

Asymptotic reaction-diffusion profiles in two-layer systems

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Introduction

Large time evolution of concentration profiles are studied analytically for reaction-diffusion systems where the reactants A and B are each initially separately contained in two immiscible solutions. They diffuse across the planar interface at $x = 0$ and react upon contact at time $t = 0$ to produce a product C. It is the goal of this paper to generalize previous analytical studies of asymptotic concentration profiles in reaction-diffusion systems by considering a general reaction rate $F(a, b)$ in an immiscible two layer system where a and b denote the concentrations of A and B respectively, and F is a non-negative function which is only zero when $a = 0$ or $b = 0$. Partition coefficients are introduced at the interface.

Reactant A is homogeneously dissolved in solvent 1 at $x < 0$ with initial concentration a_0 and reactant B is homogeneously dissolved in solvent 2 at $x > 0$ with initial concentration b_0 . The resulting system of one-dimensional reaction-diffusion equations is

$$a_t = D_a^{(i)} a_{xx} - k_a^{(i)} F(a, b), \quad b_t = D_b^{(i)} b_{xx} - k_b^{(i)} F(a, b), \quad c_t = D_c^{(i)} c_{xx} + k_c^{(i)} F(a, b) \quad (1a)$$

where the superscript i denotes the solvent. Both the sets of molecular diffusion coefficients $D_a^{(i)}$, $D_b^{(i)}$ and $D_c^{(i)}$ and kinetic constants $k_a^{(i)}$, $k_b^{(i)}$ and $k_c^{(i)}$ depend on the solvent. Using the partition coefficients p_a , p_b and p_c the interfacial equilibrium conditions are

$$p_a a^{(2)} = a^{(1)}, \quad p_b b^{(2)} = b^{(1)}, \quad p_c c^{(2)} = c^{(1)}. \quad (1b)$$

Additionally, on the interface a flux balance is required for each species. The concentrations gradients are assumed to approach zero at infinity.

Large time asymptotics

As the reaction rate F is only zero when either $a = 0$ or $b = 0$, one of the reactants must be virtually exhausted outside the reaction zone. Following the approach by Gálfi and

Rácz [1] the reaction zone will be treated like a single point where both a and b vanish. The reaction front position is given by

$$x_f = 2\alpha\sqrt{D_a^{(2)}t}. \quad (2)$$

where α is a constant. The reaction front is assumed to invade solvent 2 so that $\alpha \geq 0$. By generalising the works of Koza [2] and Sinder and Pelleg [3] to immiscible liquids the concentration fields are given by

$$\frac{a^{(1)}}{a_0} = 1 - q \frac{\text{erfc}(-q\eta)}{q + p_a \text{erf}(\alpha)}, \quad b^{(1)} = 0, \quad c^{(1)} = h \frac{\hat{s} p_c \text{erfc}(-\hat{s}\eta)}{\hat{s} + s p_c \text{erf}(s\alpha)} \quad \text{for } \eta < 0 \quad (3a)$$

$$\frac{a^{(2)}}{a_0} = \frac{\text{erfc}(\eta) - \text{erfc}(\alpha)}{q + p_a \text{erf}(\alpha)}, \quad b^{(2)} = 0, \quad c^{(2)} = h \frac{\hat{s} + s p_c \text{erf}(s\eta)}{\hat{s} + s p_c \text{erf}(s\alpha)} \quad \text{for } 0 < \eta < \alpha \quad (3b)$$

$$a^{(2)} = 0, \quad \frac{b^{(2)}}{b_0} = 1 - \frac{\text{erfc}(r\eta)}{\text{erfc}(r\alpha)}, \quad c^{(2)} = h \frac{\text{erfc}(s\eta)}{\text{erfc}(s\alpha)} \quad \text{for } \eta > \alpha \quad (3c)$$

where $q = \sqrt{D_a^{(2)}/D_a^{(1)}}$, $r = \sqrt{D_a^{(2)}/D_b^{(2)}}$, $s = \sqrt{D_a^{(2)}/D_c^{(2)}}$, $\hat{s} = \sqrt{D_a^{(2)}/D_c^{(1)}}$ and h is a constant. Balancing the reaction rates with the fluxes at the reaction front yields

$$r e^{\alpha^2(r^2-1)} \text{erfc}(r\alpha) = \frac{k_a^{(2)} b_0}{k_b^{(2)} a_0} [q + p_a \text{erf}(\alpha)] \quad \text{and} \quad h = \frac{a_0 k_c^{(2)} s e^{\alpha^2(s^2-1)} \text{erfc}(s\alpha) [\hat{s} + s p_c \text{erf}(s\alpha)]}{k_a^{(2)} [q + p_a \text{erf}(\alpha)] [\hat{s} + s p_c]} \quad (4)$$

Equations (3) and (4) were derived by Trevelyan *et al.* [4] when $F = a^n b^m$. Typical solutions are illustrated in figure 1.

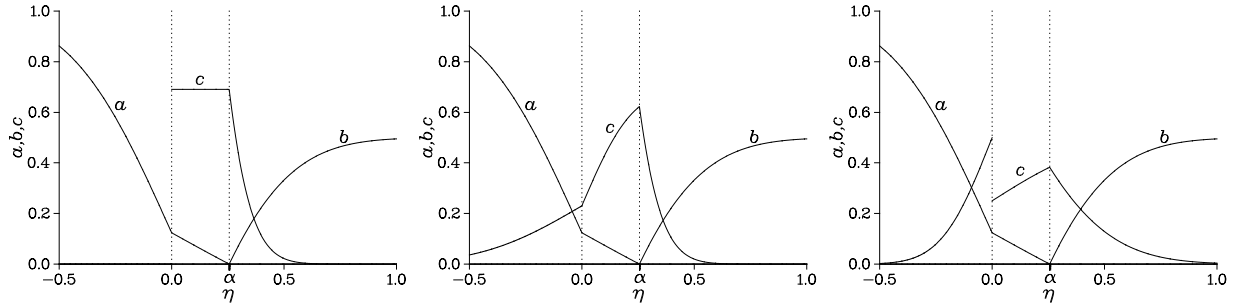


FIG. 1: Analytical outer solutions for (a) $p_c = 0$, $\hat{s} = 2$, $s = 4$ (b) $p_c = 1$, $\hat{s} = 2$, $s = 4$ and (c) $p_c = 2$, $\hat{s} = 4$, $s = 2$. The dotted lines denote the interface at $\eta = 0$ and the reaction front at $\eta = \alpha$. The remaining parameter values are $q = r = 2$, $p_a = a_0 = 1$, $b_0 = \frac{1}{2}$, $k_a^{(2)} = k_b^{(2)} = k_c^{(2)}$. Equation (4) yields $\alpha \simeq 0.2562$.

Reaction front properties

The condition that $\alpha \geq 0$, using equation (4), requires

$$\frac{b_0 k_a^{(2)}}{a_0 k_b^{(2)}} \leq \sqrt{\frac{D_a^{(1)}}{D_b^{(2)}}} \quad (5)$$

with a stationary front occurring at equality. Equation (5) reveals that the direction of the front is independent of $D_a^{(2)}$ and hence the reaction front formed between two immiscible liquids can travel in the opposite direction to when carried out in two miscible liquids.

With $\alpha > 0$, the reaction front travels faster when $D_a^{(2)}$, $D_a^{(1)}$, a_0 or $k_b^{(2)}$ are increased or when $D_b^{(2)}$, p_a , b_0 or $k_a^{(2)}$ are decreased. The effects on the width of the reaction front depends on F . When $F = ab$, corresponding to the reaction $A + B \rightarrow C$, the width of the reaction front increases when $D_a^{(2)}$, $D_b^{(2)}$ or p_a are increased or when $D_a^{(1)}$, a_0 , b_0 , $k_a^{(2)}$ or $k_b^{(2)}$ are decreased.

Conclusions

This study examines reaction-diffusion profiles in a two layer system when the reactants are initially separated. The speed of the front can be increased by choosing physical parameters favouring transport of the invading species in the invaded fluid. The direction of the front is found to depend on the diffusion coefficient of the invading species in its initial fluid but not on its value in the invading fluid. This has the important consequence that a reaction front in immiscible fluids can travel in the opposite direction to the reaction front formed in miscible fluids for a given fixed range of parameter values. The size of the invading species partition coefficient affects the magnitude of the front speed but it can not alter the direction of front.

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- [1] L. Gálfi and Z. Rácz, Phys. Rev A **38**, 3151 (1988).
 - [2] Z. Koza, J. Stat. Phys. **85**, 179 (1996).
 - [3] M. Sinder and J. Pelleg, Phys. Rev. E **62**, 3340 (2000).
 - [4] P.M.J. Trevelyan, D.E. Strier and A. De Wit, Phys. Rev. E, **78**, 026122 (2008).