi s e^{\alpha^2 s^2} \operatorname{erfc}(s\alpha) \operatorname{erfc}(-s\alpha)}{2e^{\alpha^2} \operatorname{erfc}(-\alpha)}. \quad (20)$$

The first equation is equivalent to Eq. 24 of Koza [9] when  $\psi = \frac{m}{n}$ , it must be numerically solved for  $\alpha$ . The second equation is a generalized version of Eq. (14) Sinder and Pelleg [10] for the reaction  $A+B \rightarrow C$ , it defines  $h$ , the maximum concentration of the product. The final two equations in Eq. (19) provide matching conditions for the first order outer solutions.

The matching conditions for the integrals of the zeroth order outer solutions are required. We define the integrals

$$I_A = \int_{-\infty}^Z \mathcal{A}_0 dZ, \quad I_B = \int_{-\infty}^Z \mathcal{B}_0 dZ, \quad I_C = \int_0^Z \mathcal{C}_0 dZ.$$

Using the matching conditions as  $Z \rightarrow -\infty$  from Eq. (16) we obtain

$$I_A \rightarrow \beta_a + Z\bar{a}_1 + \frac{Z^2}{2}\bar{a}_{0\eta}, \quad I_C \rightarrow \beta_c^L + Z\bar{c}_1^L + \frac{Z^2}{2}\bar{c}_{0\eta}^L, \quad (21a)$$

and as  $Z \rightarrow \infty$  from Eq. (17) we obtain

$$I_B \rightarrow \beta_b + Z\bar{b}_1 + \frac{Z^2}{2}\bar{b}_{0\eta}, \quad I_C \rightarrow \beta_c^R + Z\bar{c}_1^R + \frac{Z^2}{2}\bar{c}_{0\eta}^R \quad (21b)$$

with  $I_B \rightarrow 0$  as  $Z \rightarrow -\infty$ ,  $I_A \rightarrow 0$  as  $Z \rightarrow \infty$  and where  $\beta_a$ ,  $\beta_b$ ,  $\beta_c^L$ , and  $\beta_c^R$  are four unknown constants. Integrating Eq. (18) and using the conditions as  $Z \rightarrow -\infty$  in Eq. (21a) yields

$$I_A - \beta_a - Z\bar{a}_1 - \frac{Z^2}{2}\bar{a}_{0\eta} = \frac{I_B}{\psi r^2} = \frac{\beta_c^L + Z\bar{c}_1^L + \frac{Z^2}{2}\bar{c}_{0\eta}^L - I_C}{\xi s^2}.$$

Then using the conditions as  $Z \rightarrow \infty$  in Eq. (21b) yields the conditions

$$-\beta_a = \frac{\beta_b}{\psi r^2} = \frac{\beta_c^L - \beta_c^R}{\xi s^2}. \quad (22)$$

### 2. First order

The first order inner equations in Eq. (13) are

$$4\mathcal{N}_1 = \mathcal{A}_{1ZZ} + 2\alpha\mathcal{A}_{0Z} = \frac{\mathcal{B}_{1ZZ}}{\psi r^2} + \frac{2\alpha}{\psi}\mathcal{B}_{0Z} = -\frac{\mathcal{C}_{1ZZ}}{\xi s^2} - \frac{2\alpha}{\xi}\mathcal{C}_{0Z}.$$

Two of these equations are linear allowing them to be directly integrated twice then using the conditions as  $Z \rightarrow -\infty$  from Eq. (16) yields

$$\begin{aligned} \frac{\mathcal{B}_1 + 2r^2\alpha I_B}{\psi r^2} &= \mathcal{A}_1 + 2\alpha I_A - (\bar{a}_{1\eta} + 2\alpha\bar{a}_1)Z - \bar{a}_2 - 2\alpha\beta_a \\ &= \frac{(\bar{c}_{1\eta}^L + 2s^2\alpha\bar{c}_1^L)Z + \bar{c}_2^L + 2s^2\alpha\beta_c^L - \mathcal{C}_1 - 2s^2\alpha I_C}{\xi s^2}, \end{aligned}$$

where the results  $\bar{a}_{0\eta\eta} + 2\alpha\bar{a}_{0\eta} = 0$  and  $\bar{c}_{0\eta\eta}^L + 2s^2\alpha\bar{c}_{0\eta}^L = 0$  have been used. Then using the conditions as  $Z \rightarrow \infty$  from Eq. (17) yields the conditions

$$\frac{\bar{b}_{1\eta}}{\psi r^2} + 2\alpha\bar{a}_1(1-r^2) = -\bar{a}_{1\eta} = \frac{\bar{c}_{1\eta}^L - \bar{c}_{1\eta}^R}{\xi s^2} + 2\alpha\bar{a}_1(1-s^2), \quad (23)$$

$$\frac{\bar{b}_2}{\psi r^2} + 2\alpha\beta_a(1-r^2) = -\bar{a}_2 = \frac{\bar{c}_2^L - \bar{c}_2^R}{\xi s^2} + 2\alpha\beta_a(1-s^2), \quad (24)$$

where Eqs. (19) and (22) and the results  $\bar{b}_{0\eta\eta} + 2r^2\alpha\bar{b}_{0\eta} = 0$  and  $\bar{c}_{0\eta\eta}^R + 2s^2\alpha\bar{c}_{0\eta}^R = 0$  have been used.

The matching conditions for the first order outer solutions, see Eq. (7), are given by Eqs. (19) and (23). These two homogeneous boundary conditions lead to a trivial solution with  $f_1 = g_1 = h_1 = h_2 = 0$ , i.e.,

$$a_1 \equiv b_1 \equiv c_1^L \equiv c_1^R = 0.$$

Thus to obtain the first nontrivial correction to the outer solution the next term in the expansion is needed which requires an additional matching condition from the second order inner solution.

### 3. Second order

The second order inner equations in Eq. (13) are

$$\begin{aligned} 4\mathcal{N}_2 &= \mathcal{A}_{2ZZ} + 2\alpha\mathcal{A}_{1Z} + 4\sigma\mathcal{A}_0 + (2-4\sigma)Z\mathcal{A}_{0Z} \\ &= \frac{\mathcal{B}_{2ZZ}}{\psi r^2} + \frac{2\alpha}{\psi}\mathcal{B}_{1Z} + \frac{4\sigma}{\psi}\mathcal{B}_0 + (2-4\sigma)\frac{Z}{\psi}\mathcal{B}_{0Z} \\ &= -\frac{\mathcal{C}_{2ZZ}}{\xi s^2} - \frac{2\alpha}{\xi}\mathcal{C}_{1Z} - \frac{4\sigma}{\xi}\mathcal{C}_0 - (2-4\sigma)\frac{Z}{\xi}\mathcal{C}_{0Z}. \end{aligned}$$

Two of these equations are linear, after integrating once and using the conditions as  $Z \rightarrow -\infty$  from Eq. (16) yields

$$\begin{aligned} \mathcal{A}_{2Z} - \bar{a}_{2\eta} + 2\alpha(\mathcal{A}_1 - \bar{a}_2) + (2-4\sigma)Z\mathcal{A}_0 + (8\sigma-2)(I_A - \beta_a) \\ &= \frac{\mathcal{B}_{2Z}}{\psi r^2} + \frac{2\alpha}{\psi}\mathcal{B}_1 + (2-4\sigma)\frac{Z}{\psi}\mathcal{B}_0 + (8\sigma-2)\frac{I_B}{\psi}, \\ &= \frac{\bar{c}_{2\eta}^L - \mathcal{C}_{2Z}}{\xi s^2} + \frac{2\alpha}{\xi}(\bar{c}_2^L - \mathcal{C}_1) - (2-4\sigma)\frac{Z}{\xi}\mathcal{C}_0 \\ &\quad - (8\sigma-2)\frac{I_C - \beta_c^L}{\xi}, \end{aligned}$$

where the results  $\bar{a}_{0\eta\eta\eta} + 2\alpha\bar{a}_{0\eta\eta} + 2\bar{a}_{0\eta} = 0$ ,  $\bar{a}_{1\eta\eta} + 2\alpha\bar{a}_{1\eta} + 4\sigma\bar{a}_1 = 0$ ,  $\bar{c}_{0\eta\eta\eta}^L + 2s^2\alpha\bar{c}_{0\eta\eta}^L + 2s^2\bar{c}_{0\eta}^L = 0$ , and  $\bar{c}_{1\eta\eta}^L + 2\alpha s^2\bar{c}_{1\eta}^L + 4\sigma s^2\bar{c}_1^L = 0$  have been used. Then using the conditions as  $Z \rightarrow \infty$  from Eq. (17) yields the conditions

$$\begin{aligned} -\bar{a}_{2\eta} - 2\alpha\bar{a}_2 &= \frac{\bar{c}_{2\eta}^L - \bar{c}_{2\eta}^R}{\xi s^2} + \frac{2\alpha}{\xi}(\bar{c}_2^L - \bar{c}_2^R) + (8\sigma-2)\beta_a(1-s^2), \\ &= \frac{\bar{b}_{2\eta}}{\psi r^2} + \frac{2\alpha}{\psi}\bar{b}_2 + (8\sigma-2)\beta_a(1-r^2), \end{aligned} \quad (25)$$

where Eq. (22) and the results  $\bar{b}_{0\eta\eta\eta} + 2r^2\alpha\bar{b}_{0\eta\eta} + 2r^2\bar{b}_{0\eta} = 0$ ,  $\bar{b}_{1\eta\eta} + 2r^2\alpha\bar{b}_{1\eta} + 4r^2\sigma\bar{b}_1 = 0$ ,  $\bar{c}_{0\eta\eta\eta}^R + 2s^2\alpha\bar{c}_{0\eta\eta}^R + 2s^2\bar{c}_{0\eta}^R = 0$ , and  $\bar{c}_{1\eta\eta}^R + 2\alpha\bar{c}_{1\eta}^R + 4\sigma\bar{c}_1^R = 0$  have been used.

The matching conditions on the second order outer solutions given in Eq. (8) are given by Eqs. (24) and (25). First we obtain

$$f_2 = \frac{2\beta_a(r^2-1)\left(2r^2\alpha^2+1-4\sigma+r\alpha\frac{W_\eta(r\alpha)}{W(r\alpha)}\right)}{W(-\alpha)\left(2\alpha(r^2-1)+\frac{W_\eta(-\alpha)}{W(-\alpha)}+r\frac{W_\eta(r\alpha)}{W(r\alpha)}\right)}, \quad (26a)$$

$$g_2 = \frac{2\beta_a\psi(1-r^2)\left(2\alpha^2+1-4\sigma-\alpha\frac{W_\eta(-\alpha)}{W(-\alpha)}\right)}{W(r\alpha)\left(2\alpha(r^2-1)+\frac{W_\eta(-\alpha)}{W(-\alpha)}+r\frac{W_\eta(r\alpha)}{W(r\alpha)}\right)}, \quad (26b)$$

where for convenience we use  $W$  to denote the function  $W_{2\sigma}$ . Equation (26) define the outer solutions  $a_2$  and  $b_2$ . Then we can obtain the solutions for  $c_2^L$  and  $c_2^R$  from the constants



$$h_3 = \frac{\xi s W(s\alpha) f_2 W(-\alpha) \left( 2\alpha - \frac{W_\eta(-\alpha)}{W(-\alpha)} - s \frac{W_\eta(s\alpha)}{W(s\alpha)} \right)}{W(s\alpha) W_\eta(-s\alpha) + W_\eta(s\alpha) W(-s\alpha)} + \frac{2\xi s W(s\alpha) \alpha \beta_a (1-s^2) \left( 1 - s \frac{W_\eta(s\alpha)}{W(s\alpha)} \right)}{W(s\alpha) W_\eta(-s\alpha) + W_\eta(s\alpha) W(-s\alpha)}, \quad (27a)$$

$$h_4 = \frac{\xi s W(-s\alpha) f_2 W(-\alpha) \left( 2\alpha - \frac{W_\eta(-\alpha)}{W(-\alpha)} + s \frac{W_\eta(-s\alpha)}{W(-s\alpha)} \right)}{W(s\alpha) W_\eta(-s\alpha) + W_\eta(s\alpha) W(-s\alpha)} + \frac{2\xi s W(-s\alpha) \alpha \beta_a (1-s^2) \left( 1 + s \frac{W_\eta(-s\alpha)}{W(-s\alpha)} \right)}{W(s\alpha) W_\eta(-s\alpha) + W_\eta(s\alpha) W(-s\alpha)}. \quad (27b)$$

The first nontrivial correction to the outer solution has now been obtained. Notice, however, that when  $r=1$  then  $f_2=g_2=0$  so that  $a_2=b_2=0$ .

### III. REACTION FRONT

Chopard *et al.* [12] defined the position of the reaction front as the first moment of the reaction rate, namely,

$$x_f = \frac{\int_{-\infty}^{\infty} a^n b^m dx}{\int_{-\infty}^{\infty} a^n b^m dx}.$$

Using the  $\eta$  and  $Z$  coordinates we obtain

$$x_f = 2\sqrt{t} \left( \alpha + \frac{\int_{-\infty}^{\infty} \mathcal{N} Z dZ}{t^\sigma \int_{-\infty}^{\infty} \mathcal{N} dZ} \right).$$

For large times the above equation can be expanded. Using Eq. (13a) with the corresponding boundary condition (16a) it is found that  $\int_{-\infty}^{\infty} \mathcal{N}_0 Z dZ = 0$  and  $\int_{-\infty}^{\infty} \mathcal{N}_1 dZ = 0$ , hence the large time asymptotic reaction front position is given by

$$x_f = 2\sqrt{t} [\alpha + \alpha_2 t^{-2\sigma} + \alpha_3 t^{-3\sigma} + O(t^{-4\sigma})], \quad (28)$$

where

$$\alpha_2 = \frac{\int_{-\infty}^{\infty} \mathcal{N}_1 Z dZ}{\int_{-\infty}^{\infty} \mathcal{N}_0 dZ} \quad \text{and} \quad \alpha_3 = \frac{\int_{-\infty}^{\infty} \mathcal{N}_2 Z dZ}{\int_{-\infty}^{\infty} \mathcal{N}_0 dZ}.$$

Equations (13a) and (16a) yield the result that  $\int_{-\infty}^{\infty} \mathcal{N}_0 dZ = -\frac{1}{4} \bar{a}_{0\eta}$ . Additionally using Eq. (21a) and (21b) yields the result that  $\int_{-\infty}^{\infty} \mathcal{N}_1 Z dZ = \frac{1}{4} (\bar{a}_2 + 2\alpha\beta_a)$ , hence  $\alpha_2 = -(\bar{a}_2 + 2\alpha\beta_a) / \bar{a}_{0\eta}$ . Using  $\bar{a}_2 = f_2 W(-\alpha)$  and  $\bar{a}_{0\eta} = -2/\sqrt{\pi}$  we have

$$\alpha_2 = \sqrt{\pi} \beta_a \left[ \alpha + \frac{(r^2 - 1) \left( 2r^2 \alpha^2 + 1 - 4\sigma + r\alpha \frac{W_\eta(r\alpha)}{W(r\alpha)} \right)}{2\alpha(r^2 - 1) + \frac{W_\eta(-\alpha)}{W(-\alpha)} + r \frac{W_\eta(r\alpha)}{W(r\alpha)}} \right], \quad (29)$$

where  $\beta_a = -\frac{1}{4} \sqrt{\pi} I / [\pi \psi^m r^{2m}]^{2\sigma}$  from Appendix B and the constant  $I$ , which depends on  $n$  and  $m$ , must be numerically determined from Eq. (B2) by first solving system (B1).

As the function  $W$  employed here is not a standard function,  $\alpha_2$ , in general, must be evaluated numerically, except in certain special cases. Two such special cases follow.

#### A. Equal diffusion coefficients

We recall the special case when both reactants diffuse at the same rate, i.e.,  $r=1$ , leads to  $a_2=b_2=0$ . In this case, Eqs. (20) and (29) reduce to

$$\text{erf}(\alpha) = \frac{\psi - \phi}{\psi + \phi} \quad \text{and} \quad \alpha_2 = -\frac{\pi I \alpha}{4[\pi \psi^m]^{2\sigma}}$$

so that the large time asymptotic reaction front location can be approximated by

$$x_f \approx 2\sqrt{t} \text{erf}^{-1} \left( \frac{\psi - \phi}{\psi + \phi} \right) \left[ 1 - \frac{\pi I}{4(\pi \psi^m t)^{2\sigma}} \right]. \quad (30)$$

This shows that the first correction to the front position is always of the opposite sign to the leading order term so that approximating the front position  $x_f$  by  $2\alpha\sqrt{t}$  will overestimate the distance between the reaction front and its initial position. Further, Eq. (30) suggests that the front position crosses the point  $x_f=0$  at the time

$$t \approx \frac{(\pi I/4)^{1/2\sigma}}{\pi \psi^m}$$

provided  $\psi \neq \phi$  and further provided that  $\sigma < \frac{1}{4}$  we can infer that the front position changed direction at the earlier time

$$t \approx \frac{\left[ \pi I \left( \frac{1}{4} - \sigma \right) \right]^{1/2\sigma}}{\pi \psi^m}.$$

However, such results are only valid if they yield a sufficiently large value of  $t$  otherwise higher order terms in the expansion become important and may invalidate these predictions. The prediction of multiple turning points in the reaction front position for unequal diffusion coefficients when  $n=m=1$  was addressed by Taitelbaum *et al.* [13] who performed an expansion in small  $t$ . When  $r > 1$ , so that species  $A$  diffuses faster than species  $B$ , the front initially invades the liquid containing species  $B$ , the reverse holds when  $r < 1$ .

#### B. Class of slower fronts

When  $\phi = r\psi$ , Eq. (20) yields  $\alpha=0$ , however, this infact does not necessarily lead to a stationary front, since from Eq. (29) we obtain

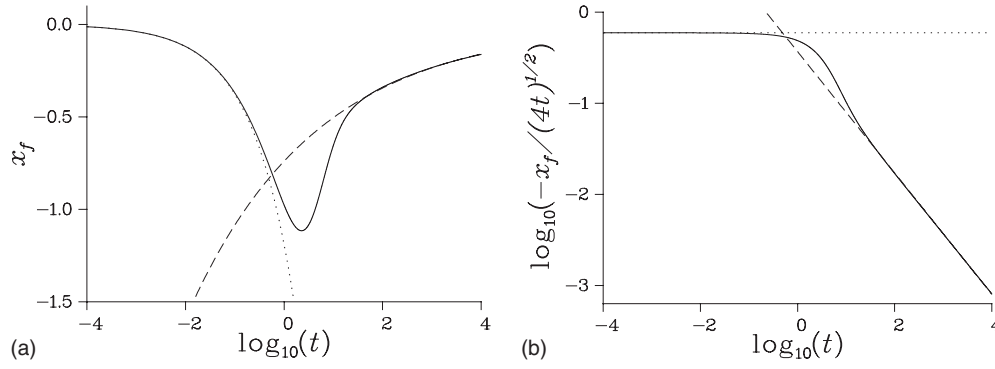


FIG. 1.  $x_f$  and  $\log_{10}(-x_f/\sqrt{4t})$  against  $\log_{10}(t)$  for the parameter values given by  $S_1$ . The dashed line in (a) is  $2\alpha_2 t^{-1/6}$  and in (b) is  $\log_{10}(-\alpha_2) - \frac{2}{3} \log_{10}(t)$ , while the dotted line in (a) is  $2\gamma\sqrt{t}$  and in (b) is  $\log_{10}(-\gamma)$ , where  $\alpha_2 \approx -0.36981$  and  $\gamma \approx -0.594499$ .

$$\alpha_2 = \frac{\pi I(r-1)\Gamma\left(\frac{3}{2} - 2\sigma\right)}{4(\pi\psi^m r^{2m})^{2\sigma}\Gamma(1-2\sigma)} \quad (31)$$

so the speed of the reaction front no longer scales with  $\sqrt{t}$  but in fact scale with  $t^{1/2-2\sigma}$  provided that the reactants have different diffusion coefficients, i.e.,  $r \neq 1$ . Throughout this study  $n$  and  $m$  have been treated as positive constants so that  $\sigma < 1$ , however, the term  $\Gamma(\frac{3}{2}-2\sigma)/\Gamma(1-2\sigma)$  is singular at  $\sigma = \frac{3}{4}$  and so in fact the expression for  $\alpha_2$  is only valid for  $0 < \sigma < \frac{3}{4}$ , i.e.,  $n+m > \frac{1}{3}$ . Further, we notice that the term  $\Gamma(\frac{3}{2}-2\sigma)/\Gamma(1-2\sigma)$  is zero at  $\sigma = \frac{1}{2}$ , i.e.,  $n+m=1$  which yields  $\alpha_2=0$ . However, physically the term  $n+m$  is usually greater than unity, hence, over the range  $0 < \sigma < \frac{1}{2}$  the term  $\Gamma(\frac{3}{2}-2\sigma)/\Gamma(1-2\sigma)$  can be considered as a positive monotonic decreasing function of  $\sigma$ .

Equation (28) shows that whenever  $\sigma > \frac{1}{4}$ , i.e.,  $n+m < 3$  then

$$\alpha = 0 \Rightarrow x_f \rightarrow 0 \text{ as } t \rightarrow \infty.$$

A special case of this result was demonstrated numerically by Jiang and Ebner [14] for the case when  $n=m=1$ .

### 1. $A+B \rightarrow C$

The most common types of reactions are of the form  $A+B \rightarrow C$  so that  $n=m=1$  and  $\psi=1$ , hence,  $\sigma = \frac{1}{3}$ . In this case, with  $\phi=r$ , we find that

$$\alpha_2 = \frac{\pi^{1/3} I(r-1)\Gamma\left(\frac{5}{6}\right)}{4r^{4/3}\Gamma\left(\frac{1}{3}\right)} \text{ thus } x_f \approx 2\alpha_2 t^{-1/6}$$

which shows that the reaction front returns to its initial position for large times. From Appendix B,  $I \approx 1.90250$ , hence the large time asymptotic front position is given by

$$x_f \approx 0.58703 \frac{r-1}{r^{4/3}} t^{-1/6}. \quad (32)$$

### 2. $A+2B \rightarrow C$

The second most common type of reaction are of the form  $A+2B \rightarrow C$  so that  $n=1$  and  $m=2$  with  $\psi=2$ , hence,  $\sigma = \frac{1}{4}$ . In this case, with  $\phi=2r$ , we find that

$$\alpha_2 = \frac{I(r-1)}{8r^2} \text{ thus } x_f \approx 2\alpha_2$$

which shows that the reaction front position approaches a finite distance from its initial position. From Appendix B,  $I \approx 3.29668$ , hence the large time asymptotic front position is given by

$$x_f \approx 0.82417 \frac{r-1}{r^2} \quad (33)$$

which requires a higher order expansion to determine the approach of  $x_f$  to this finite position, but this will not be carried out here. We note that whenever  $\phi=r\psi$  and  $n+m=3$  the reaction front will approach a point a finite distance away from its initial position as long as  $r \neq 1$ . We note that for an elementary reaction this is only possible for  $n=1$  and  $m=2$ , i.e.,  $A+2B \rightarrow C$ .

### 3. $2A+2B \rightarrow C$

Another possibility for a reaction is of the form  $2A+2B \rightarrow C$  so that  $n=m=2$  with  $\psi=1$ , hence,  $\sigma = \frac{1}{5}$ . In this case, with  $\phi=r$ , we find that

$$\alpha_2 = \frac{\pi^{3/5} I(r-1)\Gamma\left(\frac{11}{10}\right)}{4r^{8/5}\Gamma(3/5)} \text{ thus } x_f \approx 2\alpha_2 t^{1/10},$$

which shows that the reaction front position approaches infinity. From Appendix B,  $I \approx 3.76155$ , hence the large time asymptotic front position is given by

$$x_f \approx 2.38790 \frac{r-1}{r^{8/5}} t^{1/10}. \quad (34)$$

We note that whenever  $r \neq 1$ ,  $\phi=r\psi$  and  $n+m > 3$  the position of the reaction front will tend to infinity even though  $\alpha=0$ .

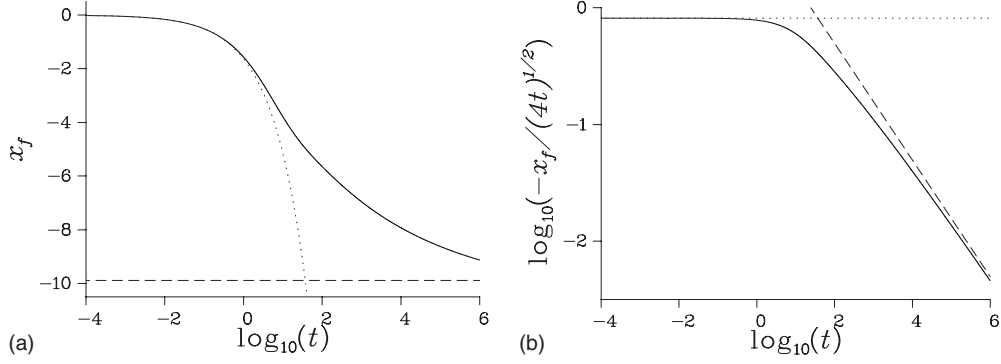


FIG. 2.  $x_f$  and  $\log_{10}(-x_f/\sqrt{4t})$  against  $\log_{10}(t)$  for the parameter values given by  $S_2$ . The dashed line in (a) is  $2\alpha_2$  and in (b) is  $\log_{10}(-\alpha_2) - \frac{1}{2}\log_{10}(t)$ , while the dotted line in (a) is  $2\gamma\sqrt{t}$  and in (b) is  $\log_{10}(-\gamma)$  where  $\alpha_2 \approx -4.94502$  and  $\gamma \approx -0.814274$ .

IV. RESULTS

In order to illustrate the new types of reaction front speeds that can occur we set  $\phi = \psi r$  so that  $\alpha = 0$ . Further, we set  $\phi = \frac{1}{2}$  and  $\psi = m/n$ , so that  $r = n/(2m)$ . Additionally the parameter values  $s = 1$  and  $\xi = 1/n$  were chosen, however, these two parameters do not effect the position of the reaction front. Three parameter sets are now considered:  $S_1 = \{n = 1, m = 1\}$ ,  $S_2 = \{n = 1, m = 2\}$ , and  $S_3 = \{n = 2, m = 2\}$ .

In Figs. 1(a), 2(a), and 3(a) the position of the reaction front  $x_f$ , obtained numerically by solving system (1) for the parameters sets  $S_1$ ,  $S_2$ , and  $S_1$ , respectively, is plotted against  $\log_{10}(t)$ . The large time analytical asymptotic prediction of the reaction front position is shown by a dashed line. There is very good agreement between the numerically obtained reaction front position and the asymptotic limit in Figs. 1(a) and 3(a), however, in Fig. 2(a), the reaction front has not yet reached its asymptotic position, but if the numerics were continued for much larger times it is anticipated that the numerical solution would get closer and closer to the asymptotic limit.

By simply plotting  $x_f$  and comparing the numerical solution with the asymptotic limit it is difficult to determine whether the actual rates predicted by Eq. (28) are true. As  $\alpha = 0$  and by truncating to the remaining leading order term in Eq. (28) we obtain

$$\frac{x_f}{2\sqrt{t}} = \alpha_2 t^{-2\sigma} + O(t^{-3\sigma}).$$

Hence, as  $x_f$  is negative,  $\log_{10}(-x_f/\sqrt{4t})$  should approach  $\log_{10}(-\alpha_2) - 2\sigma \log_{10}(t)$  for large  $t$ , and this theory is tested by plotting  $\log_{10}(-x_f/\sqrt{4t})$  against  $\log_{10}(t)$  in Figs. 1(b), 2(b), and 3(b). Again there is very good agreement between the numerically obtained reaction front position and the asymptotic limit in Figs. 1(b) and 3(b), however, in Fig. 2(b), it takes a very long time for the numerical solution to approach the asymptotic limit.

In order to ensure that the numerical results have the correct initial front position the small time asymptotic limit, given in Appendix C, is also plotted using a dotted line to correspond to  $x_f = 2\gamma\sqrt{t}$  in Figs. 1–3. For very small times, not illustrated, the numerical solution was insufficiently accurate, however, by  $t = 10^{-4}$  the numerical solution is found to agree well with the small time limit.

In conclusion, the numerical solutions are found to approach the predicted asymptotic limit when  $\alpha = 0$ . When  $\alpha \neq 0$  the results are numerically found to hold with correct limits obtained by plotting  $\log_{10}(\alpha - x_f/\sqrt{4t})$ . The theory has shown that the reaction front position is no longer forced to scale as  $\sqrt{t}$  but instead can scale as  $t^{1/2-2\sigma}$ , which can approach zero, infinity, or a non-zero finite value.

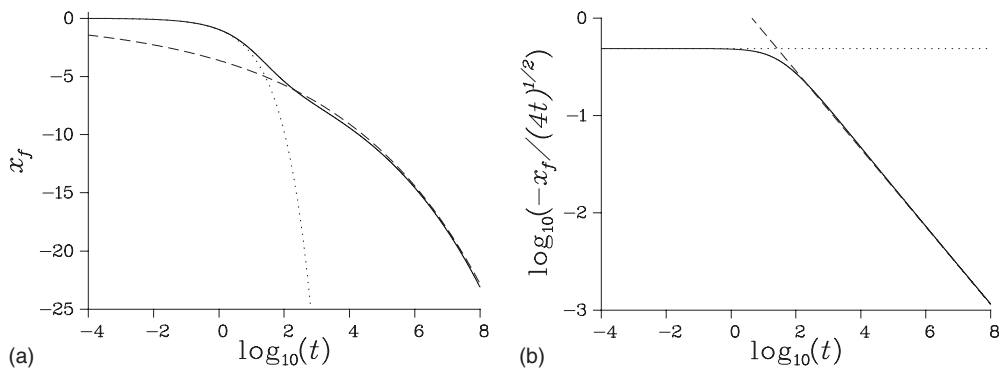


FIG. 3.  $x_f$  and  $\log_{10}(-x_f/\sqrt{4t})$  against  $\log_{10}(t)$  for the parameter values given by  $S_3$ . The dashed line in (a) is  $2\alpha_2 t^{1/10}$  and in (b) is  $\log_{10}(-\alpha_2) - \frac{1}{5}\log_{10}(t)$ , while the dotted line in (a) is  $2\gamma\sqrt{t}$  and in (b) is  $\log_{10}(-\gamma)$ , where  $\alpha_2 \approx -1.80969$  and  $\gamma \approx -0.488357$ .



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## APPENDIX A

Consider the following integral:

$$\begin{aligned} \int_{-L}^L Z^2 \mathcal{A}_{0ZZ} dZ &= [Z^2 \mathcal{A}_{0Z} - 2Z \mathcal{A}_0]_{-L}^0 + 2 \int_{-L}^0 \mathcal{A}_0 dZ \\ &+ [Z^2 \mathcal{A}_{0Z} - 2Z \mathcal{A}_0]_0^L + 2 \int_0^L \mathcal{A}_0 dZ \\ &= [Z^2 (\mathcal{A}_{0Z} + \bar{a}_{0\eta}) - 2Z (\mathcal{A}_0 - \bar{a}_1)]_{-L}^0 \\ &+ 2 \int_{-L}^0 \mathcal{A}_0 - Z \bar{a}_{0\eta} - \bar{a}_1 dZ \\ &+ [Z^2 \mathcal{A}_{0Z} - 2Z \mathcal{A}_0]_0^L + 2 \int_0^L \mathcal{A}_0 dZ. \end{aligned}$$

Hence, letting  $L \rightarrow \infty$  using  $\mathcal{A}_0 \rightarrow \bar{a}_1 + Z \bar{a}_{0\eta}$  as  $Z \rightarrow -\infty$  and  $\mathcal{A}_0 \rightarrow 0$  as  $Z \rightarrow \infty$  we obtain

$$\int_{-\infty}^{\infty} \frac{Z^2}{2} \mathcal{A}_{0ZZ} dZ = \int_{-\infty}^0 \mathcal{A}_0 - Z \bar{a}_{0\eta} - \bar{a}_1 dZ + \int_0^{\infty} \mathcal{A}_0 dZ. \quad (\text{A1})$$

Now consider

$$\begin{aligned} I_A &= \int_{-\infty}^Z \mathcal{A}_0 dZ = \int_{-\infty}^0 \mathcal{A}_0 dZ + \int_0^Z \mathcal{A}_0 dZ \\ &= \int_{-\infty}^0 \mathcal{A}_0 dZ + \int_0^Z \mathcal{A}_0 - Z \bar{a}_{0\eta} - \bar{a}_1 dZ + \frac{Z^2}{2} \bar{a}_{0\eta} + Z \bar{a}_1. \end{aligned} \quad (\text{A2})$$

Recalling that  $I_A \rightarrow \beta_a + Z \bar{a}_1 + \frac{Z^2}{2} \bar{a}_{0\eta}$  as  $Z \rightarrow -\infty$  and  $I_A \rightarrow 0$  as  $Z \rightarrow \infty$ , and letting  $Z \rightarrow -\infty$  we obtain

$$\beta_a = \int_{-\infty}^0 \mathcal{A}_0 dZ + \int_0^{-\infty} \mathcal{A}_0 - Z \bar{a}_{0\eta} - \bar{a}_1 dZ. \quad (\text{A3})$$

Hence from Eq. (A1) we obtain

$$\beta_a = -\frac{1}{2} \int_{-\infty}^{\infty} Z^2 \mathcal{A}_{0ZZ} dZ. \quad (\text{A4})$$

## APPENDIX B

The inner solutions  $a_I$ ,  $b_I$ , and  $c_I$ , to leading order are proportional to the functions  $\mathcal{A}_0$ ,  $\mathcal{B}_0$ , and  $\mathcal{C}_0$ . Using Eq. (18)

with  $a_1 = b_1 = c_1^L = c_1^R = 0$  the solutions for  $\mathcal{B}_0$  and  $\mathcal{C}_0$  are given by

$$\mathcal{B}_0 = \psi r^2 (\mathcal{A}_0 - Z \bar{a}_{0\eta}), \quad \mathcal{C}_0 = Z c_0^L + \xi s^2 (Z a_{0\eta} - \mathcal{A}_0).$$

Hence, the differential equation for  $\mathcal{A}_0$  can be written as

$$4(\psi r^2)^m \mathcal{A}_0^n (\mathcal{A}_0 - Z \bar{a}_{0\eta})^m = \mathcal{A}_{0ZZ}$$

with the boundary condition in Eq. (16a) and  $\mathcal{A}_0 \rightarrow 0$  as  $Z \rightarrow \infty$ . By writing  $\mathcal{A}_0 = -\bar{a}_{0\eta} \lambda G$  and  $Z = \lambda z$  where  $\lambda = -(\bar{a}_{0\eta}^2 / 4 \psi^m r^{2m})^\sigma / \bar{a}_{0\eta}$  yields the system

$$G_{zz} = G^n (G + z)^m, \quad (\text{B1a})$$

$$G \rightarrow -z \text{ as } z \rightarrow -\infty \text{ and } G \rightarrow 0 \text{ as } z \rightarrow \infty. \quad (\text{B1b})$$

This system of equations is identical to system (27) by Magnin [15]. Using Eq. (B1) we have  $\int_{-\infty}^{\infty} G_{zz} dz = 1$  and  $\int_{-\infty}^{\infty} z G_{zz} dz = 0$ . Returning to  $\beta_a$  in Eq. (A4), using  $G$  we can write

$$\beta_a = \frac{1}{2} \bar{a}_{0\eta} \lambda^2 I \text{ where } I = \int_{-\infty}^{\infty} z^2 G_{zz} dz. \quad (\text{B2})$$

Thus,  $I$  is the second moment of  $G_{zz}$  and thus represents a measure of the square of the width of the reaction front. As  $I$  depends on  $n$  and  $m$  the notation  $I_{n,m}$  will be used for convenience. By numerically solving system (B1) for values of  $n$  and  $m$  allows  $I_{n,m}$  to be evaluated. It is found that  $I_{1,1} \approx 1.90250$ ,  $I_{1,2} = I_{2,1} \approx 3.29668$ , and  $I_{2,2} \approx 3.76155$ .

## APPENDIX C

For small times the reaction term can be neglected so that the system is in a purely diffusing regime, thus the reactant concentrations are given by

$$a = \frac{1}{2} \operatorname{erfc}(\eta) \quad \text{and} \quad b = \frac{\phi}{2} \operatorname{erfc}(-r\eta).$$

This problem was address in more detail by Taitelbaum *et al.* [13], however, here, for simplicity, only the zeroth order small time solution is employed. Thus, to leading order, the position of the reaction front at the early stages is given by  $x_f \approx 2\gamma\sqrt{t}$ , where

$$\gamma_{n,m}(r) = \frac{\int_{-\infty}^{\infty} \operatorname{erfc}^n(\eta) \operatorname{erfc}^m(-r\eta) \eta d\eta}{\int_{-\infty}^{\infty} \operatorname{erfc}^n(\eta) \operatorname{erfc}^m(-r\eta) d\eta},$$

which must be evaluated numerically. We note that  $\gamma_{1,1}(\frac{1}{2}) \approx -0.594499$ ,  $\gamma_{1,2}(\frac{1}{4}) \approx -0.814274$ , and  $\gamma_{2,2}(\frac{1}{2}) \approx -0.488357$ .

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