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Reactions in systems with mixing

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Abstract. We study the evolution of the concentrations of reactants which perform the irreversible reaction $A + B \rightarrow 0$. The reactants are initially separated and are contained in a system undergoing mechanical mixing. We introduce a continuous mixing model which is related to Baker's transformation: the continuous aspect makes it possible to implement mixing in a reaction-diffusion scheme. Furthermore, under very weak requirements, we succeed in presenting analytical expressions for the decay: we show that the initial reaction stages are controlled by mixing so that the concentration of reactants follows the mixing (exponential) time pattern. Furthermore we show that for the usual values of the pertinent parameters (size of the system, diffusion constants, microscopic reaction rates) the standard diffusion-controlled mechanism is recovered only when the reactants are completely mixed.

1. Introduction

In recent years the investigation of diffusion-controlled reactions in different physical and chemical systems has received much attention. In particular, it was found that even for the simplest irreversible bimolecular reactions in systems without external stirring, in which the reactants diffuse and react on contact, the decay of concentrations does not, in general, obey the formal kinetics predictions; the long-time behaviour is mainly governed by the initial fluctuations of reactant concentrations [1-6]. Usually it is assumed that under vigorous stirring and for slow (reaction-controlled) reactions the system should become homogeneous, and that the standard classical kinetics should apply. For less intensive stirring the problem of reactions in systems with mixing is much more complicated.

As discussed by Ottino *et al* [7-9] the mechanical mixing of two liquids in laminar flows produces a quasi-one-dimensional lamellar structure of the (initially separated) A and B reactants. In [10-12] one envisages a thermally activated $A + B \rightarrow 0$ reaction. Then, by keeping for $t < 0$ the temperature low one may mix the non-reacting liquids. At $t = 0$ mixing stops and the irreversible reaction is switched on by heating the system. Mixing of non-reacting liquids is well represented by a structure consisting of alternating striations of the two different liquids. The characteristic striation thickness becomes smaller via mixing; thus both the mean thickness and also the distribution of striation thicknesses depend on the mixing device used and on the overall time of mixing.

Note that in this model mixing and reaction are separated in time. A numerical study of this model (reaction in a medium with striations) was presented by Muzzio

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and Ottino [10, 11], who asserted that the model reproduces well the geometrical properties of mixed substances. We have studied the same model analytically and showed that the decay law of the reactants' concentrations may depend in a subtle manner on the initial distribution of striation thicknesses [12].

We note also that in [13] and [14] numerical investigations of reactions under mixing are reported; there the particles are mixed by randomly picking some of them from time to time and placing them in new positions. The works show that under this procedure the classical kinetics results are recovered. However we hasten to note that this very interesting model does not closely follow real mixing, where one usually cannot take particles out from the system, reshuffle them and reinsert them at precise spots. Also the size of the systems used in computer simulations may be too small to highlight the (highly complex) intermediate-time range where the components are not yet fully mixed, but where particles already react significantly. We will focus on this situation in the present work.

We note that in all mixing processes the layers containing different reactants get folded and squeezed. As already stated, laminar mixing of two liquids often produces a lamellar structure of alternating striations. The distribution of thicknesses of these striations depends on the mixing device used: thus the mean value of the thickness becomes smaller with increasing mixing time.

We shall consider a system consisting of equal amounts of liquids which contain equal concentrations (say $c_0 \sim 10^{22} \text{ cm}^{-3}$) of reactants A and B . The hydrodynamic properties of the liquids are assumed to be independent of the A and B concentrations. Furthermore the reaction $A + B \rightarrow 0$ is taken to occur irreversibly, without disturbing the physical properties (temperature, viscosity etc) of the liquid. To fix the ideas on the characteristic macroscopic scales we envisage a teacup, stirred with a teaspoon. The typical length scale l_0 is then 1 cm and the typical time τ_0 is 1 s. For simplicity we take the diffusion coefficients D of the particles to be equal; for aqueous solution values around $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ are usual (e.g. [15]).

2. From Baker's transformation to a continuous model of mixing

The simplest model of mixing corresponds to the so-called Baker's transformation (e.g. [9, p 119]). The transformation maps a unit square into itself. It can be formulated in various forms, for example as the mapping $(x, y) \rightarrow (x', y')$, according to the rule:

$$y' = \{2y\} \quad x' = (x + [y'])/2 \quad (1)$$

where $\{y\}$ and $[y]$ denote the fractional and the whole parts of y , respectively, i.e. for π one has $[\pi] = 3$ and $\{\pi\} = 0.14159\dots$. Of course, the transformation is volume-conserving. It corresponds to an ideal mixing device, whose mixing cycle consists of the three stages (i) squeezing, (ii) cutting and (iii) fusing. We shall denote the time to complete one cycle by τ_0 . This transformation is not realized in flow systems because it is discrete and discontinuous. Nevertheless, it displays the main features of mixing. The stages of the mixing cycle corresponding to (1) are shown in figure 1.

As three-dimensional analogues of Baker's transformation we have several choices. We can take, for instance,

$$(x, y, z) \rightarrow (x', y', z') \quad (2a)$$

with $z' = z$ and x and y given by (1) or

$$y' = \{2y\} \quad z' = \{2z\} \quad x' = (x + [y'] + [z'])/4. \quad (2b)$$

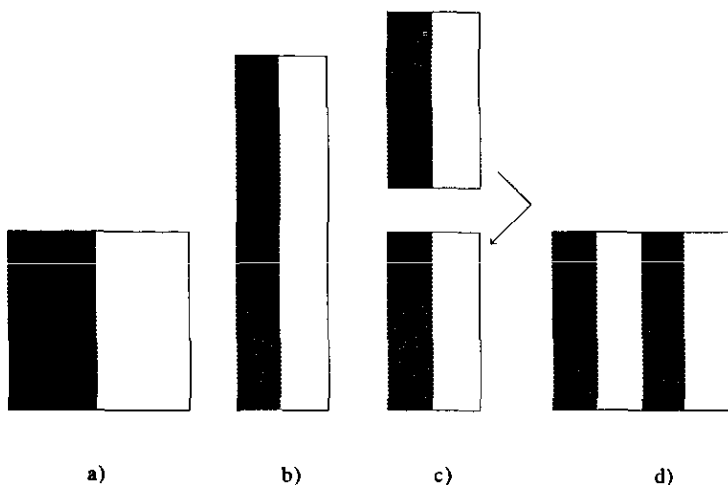


Figure 1. Baker's transformation: (a) initial configuration, (b) squeezing, (c) cutting and (d) fusing; (b)-(d) correspond to one step of the transformation.

If we have, for example, equal amounts of two liquids (black, *A* and white, *B* in figure 1), the repeated application of Baker's transformation produces a lamellar structure. Thus, if the initial boundary was a vertical plane at $x = \frac{1}{2}$, after n transformations, (1) or (2a), the system will consist of 2^n alternating parallel *A* and *B* layers of equal width. We will consider the substances as being fully mixed at the time T , when the striation thickness becomes comparable with the intermolecular distances (of the order of 1 Å). Thus $T \approx -\tau_0 \log_2 10^{-8} \approx 26$ s.

To fix the ideas let us look at striations which are nearly vertical. Of course, the boundaries between the components are not ideally plane (the left column of figure 2 shows the case of a piecewise-flat boundary). After some iterations of Baker's transformation the boundaries between layers will flatten out; however, the layers themselves will display the random thicknesses which follow from the distribution $p_0(h)$ of the initial layer widths h . Denoting the distribution of striation thicknesses after the n th iteration by $p_n(h)$ one has

$$p_n(x) = 2^n p_0(2^n x). \quad (3)$$

Of course, in reality the random form of the initial boundaries is not the only origin of random thicknesses of striations. Other obvious sources of randomness in the mixed patterns are the influence of thermal motion and the randomness introduced by (possibly chaotic) aspects of the mixing procedure, say in a turbulent flow.

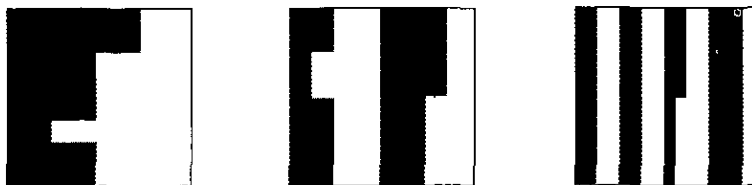


Figure 2. Evolution of a piecewise-flat boundary during the two first steps of Baker's transformation.

Although Baker's transformation is very simple, its discrete nature makes it awkward to use it directly in a reaction-diffusion scheme. We aim at obtaining a continuous scheme, more in line with differential equations. For this we start by noticing the correspondence between a system undergoing Baker's transformation and a system to whom we attach statistical copies of itself. (There are several ways to proceed, which all lead to models of the same nature.)

For macroscopic systems, during the whole time of the reaction the diffusion length $l_D = \sqrt{Dt}$ is much smaller than the system's size l_0 . We are thus free to specify the boundary conditions as we wish. Taking our volume to be a square (or a cube), we can attach copies of it at each boundary. Thus we view our original volume as being immersed in a sea of copies filling the whole plane (or space). Now let us focus on the infinite subsystem along the x -axis; it is a linear array of copies of the initial volume. Baker's transformation now shortens the x -length by a factor of two. Physically we can consider each stage of Baker's transformation as being due to the application of pressure along the x -axis, the pressure being such that all x -distances are shortened by half. In two dimensions we imagine half (in the case of the three-dimensional transformation (2b) three-quarters) of the material to be squeezed out. We can now look at our array of copies through the window corresponding to the size of the initial volume. Evidently, for *identical* copies of the system and strictly vertical planes we recover Baker's transformation. However, here we can easily generalize the procedure by taking *statistical* copies of the original system. This corresponds to the ensemble idea in statistical mechanics and leads to an important new aspect: for *identical* copies Baker's transformation leads to correlations between distant sites of the system, because after a few transformations distant regions behave in identical ways. For *statistical* copies such correlations do not arise. Also note that because of statistical fluctuations and because we view the development through a restricted window, the amounts of different reactants inside the window are only equal *on the average*, but are not exactly equal at each moment. This, however, makes no difference when only ensemble averaged quantities are considered, as long as the diffusion length is small compared with the system's size.

As a last step, we can now dispense from considering a discrete model, and we view the squeezing to occur continuously, as exemplified in figure 3. Our extension of

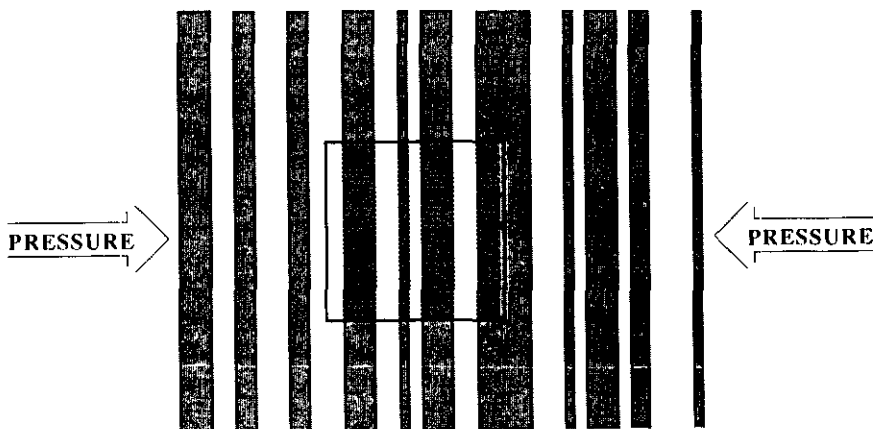


Figure 3. The model of mixing used: an array of parallel striations under pressure seen through a window.

Baker's model for mixing is thus a lamellar system with an initial distribution of striation thicknesses $p_0(x)$ which undergoes a contraction along the x -axis. In line with our ideas we shall mainly consider a continuous contraction which renders the characteristic scale of a system ϵ times smaller each τ seconds. We note that similar results are obtained when the contractions occur at discrete time intervals, where the distances change by a factor of 2 at times $t = n\tau_0$, and $\tau_0 = \tau \ln 2$. Note that the local structure and the statistical properties of the striations (but *not* their widths) are preserved at all times.

To finish specifying the model we have to discuss the initial distribution of layers. We take the initial thicknesses of different layers as being independent random variables, given by the distribution $p_0(x)$. For simplicity we take the same distribution $p_0(x)$ for both reactants. Here we introduce the first two moments L and S of $p_0(x)$ which will be repeatedly used in the following:

$$L = \int_0^\infty x p_0(x) dx \quad S = \int_0^\infty x^2 p_0(x) dx. \quad (4)$$

As our model deals with the two layers of liquid whose total width is equal to the system's size l_0 , both L and S are finite. In other problems one also encounters the case of infinite S , as discussed by us in [12].

The main result of this section is that we are able to model mixing through a continuous one-dimensional spatial transformation. This allows us to implement the transformation readily into a reaction-diffusion scheme, as we now proceed to show.

3. The main equations

The bimolecular irreversible reaction $A + B \rightarrow 0$ in a system without external constraints can be described by the following pair of differential equations:

$$\frac{\partial c_A}{\partial t} = D\Delta c_A - \kappa c_A c_B \quad \frac{\partial c_B}{\partial t} = D\Delta c_B - \kappa c_A c_B \quad (5)$$

where $c_A(\mathbf{r}, t)$ and $c_B(\mathbf{r}, t)$ are the local concentrations of reactants, D is the diffusion constant, and κ denotes the microscopic reaction rate constant. The form $\kappa c_A c_B$ is a widely-used approximation for the reaction term; see [6] and [12] for the discussion of its limitations.

The squeezing of the system may now be described by introducing the field of velocities of the liquid. The full hydrodynamical description of such a field, corresponding to real squeezing, is complicated, but fortunately we do not need such a full description. In an infinite system under constant pressure the liquid motion can be viewed as being a homogeneous dilational flow whose velocity field is $v_i = \sum_k \alpha_{ik} x_k$ (where $\sum_i \alpha_{ii} = 0$ due to incompressibility) (see e.g. [16]). Moreover, in our model the system is always an array of parallel striations perpendicular to the x -axis; the external pressure is applied parallel to the x -axis. Therefore the problem can be treated as essentially one-dimensional and only the x -component of the velocity is significant. In the case of a continuous contraction this component depends on the location x with $\alpha_{xx} = 1/\tau$:

$$v(x) = -x/\tau. \quad (6)$$

To see this consider a liquid domain first located at x_0 at time 0. Through the contraction its coordinate changes. The position of the domain at time t is $x(t) = x_0 \exp(-t/\tau)$. The velocity v of the domain is $v = -x_0 \exp(-t/\tau)/\tau = -x/\tau$. Note thus that the velocity depends only on the current location (it does *not* depend on time or on the *initial* location of the domain).

We now envisage the reaction to occur in a system with the superimposed velocity field v , given by (6). Now, when one considers a reaction in a moving liquid (5) holds locally in the system of coordinates moving together with the liquid domain considered (Lagrangian coordinates, \mathbf{R} , e.g. [9, p 20]).

We need, however, a description of the process in a fixed frame corresponding to our window (Eulerian coordinates \mathbf{r}). Therefore we need to relate functions f in the moving frame to the properties of f in the fixed coordinate frame. The procedure is as usual: one takes the moving and the fixed coordinate systems to coincide at $t=0$. Thus the Eulerian coordinates of the liquid domain considered are

$$\mathbf{r}(t) = \mathbf{r}(0) + \int_0^t \mathbf{v}(\mathbf{r}(t'), t') dt' \quad (7)$$

where $\mathbf{v}(\mathbf{r}, t)$ is local liquid velocity and $\mathbf{r}(0) = \mathbf{R}$. Now

$$\frac{\partial}{\partial t} f(\mathbf{r}(t), t) = \frac{\partial f(\mathbf{r}, t)}{\partial t} + \frac{\partial \mathbf{r}(t)}{\partial t} \cdot \nabla f(\mathbf{r}, t) = \frac{\partial f(\mathbf{r}, t)}{\partial t} + \mathbf{v} \cdot \nabla f(\mathbf{r}, t) \quad (8)$$

where $\partial/\partial t$ and ∇ are the partial time derivative and the gradient of f as functions of the variables (\mathbf{r}, t) . One can now introduce the operator (called *material* derivative in [7])

$$\frac{\mathcal{D}}{\mathcal{D}t} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \quad (9)$$

which gives the partial time derivative in a coordinate system moving with the liquid domain. Hence in an imposed velocity field one has, as a generalization of (5), but now restricted to one dimension:

$$\begin{aligned} \frac{\mathcal{D}c_A}{\mathcal{D}t} &= \frac{\partial c_A}{\partial t} + v \frac{\partial c_A}{\partial x} = D \frac{\partial^2 c_A}{\partial x^2} - \kappa c_A c_B \\ \frac{\mathcal{D}c_B}{\mathcal{D}t} &= \frac{\partial c_B}{\partial t} + v \frac{\partial c_B}{\partial x} = D \frac{\partial^2 c_B}{\partial x^2} - \kappa c_A c_B. \end{aligned} \quad (10)$$

Here one usually has to assume that the gradient of velocity is small enough, namely, that the characteristic reaction rates which correspond to particles' collisions due to the velocity gradient and to the inertial forces (disregarded here) are small compared with the diffusion-controlled reaction rate κ . When both reactants are moving the last quantity is given by $\kappa = 8\pi D r_0$ where r_0 is the reaction radius. In the case of purely diffusion-controlled reactions κ is around $10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for a reaction radius r_0 around 10^{-8} cm .

If we rewrite now (10) as a pair of equations for $q(x, t) = c_A(x, t) - c_B(x, t)$ and for $s(x, t) = c_A(x, t) + c_B(x, t)$ we obtain

$$\frac{\mathcal{D}q}{\mathcal{D}t} = \frac{\partial q}{\partial t} - \frac{x}{\tau} \frac{\partial q}{\partial x} = D \frac{\partial^2 q}{\partial x^2} \quad (11)$$

and

$$\frac{\partial s}{\partial t} = \frac{\partial s}{\partial t} - \frac{x}{\tau} \frac{\partial s}{\partial x} = D \frac{\partial^2 s}{\partial x^2} - \frac{\kappa}{2} (s^2 - q^2). \quad (12)$$

Here we see that the first equation is a linear equation of one variable and that the second one contains $q(x, t)$ as a parameter. These forms are simple enough to be amenable to a theoretical analysis.

4. The case of extremely fast reactions

First let us consider the case of a very fast reaction $\kappa \rightarrow \infty$. The experimental relevance and the theoretical significance of this model is considered in [9, pp 13 and 282ff]. The results of this section are also of much importance in our considerations of the case of finite reaction rates, to be discussed in section 5. According to (12) the limiting case $\kappa \rightarrow \infty$ corresponds to $s^2 = q^2$, or $s = |q|$ everywhere. This means that the system consists of domains occupied either by A or by B particles; the lines (surfaces) for which $q = 0$ give the boundaries between the domains. One hence has:

$$c_A = q\theta(q) \quad c_B = -q\theta(-q) \quad (13)$$

and one can describe the reaction-diffusion process under mixing with the help of only one linear equation, namely, equation (11). Furthermore (11) can be reduced to a simple diffusion equation with partial, not material, derivatives. This can be achieved by a change of variables, whereby (ξ, η) are related to (x, t) via

$$\xi = x\psi(t) \quad \eta = \int_0^t \psi^2(t) dt \quad (14)$$

with

$$\psi(t) = \exp(t/\tau). \quad (15)$$

Equation (15) is normalized in such a way that for $t = 0$ (ξ, η) and (x, t) coincide. In the variables ξ and η one has instead of (11)

$$\frac{\partial q}{\partial \eta} = D \frac{\partial^2 q}{\partial \xi^2} \quad (16)$$

which can be seen by using

$$\frac{\partial}{\partial t} = \psi^2(t) \frac{\partial}{\partial \eta} + x\psi'(t) \frac{\partial}{\partial \xi} \quad \text{and} \quad \frac{\partial}{\partial x} = \psi(t) \frac{\partial}{\partial \xi}$$

in (11). From (14) and (15), η obeys

$$\eta(t) = [\exp(2t/\tau) - 1]\tau/2. \quad (17)$$

The generalization to cases where the contraction rate is time-dependent is rather obvious: then $\psi(t)$ is given by

$$\psi(t) = \exp\left(-\int_0^t [v(x, t)/x] dt\right) \quad (18)$$

instead of (15). The generalization of the following theory to such time-dependent contraction is quite straightforward, and we will restrict ourselves to the simpler form, equation (15).

Equation (16) can be easily solved using its Green's function. The Green's function of (16) is

$$G(\xi, \eta) = (4\pi D\eta)^{-1/2} \exp(-\xi^2/4D\eta). \quad (19)$$

Because of the coincidence of both sets of variables at $t=0$ the initial realization of the A and B domains, $q(x, 0)$, is the same for $\eta = 0$ in the (ξ, η) variables. The temporal development of $q(\xi, \eta)$ is thus

$$q(\xi, \eta) = \int_{-\infty}^{\infty} q(x, 0) G(\xi - x, \eta) dx. \quad (20)$$

Note that the initial distribution of $q(x, 0)$ is bimodal: $q = c_0$ in the A lamellae and $q = -c_0$ in the B lamellae. Furthermore, since the initial distribution of $q(x, 0)$ has a finite correlation length l the integral in (20) can be approximated by a sum of Ξ_G/l independent variables. Here $\Xi_G \sim \sqrt{D\eta}$ is the characteristic scale of the Green's function, equation (19). Thus for $\Xi_G \gg l$ the distribution of $q(\xi, \eta)$ will tend to a Gaussian, according to the central limit theorem. In the intermediate time regime, for which $\Xi_G \sim l$ the distribution is 'smoothed' bimodal. Moreover during the whole time development the mean value of q vanishes: $\langle q(\xi, \eta) \rangle = 0$.

The set of transformations, equation (14) (the so-called 'warped-time transformation'), was first introduced by Ranz [17]. They are widely used for the description of diffusion in liquid flows (see e.g. [9]). We would like to stress here a very important property of these transformations, namely the conservation of spatial averages. This property makes possible the further theoretical analysis.

Note that since the change of variables from (x, t) to (ξ, η) is linear in x and since the variable η depends only on t (but not on x) all the spatial averages are the same when averaging over x or over ξ ; furthermore both coincide with the ensemble averaging over the initial conditions:

$$\begin{aligned} \langle f(q(x, t)) \rangle &= \lim_{\lambda_0 \rightarrow \infty} \frac{1}{2\lambda_0} \int_{-\lambda_0}^{\lambda_0} f(q(x, t)) dx \\ &= \lim_{\lambda \rightarrow \infty} \frac{1}{2\lambda} \int_{-\lambda}^{\lambda} f(q(\xi, \eta(t))) d\xi = \langle f(q(\xi, \eta(t))) \rangle \end{aligned} \quad (21)$$

where f is an arbitrary function of q only, $\lambda = \lambda_0 \exp(t/\tau)$ and the symbol $\langle \dots \rangle$ denotes the ensemble average.

In the case of extremely fast reactions one finds domains occupied by A or by B molecules, exclusively. The overall reactant concentrations $c(t)$ therefore obey:

$$c(t) = \langle c_A(x, t) \rangle = \langle c_B(x, t) \rangle = \langle |q(x, t)| \rangle / 2. \quad (22)$$

According to (21), $\langle |q(x, t)| \rangle = \langle |q(\xi, \eta(t))| \rangle$, and $\langle |q(\xi, \eta(t))| \rangle$ is bounded by the inequalities

$$\sqrt{2/\pi} \langle q^2(\xi, \eta(t)) \rangle^{1/2} \leq \langle |q(\xi, \eta(t))| \rangle \leq \langle q^2(\xi, \eta(t)) \rangle^{1/2} \quad (23)$$

following from the relations between $\langle q^2 \rangle$ and $\langle |q| \rangle$ for the limiting cases of bimodal and Gaussian distributions. Hence

$$\frac{1}{\sqrt{2\pi}} \langle q^2(\xi, \eta(t)) \rangle \leq c(t) \leq \frac{1}{2} \langle q^2(\xi, \eta(t)) \rangle. \quad (24)$$

The difference between the upper and the lower bounds is only 25%. If we accept this order of accuracy, the only thing needed in order to evaluate $c(t)$ for infinitely fast reactions is to calculate $\langle q^2(\xi, \eta(t)) \rangle$ —the second moment of the distribution of q at time t . From (20) one has by a simple change of variables

$$q(\xi, \eta) = \int_{-\infty}^{\infty} q(\xi - \zeta, 0) G(\zeta, \eta) d\zeta \tag{25}$$

and thus

$$\begin{aligned} \langle q^2(\eta) \rangle &= \langle q(\xi, \eta) q(\xi, \eta) \rangle \\ &= \left\langle \iint G(\zeta, \eta) q(\xi - \zeta, 0) q(\xi - \vartheta, 0) G(\vartheta, \eta) d\zeta d\vartheta \right\rangle \\ &= \iint G(\zeta, \eta) \langle q(\xi - \zeta, 0) q(\xi - \vartheta, 0) \rangle G(\vartheta, \eta) d\zeta d\vartheta. \end{aligned} \tag{26}$$

Here we could interchange integration and averaging, because $G(\xi, \eta)$ is a non-random function which does not depend on the particular realization of the disorder.

For systems which are statistically homogeneous on average, the initial correlation function $g(x_1, x_2)$ of the q defined through

$$g(x_1, x_2) = \langle q(x_1, 0) q(x_2, 0) \rangle \tag{27}$$

depends only on the difference of the arguments x_1 and x_2 , i.e. $g(x_1, x_2) = g(x_1 - x_2)$. Hence

$$\langle q^2(\eta) \rangle = \iint G(\zeta, \eta) g(\zeta - \vartheta) G(\vartheta, \eta) d\zeta d\vartheta. \tag{28}$$

One can now remark on the double convolution on the RHS of (28), since $G(\xi, \eta)$ is symmetric in ξ . This allows us to express $\langle q^2(t) \rangle$ in terms of the Fourier transforms of g and G . Setting $\Gamma(k) = \int g(x) \exp(ikx) dx$ for the Fourier transform of g , and using the explicit Fourier transform $\exp(-2D\eta k^2)$ of $G(\xi, \eta)$, equation (19), one obtains

$$\langle q^2(\eta) \rangle = \frac{1}{2\pi} \int \Gamma(k) \exp(-2D\eta k^2) dk. \tag{29}$$

For small times corresponding to $\eta \ll l^2/D$ one has $\langle q^2(\eta) \rangle = (1/2\pi) \int \Gamma(k) dk = g(0) = c_0^2$ as initially $q(x) = \pm c_0$. At larger times one can make use of the very fast (exponential) growth of $\eta(t)$, see (17). Changing the variable in (28) into $\chi = \sqrt{2D\eta} k$ one obtains

$$\langle q^2(\eta) \rangle = \frac{1}{2\pi\sqrt{2D\eta}} \int_{-\infty}^{\infty} \Gamma(\chi/\sqrt{2D\eta}) e^{-\chi^2} d\chi = [8\pi D\eta]^{-1/2} \Gamma(0). \tag{30}$$

The time dependence $\langle q^2(t) \rangle$ follows now from the explicit form of $\eta(t)$, equation (17). Now it only remains to evaluate the quantity $\Gamma(0) = \int g(x) dx$. The correlation function $g(x)$ of concentrations in a lamellar system was calculated in [12]. According to the results of this work, for finite S and L with $S \neq L^2$ (this is the general case) one has

$$\Gamma(0) = c_0^2 \frac{S - L^2}{L}. \tag{31}$$

From (31) we now immediately obtain via (30)

$$\langle q^2(t) \rangle = c_0^2 \frac{S - L^2}{L} [4\pi D\tau(\exp(2t/\tau) - 1)]^{-1/2}. \tag{32}$$

As $c(t) \approx \langle q^2(t) \rangle^{1/2}$, in accordance with (24) we have

$$c(t) = a^{1/2} [\exp(2t/\tau) - 1]^{-1/2} \quad (33)$$

with $a = c_0^2(S - L^2)/L\sqrt{4\pi D\tau}$. For large enough times (of the order of a few units of τ), when $\exp(t/\tau) \gg 1$, the decay of $c(t)$ is exponential:

$$c(t) = a^{1/2} \exp(-t/2\tau) \quad (34)$$

and follows the mixing pattern. A heuristic derivation of (33), which also shows that (31) is very reasonable, is given in the appendix.

5. The case of a finite reaction rate

In the previous section we derived that for very fast reactions the decay is exponential. This is, of course, related to our mixing model, which enforced an exponential decay on the pattern of striation lengths. Evidently, this mimics the situation when after long stirring the initial distribution of reactants is forgotten and the system becomes homogeneous. In this section we focus on reactions where κ is not infinite: this allows us both to assess the range of validity of the model of extremely fast reactions, and also to display the temporal range in which mixing destroys the influence of the initial conditions.

We first remark that for an ensemble-averaged situation $\langle s \rangle$ is independent of x . Hence also $\langle \partial s / \partial x \rangle = 0$, which implies that both $\langle D\Delta s \rangle$ and $\langle v\nabla s \rangle$ vanish. We now turn back to (12). By averaging this equation over the ensemble of realizations one obtains

$$\frac{d\langle s \rangle}{dt} = -\frac{\kappa}{2} (\langle s^2 \rangle - \langle q^2 \rangle). \quad (35)$$

Now we approximate in this expression $\langle s^2 \rangle$ by $\langle s \rangle^2$. We note that s is independent of x both in the initial state, where (apart from the boundaries between the domains) $s(x, 0) = c_0$ and also in the late, fully mixed states of the reaction. In both these limiting cases the relation $\langle s^2 \rangle = \langle s \rangle^2$ is well-obeyed. In the intermediate regime $\langle s^2 \rangle$ and $\langle s \rangle^2$ can differ only by a factor of order of unity, since the distribution of s is well-behaved. Setting $\langle s^2 \rangle = \langle s \rangle^2$ in (35) we obtain instead of (12) an ordinary differential equation:

$$\frac{d\hat{s}(t)}{dt} = -\frac{\kappa}{2} (\hat{s}^2(t) - \hat{q}^2(t)) \quad (36)$$

where we set $\hat{s}(t) = \langle s(x, t) \rangle = \langle s^2(x, t) \rangle^{1/2}$ and $\hat{q}(t) = \langle q^2(t) \rangle^{1/2}$. Now we shall show that at large times (when \hat{q} tends to 0), equation (36) has the solution $\hat{s}(t) = 2/\kappa t$, while at small times one has $\hat{s} \approx \hat{q}$, in accordance with (24). We shall also evaluate the characteristic time for the crossover.

We first note that for the times larger than a few τ -units one has $\hat{q}^2(t) = a \exp(-t/\tau)$ (see (32)). Substituting this form into (36) and introducing as a new variable $z = \exp(-t/\tau)$ we obtain in this time regime the equation

$$\frac{d\hat{s}}{dz} = \frac{\kappa\tau}{2z} \hat{s}^2 - \frac{a\kappa\tau}{2}. \quad (37)$$

Equation (35) is a Riccati equation [18, p 21] and can be reduced to a second-order linear equation for the auxiliary function $\phi(z)$, where

$$\phi(z) = \exp\left(-\int_0^z \frac{\kappa\tau\hat{s}(z')}{2z'} dz'\right). \quad (38)$$

This new equation reads as follows:

$$z^2 \frac{d^2 \phi}{dz^2} + z \frac{d\phi}{dz} - z \frac{a\tau^2 \kappa^2}{4} \phi = 0 \quad (39)$$

and is a Bessel equation [18, p 440]. Its general solution is

$$\phi(z) = C_1 J_0(i\tau\kappa\sqrt{az}) + C_2 Y_0(i\tau\kappa\sqrt{az}) \quad (40)$$

where $J_0(x)$ and $Y_0(x)$ are the Bessel and the Weber's functions of zeroth order and C_1 and C_2 are arbitrary constants. Now, since $\hat{s}(z)$ is a real function, $\phi(z)$ is also real. To simplify (40) one can express it in terms of modified Bessel functions since one has $J_0(ix) = I_0(x)$ and $Y_0(ix) = iI_0(x) - (2/\pi)K_0(x)$ (see [19, equations (9.6.3) and (9.6.5)]). In order to obtain a real solution $\phi(z)$ one must thus take $C_1 = -iC_2$ with C_2 real. In this case one has

$$\phi(z) = -C_2 \frac{2}{\pi} K_0(x). \quad (41)$$

From (38) we obtain now $\hat{s}(z)$ as

$$\hat{s}(z) = -(2z/\kappa\tau)\phi'(z)/\phi(z) \quad (42)$$

ϕ' being the derivative of ϕ . Making use of the relation $K_0'(x) = -K_1(x)$, [19, equation (9.6.27)], one obtains therefore

$$\hat{s}(z) = \sqrt{az} \frac{K_1(\kappa\tau\sqrt{az})}{K_0(\kappa\tau\sqrt{az})}. \quad (43)$$

As the coefficient $\kappa\tau\sqrt{a} \sim 10^{10}$ is much larger than unity, for small enough times the ratio on the RHS of (43) is close to unity. One obtains

$$s(z) = \sqrt{az} \quad (44)$$

which corresponds to $s(t) = q(t) = a^{1/2} \exp(-t/2\tau)$ for moderately long times t : these are larger than a few units of τ (so that $\hat{q}(t) = a^{1/2} \exp(-t/2\tau)$ holds well) but such that the argument $\tau\kappa\sqrt{az}$ of the Bessel functions is still large, $1 < t/\tau < 2 \ln(\tau\kappa\sqrt{a})$. For larger times $t > 2\tau \ln(\tau\kappa\sqrt{a})$ the argument in (43) becomes significantly smaller than unity. Here we have to use the forms for small values of the arguments for modified Bessel functions: $K_0(x) \sim -\ln x$, $K_1(x) \sim 1/x$ [19, equations (9.6.8) and (9.6.9)]. In this case we obtain as leading behaviour

$$\hat{s}(z) = -\frac{2\tau}{\kappa \ln z} \quad (45)$$

which corresponds to

$$\hat{s}(t) = 2/\kappa t. \quad (46)$$

This expression is the standard chemical kinetics form. The change from one type of temporal behaviour to another occurs for values of the argument of the order of unity; this corresponds to a time of the order of T_0 , given by

$$T_0 = 2\tau \ln(\tau\kappa\sqrt{a}) = 2\tau \ln \frac{c_0(S-L^2)^{1/2} \kappa\tau}{(4\pi D\tau)^{1/4} L^{1/2}}. \quad (47)$$

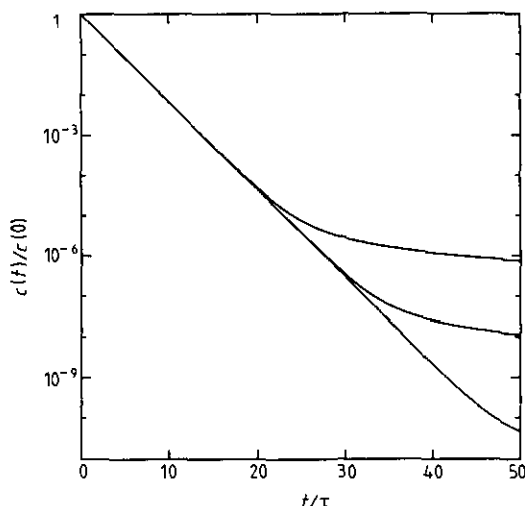


Figure 4. The evolution of the reactant concentrations $c(t)$ in a mixed system with a finite microscopical reaction rate κ . Displayed are the results for $c(0) = 10^{22} \text{ cm}^{-3}$ and for $\kappa = 10^{-18}, 10^{-16}$ and $10^{-13} \text{ cm}^3 \text{ s}^{-1}$ (top to bottom). Shown on a logarithmic scale is the ratio $c(t)/c(0)$; the time is given in units of τ , the typical mixing time.

Substituting in (47) the values of parameters discussed above we obtain for an extremely fast, purely diffusion-controlled microscopical mechanism of reaction, which corresponds to $\kappa = 10^{-13} \text{ cm}^3 \text{ s}^{-1}$.

$$T_0 \approx 37\tau \approx 53 \text{ s.} \quad (48)$$

Now T_0 is twice as large as T , the full mixing time in the absence of the reaction, see section 2, which was around 26 s.

We can also evaluate the behaviour of the concentration $c(t)$ numerically, which is given by $c(t) = \hat{s}(t)/2$. We do this by using polynomial approximations for the modified Bessel functions in different ranges of the parameters (see [19, section 9.8]). The results of the computations are shown in figure 4. All curves correspond to the same value of a , taken to be $a = 10^{46} \text{ cm}^{-6}$, but to different values of κ : these vary from $10^{-13} \text{ cm}^3 \text{ s}^{-1}$ (corresponding to a diffusion-controlled microscopical mechanism) to $10^{-18} \text{ cm}^3 \text{ s}^{-1}$ (corresponding to a rather slow, reaction-controlled mechanism). The small-time behaviour is exponential in all cases, and shows up as a straight line for the axes chosen in figure 4. At longer times the crossover effects are clearly seen. From the figure we can infer that for $\kappa = 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ the crossover time is around 50τ , somewhat larger than the value T_0 given by (47). For smaller values of κ , the crossover moves to shorter times; thus for $\kappa = 10^{-18} \text{ cm}^3 \text{ s}^{-1}$ one has a crossover regime around 20τ , still comparable with the full-mixing time T of section 2. Thus, even for this rather slow reaction, standard kinetics are recovered only when the concentration is smaller than 10^{-4} of its initial value. This again shows that the experimentally important stages of the reaction are always controlled by mixing.

6. Conclusions

We conclude that for usual mixing devices and reactions, in the range of parameters considered here, the course of reaction is governed mainly by mixing and not by

diffusion or kinetics. This mixing-controlled type of behaviour corresponds (in our model) to an exponential decay of the reactants' concentration. The standard diffusion-controlled regime (for $\kappa = 10^{-13} \text{ cm}^3 \text{ s}^{-1}$) establishes itself very late in the course of the reaction; for the parameters used here this corresponds to about a minute of mixing (in the best, ideal mixing device!). At this time the concentration of reactants is down by something like 10 orders of magnitude compared with its initial value. Of course one can choose the microscopic reaction rate to be very small so that in a reaction-controlled situation the crossover from the mixing-controlled behaviour to the large-time, $1/t$ behaviour, may occur at shorter times. Nevertheless, even in this case the mixing-controlled mechanism stays very important, provided that the reaction rate is high enough to ensure that a reasonable amount of particles react during a mixing cycle of duration τ .

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Appendix

In this appendix we will give a heuristic justification of (33), the exact derivation of which needs the use of the explicit form of $g(x)$ or $\Gamma(k)$ (see [12]). A very simple, heuristic explanation of the final result, equation (33), starts from the ideas of the scaling approach used in [3] for reactions in fully mixed but disordered systems.

If we consider (16) and treat η as the time and ξ as the space variable we can introduce a characteristic diffusion length ξ_D in ξ -space, $\xi_D \sim \sqrt{D\eta}$. The quantity ξ_D is of the same order of magnitude as the characteristic extent of the Green's function Ξ_G introduced in section 5. At time η the profile of concentrations is smoothed out by diffusion on the scale ξ_D , but fluctuations on larger scales than ξ_D survive. Thus, at time η the system can be viewed as consisting of independent compartments of length ξ_D , each compartment containing only the reactant that initially was in excess in this part. This residual amount of reactant is of the order of $c_0|\xi_A - \xi_B|$, where ξ_A and ξ_B are the total widths of the *A* and the *B* lamellae in the compartment considered. If $\xi_D \gg l_0$, the mean number of *A* and *B* striations inside a compartment of length ξ_D is $n = \frac{1}{2}\xi_D/l_0$, the mean value of the difference $\xi_A - \xi_B$ is, of course, zero and the squared dispersion of this difference, $\langle(\xi_A - \xi_B)^2\rangle$ is of the order of $2n\sigma^2$, where $\sigma^2 = S - L^2$ is the squared dispersion of the length of one striation.

The averaged amount of the residual reactant is $c_0\langle|\xi_A - \xi_B|\rangle \sim c_0\langle(\xi_A - \xi_B)^2\rangle^{1/2}$, and its average concentration $c(t) \sim c_0\langle|\xi_A - \xi_B|\rangle/\xi_D$ is of the order of

$$c(t) \sim c_0 \left(\frac{S - L^2}{L} \right)^{1/2} \xi_D^{1/2} \sim c_0 \left(\frac{S - L^2}{L} \right)^{1/2} (D\eta)^{-1/4}. \quad (\text{A1})$$

After substitution of the explicit form for η , equation (17), in (A1) we regain (33) up to the numerical coefficient $(4\pi)^{-1/4} = 0.531 \dots$

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