PROPAGATING REACTION-DIFFUSION FRONTS

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Propagating chemical waves have been experimentally characterized in the Belousov–Zhabotinskii reaction (Zhabotinskii and Zaikin, 1973; Winfree, 1972, 1974b; Field and Noyes, 1974b; Showalter et al., 1979; Smoes, 1980), in a ferroin–bromate system (Showalter, 1981), and in the iodate–arsenous acid reaction (Epik and Shub, 1955; Gribschaw et al., 1981; Hanna et al., 1981, 1982). Propagating waves have also been observed in the chlorite–iodide–malonic acid reaction (De Kepper et al., 1982).

The chemical waves in these systems can be categorized as fronts, pulses, or periodic wave trains (Ortoleva and Ross, 1974; Fife, 1979). The BZ and chlorite–iodide–malonic acid reactions exhibit pulses and wave trains that require excitable or oscillatory reaction kinetics. Pulses regenerate the kinetic state of the solution through which they propagate. Waves in the ferroin–bromate and iodate–arsenous acid reactions are frontlike, converting a reaction mixture from one kinetic state to another as they propagate. In stirred solution, these systems behave as “clock reactions.”

Fronts in the ferroin–bromate reaction have been characterized as “consumption waves” (Rinzel and Ermentrout, 1982). In stirred solution, bromide initially present as a reactant is slowly consumed to a critical concentration;

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bromous acid is then rapidly generated autocatalytically. The red solution suddenly turns blue as ferroin is oxidized to ferrin in the autocatalytic reaction. A chemical wave can be initiated in a thin film of solution before the bulk oxidation by locally depleting bromide at a positively biased Ag electrode. The result is a propagating wave that converts the reaction mixture from red to blue.

Waves in the iodate oxidation of arsenous acid are true propagating fronts. Iodide is generated autocatalytically in a reaction mixture initially containing iodide until the limiting reagent, iodate or arsenous acid, is consumed. Negligible chemical reaction occurs in a solution that initially contains very little iodide. In the limit of zero initial iodide concentration, the system is unstable only to a finite increase in iodide concentration.

A chemical wave can be initiated in a thin film of solution containing only iodate and arsenous acid by reducing iodate to iodide at a negatively biased Pt electrode, thereby initiating iodide autocatalysis locally. The resulting propagating front converts the solution from the unstable state of initial reactants to the stable state of thermodynamic equilibrium.

In this chapter we consider the propagating fronts of the iodate–arsenous acid reaction. It is an attractive system for analysis because the reaction kinetics can be accurately described in terms of a simple model. Many of the results of our analysis presented here are well known. Kolmogorov et al. (1937) and Fisher (1937) developed propagating wave-front solutions of the node–saddle type we consider. Here we apply this analysis to a real chemical system. The different though similar problem, with a saddle–saddle connection, has been thoroughly analyzed in a model for neural impulse propagation (FitzHugh, 1961; Nagumo et al., 1962) and in bistable reaction–diffusion systems (Schlögl, 1972; Nitzan et al., 1974b; Ortoleva and Ross, 1975; Tyson and Fife, 1980).

A phase-plane analysis of fronts like those exhibited in the iodate–arsenous acid system is presented in Section 11.1. A heuristic derivation of an analytic solution for certain fronts of this type is given in Section 11.2. In Section 11.3, the results are used to analyze the fronts of the iodate–arsenous acid system with arsenic acid in stoichiometric excess, and in Section 11.4 we examine higher-velocity fronts. In Section 11.5 fronts in the iodate–arsenous acid system with iodate in stoichiometric excess are analyzed. Limitations and unique features of our analyses are discussed in Section 11.6.

11.1 TRAVELING WAVE FRONTS

We begin by examining a partial differential equation describing chemical reaction and diffusion in one spatial dimension, modeling waves in a tube or in an axially symmetric thin layer of solution where the propagation is purely radial at distances far from the origin. Letting $u(x, t)$ be the concentration of
FIGURE 11.1. Solution of the reaction-diffusion equation for iodide fronts in the iodate–arsenous acid system with arsenous acid in stoichiometric excess. Concentration $u$ (M) as a function of (a) distance (mm) for a fixed time, and (b) time (s) for a fixed distance. These curves were calculated from Eq. (11.29) with $k = 11.7$ mm$^{-1}$ and $v = 2.35 \times 10^{-2}$ mm s$^{-1}$, which corresponds to Eq. (11.20) with $u_1 = 0$ M and $u_2 = c_4^0 = 5.0 \times 10^{-3}$ M.
the species of interest, the reaction-diffusion equation is

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial x^2} + f(u),$$  \hspace{1cm} (11.1)

where $D$ is the diffusion coefficient and $f$ represents the rate of reaction in the homogeneous batch system. In general, $u$ could be a vector of the various species concentrations in the reaction. However, we will pursue the analysis of Eq. (11.1) as a scalar equation. In Section 11.3 we will reduce a system of several components to a one-variable model.

We seek traveling wave-front solutions of Eq. (11.1) of the type shown in Fig. 11.1, where $u_1 = u(\infty, t) = u(x, -\infty)$ and $u_2 = u(-\infty, t) = u(x, \infty)$. The initial reaction mixture ($t \to -\infty$) or the reaction mixture ahead of the wave ($x \to \infty$) is in the unstable steady state $u_1$; the wave front represents the transition from this unstable steady state to the stable state $u_2$ of thermodynamic equilibrium.

We look for constant-velocity, constant-wave-form solutions. Letting the velocity $v$ of the front be positive, we have

$$v = \left( \frac{dx}{dt} \right)_{du=0} = -\frac{(\partial u/\partial t)_x}{(\partial u/\partial x)_t}.$$  \hspace{1cm} (11.2)

**Figure 11.2.** Reaction rate $f \,(M \, s^{-1})$ as a function of concentration $u \,(M)$ according to Eq. (11.25). Roots are at $u = c_1 = -1.0 \times 10^{-5}$, 0, and $5.0 \times 10^{-3} \, M$. Inset shows blowup of the region near origin.
Combining the constant-velocity assumption [Eq. (11.2)] with the reaction–diffusion equation [Eq. (11.1)] (or introducing a new coordinate \( x - vt \)) allows us to write the ordinary differential equation

\[
Du'' + vu' + f(u) = 0,
\]

where \( '' \) designates differentiation with respect to a moving spatial coordinate \( x - vt \) that we will denote as \( x \). Equation (11.3) is equivalent to the first-order system, Eqs. (11.4)

\[
\begin{align*}
  u' &= \gamma, \\
  \gamma' &= -\frac{v\gamma}{D} - \frac{f(u)}{D}.
\end{align*}
\]

The steady-state solutions of Eq. (11.4) are simply \( u = \dot{u}, \gamma = 0 \) where \( f(\dot{u}) = 0 \).

We now examine the steady states \( u_1 \) and \( u_2 \). The gradient \(|\gamma|\) increases between these two points and is steepest in the wave front when \( \gamma' = u'' = 0 \).

![FIGURE 11.3. Phase plane for Eq. (11.4) with \( v = 2.35 \times 10^{-7} \text{ mm s}^{-1} \), \( D = 2.0 \times 10^{-3} \text{ mm}^2 \text{ s}^{-1} \), and \( f(u) = f(c_1) \) according to Eq. (11.25). Gradient \( \gamma(M \text{ mm}^{-1}) \) as a function of concentration \( u(M) \). Trajectories (---) through a wide range of initial values converge to the node at the origin. The connection from the saddle at \( (c_4^0 = 5.0 \times 10^{-3} \text{ M}, 0) \) to the node at \( (0,0) \) represents the propagating wave-front solution. This trajectory is identical to that obtained from Eq. (11.27). The eigenvectors (-----) at these steady states are indicated.](image)
and \( f(u) = -v \gamma \). Linearizing Eq. (11.4) generates the eigenvalues

\[
\lambda = \frac{-v/D \pm \sqrt{v^2/D^2 - 4f'(\hat{u})/D}}{2}.
\]

(11.5)

For \( f'(\hat{u}) < 0 \), the two eigenvalues are of opposite sign and the steady state is a saddle point; for \( 0 < f'(\hat{u}) < v^2/4D \), both eigenvalues are negative and the steady state is a stable node. The eigenvectors corresponding to the eigenvalues \( \lambda \) are simply given by \( \gamma = \lambda (u - \hat{u}) \).

In order to depict the phase plane, we choose the function \( f \) used in Section 11.3 to describe the iodate–arsenous acid system when arsenous acid is in stoichiometric excess. Figure 11.2 shows \( f \) as a function of \( u \). Here, \((u_1, \gamma_1) = (0, 0)\) is the stable node and \((u_2, 0)\) is the saddle point. (A third physically meaningless root of \( f \) at negative concentration is shown in the enlargement of the region near the origin.) Figure 11.3 shows the \( u-\gamma \) phase plane with the two steady states of \( f \) and the corresponding eigenvectors. The eigenvectors at \( u_1 \) approach the origin with negative slopes, whereas at \( u_2 \) one eigenvector moves away from the steady state with a positive slope and the other approaches it with a negative slope. Also shown in Fig. 11.3 are the phase-plane

![Image of the phase plane](image)

**Figure 11.4.** The phase plane for Eq. (11.6) with \( v = 2.35 \times 10^{-2} \) mm s\(^{-1}\), \( D = 2.0 \times 10^{-3} \) mm\(^2\) s\(^{-1}\), and \( f(u) = f(c_1) \) according to Eq. (11.25) showing \( w \) (M s\(^{-1}\)) as a function of concentration \( u \) (M). A unique orbit connects the node at \((0, 0)\) and the saddle at \((c_2^0 = 5.0 \times 10^{-3} \ M, 0)\). The six trajectories were generated by integrating Eq. (11.6) with initial values of \( u = 1.0 \times 10^{-5} \) M and \( w \) ranging from \( 2.0 - 3.0 \times 10^{-6} \) M s\(^{-1}\).
trajectories. Note that all trajectories converge to the node at the origin. The trajectory tangent to an eigenvector at each steady state represents the wave front. Note also that the points on the trajectories with horizontal tangents trace out the shape of \( f \), as given by the relation \( \gamma = -f(u)/v \) when \( \gamma' = 0 \).

The natural choice for the direction of wave propagation is that which gives rise to a positive wave velocity. However, this choice results in some confusion

![Figure 11.5](image.png)

**FIGURE 11.5.** Reaction rate \( g \ (M \ s^{-1}) \) as a function of concentration \( u \ (M) \) according to Eq. (11.35) (--). Roots are at \( u = c_2 = 2.180 \times 10^{-3}, \ 2.186 \times 10^{-3}, \) and \( 4.1 \times 10^{-3} \ \ M. \) Also shown is the corresponding phase-plane trajectory (---) for Eq. (11.4) with \( v = 2.998 \times 10^{-2} \ mm \ s^{-1}, \ D = 2.0 \times 10^{-3} \ mm^2 \ s^{-1}, \) and \( f(u) = g(c_2). \) Gradient \( \gamma \ (M \ mm^{-1}) \) as a function of concentration \( u \ (M). \) The trajectory leads away from the steady state at \( u = c_3^0 = 2.180 \times 10^{-3} \ \ M \) toward zero concentration. This trajectory is identical to that obtained from Eq. (11.10) with \( u_1 = 2.186 \times 10^{-3} \ \ M, \ u_2 = 2.180 \times 10^{-3} \ \ M, \) and \( k = -3.91 \times 10^{3} \ M^{-1} \ mm^{-1}. \) Inset shows blowup of region near \( c_3^0 \) (dotted line represents trajectory inaccessible to the reaction).
concerning the stability of the steady states since a "stable" node in space is "unstable" in time. We can convert to the phase plane in time simply with a factor of \(-v\). Let \(w = \dot{u} = du/dt\). The first-order system now becomes

\[
\dot{u} = w, \\
\dot{w} = \frac{v^2}{D} (w - f(u)),
\]

and the corresponding eigenvalues are

\[
\lambda = \frac{v^2/D \pm \sqrt{v^2/D^2 - 4f'(\dot{u})/D}}{2}.
\]

At \(\dot{u} = u_1 = 0\), \(f' > 0\), and both eigenvalues are positive; therefore the steady state is an unstable node. At \(u_2\), \(f' < 0\), and the steady state is a saddle point. The trajectories in the \(u-w\) phase plane, shown in Fig. 11.4, leave the unstable steady state at the origin and approach the saddle at \(u_2\) along its eigenvector of negative slope. (Trajectories with initial values slightly off the true trajectory diverge along the eigenvector of positive slope as they approach the saddle point.)

![Graph showing solution of reaction-diffusion equation](image)

**FIGURE 11.6.** Solution of reaction-diffusion equation for iodine fronts in iodate-arsenous acid system with iodate in stoichiometric excess. Concentration \(u (M)\) as a function of distance (mm) for a fixed time. Curve calculated from Eq. (11.36) with \(k = -3.91 \times 10^3 \text{ M}^{-1} \text{ mm}^{-1}\) and \(v = 2.998 \times 10^{-2} \text{ mm s}^{-1}\), which corresponds to Eq. (11.20) with \(u_1 = \frac{1}{2} c_2^0 + 3k_4/5k_H = 2.186 \times 10^{-3} \text{ M}\) and \(u_2 = \frac{1}{2} c_2^0 = 2.180 \times 10^{-3} \text{ M}\).
A different type of propagating front is exhibited by the iodate–arsenous acid system when iodate is in stoichiometric excess (see Section 11.5). In this case the rate of chemical reaction \( g \) has three positive roots with a negative derivative at the smallest and largest roots. The wave front is generated between zero concentration, which is not a steady state but is the starting point for this particular reaction, and the smallest root, which corresponds to thermodynamic equilibrium. Figure 11.5 shows \( g \) and the \( u-\gamma \) phase plane for the excess iodate system. Here \( \dot{u} \) is a saddle and the trajectory moves toward lower concentration. The trajectory is truncated at \( u = 0 \) for obvious physical reasons. Note that the gradient there is at its steepest. The wave form for such a "sharp front" (Aronson, 1980) is shown in Fig. 11.6.

11.2 ANALYTIC SOLUTIONS

We begin with Eq. (11.3), \( Du'' + vu' + f(u) = 0 \). Instead of analyzing the first-order system as in Section 11.1, we will transform Eq. (11.3) into a first-order equation. Let \( u' = G(u) \). We want \( G(\dot{u}) = 0 \) for the steady states \( \ddot{u} \). Since \( u'' = G'(u)u' \), we have from Eq. (11.3)

\[
\frac{-f}{DG' + v}.
\]

Say \( u' = G \) is of degree \( n \) as a function of \( u \). Then \( G' \) is degree \( n - 1 \), and \( f = -u'(DG' + v) \) has degree \( n + (n - 1) = 2n - 1 \). For fronts in the iodate–arsenous acid system (Sections 11.3–11.5), we know that \( f \) is a cubic; therefore \( 2n - 1 = 3 \) and \( n = 2 \). We therefore choose the gradient to be a quadratic function of the concentration, which corresponds to a parabolic phase-plane trajectory.

Let our cubic function \( f \) be given by

\[
f(u) = -\alpha(u - u_1)(u - u_2)(u - u_3).
\]

Since we want a wave front between two steady states we choose

\[
G(u) = u' = k(u - u_1)(u - u_2),
\]

or any of three such possibilities, depending on which two of the three steady states are appropriate. Differentiation gives

\[
u'' = k^2(u - u_1)(u - u_2)(2u - u_1 - u_2).
\]

Substitution into Eq. (11.3) generates the linear equation

\[
Dk^2(2u - (u_1 + u_2)) + kv - \alpha(u - u_3) = 0.
\]
Therefore
\[ 2Dk^2 - \alpha = 0, \]  \hspace{1cm} (11.13)
and
\[ -Dk^2(u_1 + u_2) + kv + \alpha u_3 = 0. \]  \hspace{1cm} (11.14)
From Eq. (11.13),
\[ k = \left(\frac{\alpha}{2D}\right)^{1/2} \]  \hspace{1cm} (11.15)
(we choose the sign of \( k \) to give a negative gradient as desired), which on substitution into Eq. (11.14) gives
\[ v = (2D\alpha)^{1/2}\left[\frac{1}{3}(u_1 + u_2) - u_3\right]. \]  \hspace{1cm} (11.16)
We also see from Eqs. (11.10) and (11.15) that
\[ u' = \left(\frac{\alpha}{2D}\right)^{1/2}(u - u_1)(u - u_2). \]  \hspace{1cm} (11.17)
This first-order equation is integrated using partial fractions to yield
\[ u = \frac{u_1 - u_2}{1 - Ae^{k(u_1 - u_2)x}}, \]  \hspace{1cm} (11.18)
where \( A \) is the constant of integration. Another expression for this solution in the case where the initial value lies between \( u_1 \) and \( u_2 \) (making \( A < 0 \)) is
\[ u = \frac{u_1 + u_2}{2} + \frac{u_1 - u_2}{2}\tanh\left(-\frac{1}{2}k(u_1 - u_2)x + a\right), \]  \hspace{1cm} (11.19)
where \( a = \ln(-A) \). Equation (11.19) makes clear the nature of wave fronts generated by the cubic function \( f \). The wave front shown in Fig. 11.1 is simply a tanh curve asymptotic to the two steady states, with an initial value determined by \( a \) and a steepness determined by \( k \).
Since our spatial coordinate \( x \) is actually \( x - vt \), the solution to the reaction-diffusion equation [Eq. (11.1)] is
\[ u(x, t) = \frac{u_1 + u_2}{2} + \frac{u_1 - u_2}{2}\tanh\left(-\frac{1}{2}k(u_1 - u_2)(x - vt) + a\right), \]  \hspace{1cm} (11.20)
\[ = \frac{u_1 - u_2}{1 - Ae^{k(u_1 - u_2)(x - vt)}}. \]  \hspace{1cm} (11.20)
Equation (11.20), together with Eqs. (11.15) and (11.16) to define \( k \) and \( v \), and
a known rate equation \( f \), describes the wave-front behavior of a particular reaction-diffusion system. We now apply these results to the iodate–arsenous acid system.

### 11.3 IODIDE FRONTS IN THE IODATE–ARSENOUS ACID REACTION WITH ARSENOUS ACID IN STOICHIOMETRIC EXCESS

The iodate–arsenous acid system can be described in terms of the oxidation of iodide by iodate, Process (A), and the reduction of iodine by arsenous acid, Process (B) (De Kepper et al., 1981b; Hanna et al., 1981, 1982; Saul et al., 1984).

\[
\text{IO}_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O, \quad (A)
\]

\[
H_3\text{AsO}_3 + I_2 + H_2O = H_3\text{AsO}_4 + 2I^- + 2H^+. \quad (B)
\]

Process (A) obeys rate law \( \alpha \) (Liebafsky and Roe, 1979) and Process (B) obeys rate law \( \beta \) (Roebuck, 1902; Pendlebury and Smith, 1974).

\[
R_\alpha = -\frac{1}{5} \frac{d[I^-]}{dt} = (k_a + k_b[I^-])[I^-][\text{IO}_3^-][H^+]^2, \quad (\alpha)
\]

\[
R_\beta = -\frac{d[I_2]}{dt} = \frac{k_c[I_2][H_3\text{AsO}_3]}{[I^-][H^+]}. \quad (\beta)
\]

In this section we consider chemical waves in reaction mixtures containing arsenous acid in stoichiometric excess \([H_3\text{AsO}_3]_0 > 3[\text{IO}_3^-]_0\). For these initial conditions, the net reaction is given by Processes (A) + 3(B) or (I).

\[
\text{IO}_3^- + 3H_3\text{AsO}_3 = I^- + 3H_3\text{AsO}_4. \quad (I)
\]

The following notation is adopted for our description of chemical waves in this system:

\[
c_1 = [I^-], \quad c_2 = [I_2], \quad c_3 = [H_3\text{AsO}_3], \quad c_4 = [\text{IO}_3^-],
\]

\[
k_A = k_a[H^+]^2, \quad k_B = k_b[H^+]^2, \quad k_C = \frac{k_c}{[H^+]},
\]

and \( c_i^0 \) for initial concentrations. We consider buffered reaction mixtures; therefore hydrogen ion concentration is constant. Initial concentrations in typical wave experiments (Hanna et al., 1981, 1982) and values for \( k_a, k_b, \) and \( k_c \) (Saul et al., 1984) are given in Table 11.1.

A simple empirical rate law model can be formulated for the reaction–diffusion behavior in solutions containing a stoichiometric excess of arsenous acid.
Process (A) is rate determining, and therefore the rate of iodide autocatalysis is governed by rate law $\alpha$. The reaction–diffusion behavior is described in terms of the variable species in rate law $\alpha$ according to the stoichiometry of net reaction (I)

\[
\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} + R_\alpha, \tag{11.21}
\]

\[
\frac{\partial c_4}{\partial t} = D_4 \frac{\partial^2 c_4}{\partial x^2} - R_\alpha. \tag{11.22}
\]

Iodate and iodide are the only stoichiometrically significant iodine containing species; therefore according to net reaction (I), $c_1^0 + c_4^0 = c_1 + c_4$. Since $c_4^0 \gg c_1^0$, we have to a good approximation

\[
c_4^0 = c_1 + c_4. \tag{11.23}
\]

Combining this stoichiometric relation with Eq. (11.21) or Eq. (11.22) yields a reaction–diffusion equation in $c_1$

\[
\frac{\partial c_1}{\partial t} = D \frac{\partial^2 c_1}{\partial x^2} + (k_A + k_B c_1)c_1(c_4^0 - c_1). \tag{11.24}
\]

This scalar equation corresponds to Eq. (11.1), where

\[
f(c_1) = (k_A + k_B c_1)c_1(c_4^0 - c_1). \tag{11.25}
\]

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Excess Arsenous Acid Solutions, M</th>
<th>Excess Iodate Solutions, M</th>
<th>Rate Constants and Diffusion Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>[IO₃⁻]</td>
<td>$5.0 \times 10^{-3}$</td>
<td>$5.0 \times 10^{-3}$</td>
<td>$k_a = 4.50 \times 10^3 , M^{-3} , \text{sec}^{-1}$</td>
</tr>
<tr>
<td>[H₃AsO₃]</td>
<td>$1.55 \times 10^{-2}$</td>
<td>$1.09 \times 10^{-2}$</td>
<td>$k_b = 4.36 \times 10^5 , M^{-4} , \text{sec}^{-1}$</td>
</tr>
<tr>
<td>[H⁺]</td>
<td>$7.1 \times 10^{-3}$</td>
<td>$7.1 \times 10^{-3}$</td>
<td>$k_c = 3.20 \times 10^{-2} , M , \text{sec}^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$D = 2.0 \times 10^{-3} , \text{mm}^2 , \text{sec}^{-1}$</td>
</tr>
</tbody>
</table>
The steady states of the stirred batch reaction are

\[ c_1 = \begin{cases} -k_A/k_B \\ 0 \\ c_4^0 \end{cases} \]  \hspace{1cm} (11.26)

Of course, only the steady states 0 and \( c_4^0 \) are physically meaningful. To ensure that Eq. (11.24) is locally valid, we assume that \( D_1 = D_4 = D \) in Eqs. (11.21) and (11.22) (Hanna et al., 1982).

The analysis in Sections 11.1 and 11.2 of Eq. (11.1) with a cubic function \( f \) applies directly to Eq. (11.24). The function \( f(c_1) \) is shown in Fig. 11.2 for the rate constants and initial concentrations in Table 11.1. According to Eq. (11.10), the steady states \( u_1 = 0 \) and \( u_2 = c_4^0 \) are joined by the parabolic trajectory

\[ G(c_1) = \left( \frac{k}{c_4^0} \right) c_1(c_1 - c_4^0), \]  \hspace{1cm} (11.27)

shown in Fig. 11.3. The slopes of this parabola at 0 and \( c_4^0 \) are given by the eigenvalues \( \pm k \). Here

\[ k = \left( \frac{k_B}{2D} \right)^{1/2} c_4^0 \]  \hspace{1cm} (11.28)

differs from \( k \) of Eq. (11.15) by a factor of \( c_4^0 = -(u_1 - u_2) \). Figure 11.4 shows trajectories in the \( u-w \) phase plane calculated from Eq. (11.6) with \( f(c_1) \).

From Eq. (11.20), the solution of Eq. (11.24) is

\[ c_1(x,t) = \frac{c_4^0}{1 + Be^{-k(x-wt)}} = \frac{1}{2}c_4^0 \left( 1 + \tanh \left( -\frac{1}{2}k(x - vt) + b \right) \right), \]  \hspace{1cm} (11.29)

where \( B \) and \( b \) are arbitrary constants. Figure 11.1 shows \( c_1 \) as a function of distance and time for the rate constants and initial concentrations in Table 11.1. The wave-front-propagation velocity is given by

\[ v = kD + \left( \frac{2D}{k_B} \right)^{1/2} k_A \approx kD. \]  \hspace{1cm} (11.30)

Equation (11.30) with the values in Table 11.1 gives \( v = 2.35 \times 10^{-2} \) mm sec\(^{-1}\) in good agreement with experiment (Hanna et al., 1982). The wave form in Fig. 11.1 also agrees well with that obtained by numerically integrating a four-variable (\( \Gamma^- \), \( I_2 \), \( IO_3^- \), \( H_3AsO_3 \)) reaction-diffusion model (Saul et al., 1984). The agreement between the analytic and numerical wave forms improves as the
concentration of $H_3AsO_3$ is increased. As the $H_3AsO_3$ concentration increases, the rate of consumption of $I_2$ in Process (B) increases, and the resulting lower concentration of $I_2$ makes stoichiometric relation Eq. (11.23) a better assumption.

To calculate the eigenvalues at $u_1$ and $u_2$, it is convenient to combine Eq. (11.25) with Eqs. (11.28) and (11.30) to yield

$$f(c_1) = \frac{2Dk^2}{c_4} \left[ \left( \frac{v}{Dk} - 1 \right) \frac{c_4^0}{2} + c_1 \right] c_1 (c_4^0 - c_1)$$

(11.31)

and

$$f'(c_1) = Dk \left( \frac{v}{D} - k \right) + 2Dk \left( 3k - \frac{v}{D} \right) \frac{c_1}{c_4^0} - 6Dk^2 \left( \frac{c_1}{c_4^0} \right)^2$$

(11.32)

Therefore, $f'(0) = Dk (v/D - k)$ and $f'(c_4^0) = -Dk (v/D + k)$. From Eq. (11.5) the eigenvalues at $c_1 = 0$ are

$$\lambda = \begin{cases} k - \frac{v}{D} \\ -k \end{cases}$$

and at $c_1 = c_4^0$,

$$\lambda = \begin{cases} -k - \frac{v}{D} \\ k \end{cases}$$

Because the maximum gradient in the parabolic trajectory occurs when $c_1 = \frac{1}{2} c_4^0$ and $f(c_1) = -ve_1$, the maximum gradient is therefore $c_{1\text{max}} = -f(\frac{1}{2} c_4^0)/v = -\frac{1}{2} k c_4^0$. The parameter $k$ clearly determines the steepness of the wave front, which increases with the square of the initial iodate concentration.

### 11.4 Higher-Velocity Fronts

Although the particular analytic solution of Eq. (11.24) given by Eq. (11.29) agrees well with experiment, it is not unique. Solutions exist for this system with propagation velocities greater than or equal to some minimum velocity (Kolmogorov et al., 1937). That this minimum velocity is the propagation velocity given by Eq. (11.30) for the analytic solution Eq. (11.29) is shown in Section 11.7.

Aronson (1980) defines the minimal wave velocity, $v_{\text{min}}$, as the “asymptotic speed of propagation of disturbances from rest”. That is, steep monotonic initial conditions, such as a step function in concentration, will decay into the
tanh curve of Eq. (11.29) as the velocity increases toward $v_{\text{min}}$, given by Eq. (11.30). Shallow monotonic initial conditions that attain the unstable steady state $u_1$ in a finite distance will also evolve into the analytic solution, slowing down toward $v_{\text{min}}$ and becoming steeper. In this case the slowing down is due to the encounter of the wave front with the steady state $u_1$ ahead of it. If we remove this restriction, allowing shallow initial conditions to approach $u_1$ only in the limit, we can generate solutions of high velocity that do not necessarily decay into the analytic solution.

In Section 11.1 we found that $v = -f(u)/\gamma_{\text{max}}$ at the maximum gradient in the front. Therefore, a steep wave front implies a low propagation velocity, and the higher-velocity alternate solutions of Eq. (11.24) suggest fronts with less steep gradients. Diffusion plays an important role in fronts with very steep gradients, whereas fronts with shallow gradients allow reaction to proceed with little influence from diffusion. Thus in the iodate–arsenous acid system there are characteristically slow and steep waves, including the analytic solution, and arbitrarily fast and shallow waves, represented by the alternate solutions of the reaction-diffusion equation. In the limit the fast wave is the front of infinite velocity and zero concentration gradient; the slow wave is given by the analytic solution Eq. (11.29). All the other solutions are hybrids, with diffusion contributing somewhat to a fast wave, or an initial concentration gradient altering the wave form and velocity of a slow wave. Figure 11.7 shows the wave forms of

![Figure 11.7](image)

**Figure 11.7.** Higher velocity iodide fronts in iodate–arsenous acid system with arsenous acid in stoichiometric excess. Concentration $u (M)$ as a function of distance (mm). Calculated from Eqs. (11.4) with $v_0 = 2.35 \times 10^{-2}$ mm s$^{-1}$ (-----), $v = 2v_0$ (---), $v = 4v_0$ (-----), $v = 8v_0$ (•••••), $D = 2.0 \times 10^{-5}$ mm$^2$ s$^{-1}$, and $f(u) = f(c_1)$ according to Eq. (11.25).
fronts with velocities equal to multiples of the velocity given by Eq. (11.30) for the analytic solution. These fronts were generated by numerically integrating Eq. (11.4) with \( f(c_i) \) and the indicated velocities. The corresponding trajectories in the \( u-\gamma \) phase plane are shown in Fig. 11.8. We see that the trajectories become more shallow as \( v \) increases. As \( v \) becomes large, both eigenvalues at \( u_1 \) and \( u_2 \) approach 0 and \(-v/D\). The trajectories for the high-velocity fronts approach the steady states along the almost horizontal eigenvectors, indicating that they are little affected by diffusion.

The iodate–arsenous acid waves described by Eq. (11.29) are much like trigger wave fronts in systems with excitable or oscillatory kinetics, such as the Belousov–Zhabotinskii reaction. Very slow moving phase waves in the BZ system arising from large phase gradients evolve into trigger waves (Reusser and Field, 1979). Phase waves arising from shallow phase gradients may propagate with an arbitrarily large velocity above the trigger wave velocity. In the limit of a zero phase gradient in an oscillatory medium, a phase wave has an infinite velocity; in a nonoscillatory but excitable medium, pure trigger wave fronts are exhibited. [Tyson and Fife (1980) have shown that wave backs in an excitable or oscillatory BZ system are phase waves.] Higher-velocity waves may also result from a concentration or temperature gradient imposed on an oscillatory system. These waves are known as kinematic waves (Kopell and Howard, 1973b; Ortoleva and Ross, 1974).

If we define phase as the extent of reaction from initial reactants to thermodynamic equilibrium in the iodate–arsenous acid reaction, the arbi-

![Figure 11.8](image)

**Figure 11.8.** Phase-plane trajectories corresponding to higher-velocity iodide fronts in Fig. 11.7. Gradient \( \gamma \text{ (M mm}^{-1} \) as a function of concentration \( u \text{ (M).} \)
trarily fast and shallow waves are much like phase waves. Thus the initial conditions correspond to a negative “phase gradient” with $u_1 = 0$ approached only in the limit.

11.5 IODINE FRONTS AND TRUNCATED IODIDE FRONTS IN THE IODATE–ARSENOUS ACID REACTION WITH IODATE IN STOICHIOMETRIC EXCESS

The net reaction for the iodate oxidation of arsenous acid in reaction mixtures containing iodate in stoichiometric excess ($[\text{H}_3\text{AsO}_3]_0 < \frac{2}{3}[\text{IO}_5^-]_0$) is given by Processes 2(A) + 5(B) or

$$2\text{IO}_5^- + 5\text{H}_3\text{AsO}_3 + 2\text{H}^+ = \text{I}_2 + 5\text{H}_3\text{AsO}_4 + \text{H}_2\text{O}.$$  \hspace{1cm} (II)

As long as sufficient $\text{H}_3\text{AsO}_3$ remains in the solution for the reduction of $\text{I}_2$ to $\text{I}^-$ in Process (B), the reaction proceeds with the autocatalytic generation of iodide according to Processes (A) + 3(B) at a rate governed by rate law $\alpha$. Upon complete consumption of $\text{H}_3\text{AsO}_3$, autocatalysis is terminated and the accumulated $\text{I}^-$ is oxidized to $\text{I}_2$ in Process (A). This process is also governed by rate law $\alpha$.

The development in Section 11.3 describing iodide fronts in excess arsenous acid solutions applies also to waves in excess iodate solutions; however, now the iodide front is truncated when iodide autocatalysis is terminated. This occurs, according to net reaction (I), when $c_I = \frac{1}{2}c_0$. The subsequent consumption of iodide in Process (A) gives rise to a cusp-shaped maximum in iodide concentration (Hanna et al., 1982; Saul et al., 1984). Therefore the iodide front before (in time) or ahead (in space) of the cusp is described by Eq. (11.29) with $k$ and $v$ exactly as in an excess arsenous acid solution. However, because the front is truncated, the wave velocity given by Eq. (11.30) provides only an approximation of the experimental velocity or that obtained by numerically integrating a four-variable reaction-diffusion model (Saul et al., 1984). Another consideration in applying the development in Section 11.3 is that near the cusp, $\text{I}_2$ is generated in Process (A) faster than it is consumed in Process (B) since the rate of Process (B) is retarded by the low arsenous acid concentration. If there is a significant accumulation of $\text{I}_2$, the stoichiometric assumption Eq. (11.23) fails and Eq. (11.29) no longer accurately describes the front at this point. However, numerical integration of a four-variable model for a typical excess iodate batch reaction shows that $[\text{IO}_5^-] + [\text{I}^-]$ is equal to about 97% of $[\text{IO}_5^-]_0$ at the iodide maximum (Hanna et al., 1982, Fig. 13). Therefore Eq. (11.23) is a reasonable approximation even at the iodide cusp. Diffusion will also tend to smooth out the iodide cusp; however, our numerical studies indicate that the iodide maximum remains remarkably sharp in the chemical wave (Saul et al., 1984).

We now use the developments in Sections 11.1 and 11.2 to describe the iodine front, which appears directly after the iodide cusp. Again, our method is
to derive a one-variable model (in this case $c_2$) by combining the empirical rate law with the pertinent reaction stoichiometry. Following the complete consumption of $\text{H}_3\text{AsO}_3$, iodine is generated in Process (A) at a rate governed by rate law $\alpha$. The reaction–diffusion behavior is again described in terms of the variable species in rate law $\alpha$ according to the stoichiometry of Process (A)

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} - 5R_\alpha,$$  \hspace{1cm} (11.33)

$$\frac{\partial c_4}{\partial t} = D_4 \frac{\partial^2 c_4}{\partial x^2} - R_\alpha.$$  \hspace{1cm} (11.34)

From reaction (I), the iodide concentration at the cusp is given by $\frac{1}{3}c_3^0$, therefore, after the cusp $c_1 = \frac{1}{3}c_3^0 - \frac{4}{3}c_2$ according to Process (A). Similarly, iodate concentration at the cusp is given by $c_4^0 - \frac{1}{3}c_3^0$, therefore, after the cusp $c_4 = (c_4^0 - \frac{1}{3}c_3^0) - \frac{1}{3}c_2$. These stoichiometric relations depend on the assumption that the concentrations of $\text{H}_3\text{AsO}_3$ and $\text{I}_2$ are negligible at the iodide cusp. Substituting the relations into Eq. (11.33) or Eq. (11.34) yields a reaction-diffusion equation in $c_2$,

$$\frac{\partial c_2}{\partial t} = D \frac{\partial^2 c_2}{\partial x^2} + 3\left[k_A + k_B \left(\frac{1}{3}c_3^0 - \frac{4}{3}c_2\right)\right]\left(\frac{1}{3}c_3^0 - \frac{4}{3}c_2\right)\left(c_4^0 - \frac{1}{3}c_3^0 - \frac{1}{3}c_2\right)$$

$$= D \frac{\partial^2 c_2}{\partial x^2} + g(c_2).$$  \hspace{1cm} (11.35)

The function $g$, shown in Fig. 11.5 for the rate constants and initial concentrations in Table 11.1, is a cubic with three positive roots: $\frac{1}{3}c_3^0$, $\frac{1}{3}c_3^0 + \frac{2}{3}(k_A/k_B)$ and $3c_4^0 - c_3^0$. It is necessary to assume that $D_1 = D_2 = D_4 = D$ for Eq. (11.35) to be locally valid.

We are interested in the rise in $c_2$ from near zero to the value of $\frac{1}{3}c_3^0$ predicted by the stoichiometry of net reaction (II). The trajectory in the $u$–$\gamma$ phase plane corresponding to this rise is shown in Fig. 11.5, calculated using $u_1 = \frac{1}{3}c_3^0 + \frac{2}{3}(k_A/k_B)$ and $u_2 = \frac{1}{3}c_3^0$ in Eq. (11.10) with rate constants and initial concentrations in Table 11.1. From Eq. (11.20) (after taking the appropriate sign of $k$) a solution for the iodine front is given by

$$c_2(x, t) = \frac{\frac{1}{3}c_3^0 Me^{3/5(k_A/k_B)(x-vt)}}{Me^{3/5k_A/k_B(x-vt)} - 1},$$  \hspace{1cm} (11.36)

where

$$k = -\frac{5}{3} \left( \frac{k_B}{2D} \right)^{1/2},$$  \hspace{1cm} (11.37)

$$v = kD\left[\frac{3}{5} \left( 4c_3^0 + \frac{k_A}{k_B} \right) - 6c_4^0 \right].$$  \hspace{1cm} (11.38)
and \( M \) is an arbitrary constant. Of course, the solution is restricted to \( c_2 \geq 0 \). Equation (11.36) was obtained by substituting into Eq. (11.20) the node and saddle point of \( g, \frac{1}{3}c_3^0 + \frac{2}{3}(k_A/k_B) \) and \( \frac{1}{3}c_3^0 \), for \( u_1 \) and \( u_2 \), respectively. The wave form is little affected by the value of \( u_4 \); however, the direction of propagation is reversed with \( u_1 = 3c_4^0 - c_3^0 \) since it is dynamically stable relative to \( \frac{1}{3}c_3^0 \) (Fife, 1979).

The wave form, shown in Fig. 11.6, is a “sharp” front rather than the “change of phase” front given by a tanh curve like that in Fig. 11.1. These two different types of fronts are a result of initial conditions. The iodine front compares well with that generated by numerically integrating a four-variable reaction-diffusion model for the system (Saul et al., 1984). These calculations show, however, that the iodine front is a “change of phase” type front with an extremely sharp concentration rise at the iodide cusp. Equation (11.36) provides a remarkably accurate facsimile of the wave form because the neglect of \( I_2 \) and \( H_3AsO_3 \) at the iodide cusp corresponds to neglecting the very shallow rise in iodine concentration before the cusp.

The iodine front does not propagate freely. It is generated in the wave back of the truncated iodide front and hence has features of a phase wave. Its propagation velocity is therefore determined by the iodide front rather than that given by Eq. (11.38). The wave form generated by Eq. (11.36), shown in Fig. 11.6, corresponds to the freely propagating front for reaction-diffusion equation (11.35), with the appropriate moving boundary conditions fixing the concentration at zero ahead of the front. The actual iodine front, however, will be an altered version of this wave form, such that its velocity matches that of the truncated iodide front.

11.6 SUMMARY

Propagating fronts convert a reaction mixture from one steady state to another as they travel through a solution. In the iodate–arsenous acid reaction, the front converts a solution of initial reactants to the composition of thermodynamic equilibrium. Fronts that convert a reaction mixture from one stable steady state to another propagate in a direction determined by the relative dynamic stabilities of the steady states (Schlögl, 1972; Nitzan et al., 1974b; Ortoleva and Ross, 1975; Fife, 1979). Fronts in the iodate–arsenous acid system propagate in one direction only, converting the solution to the stable state of thermodynamic equilibrium.

The unstable steady state describing an initial reaction mixture of iodate and arsenous acid is unstable only to a finite increase in iodide concentration. Thus, according to our model, no chemical reaction may occur until some iodide is introduced into the system. This characteristic is a consequence of the location of the unstable steady state at the origin (Fig. 11.2). A chemical wave, initiated by supplying iodide locally at an electrode (Hanna et al., 1981, 1982), propagates by the diffusion of iodide into the solution ahead.
The iodate–arsenous acid reaction provides a real chemical example of wave behavior modeled by a one-variable reaction-diffusion equation. Moreover, the accessibility of an analytic solution permits a detailed analysis of the wave-form and propagation velocity dependence on initial reactant concentrations and rate constants.

Our model of the system is highly idealized; however, it provides a remarkably accurate description of the iodide fronts in excess arsenous acid solutions. A deficiency of the one-variable analysis is that it does not account for the velocity dependence on arsenous acid concentration that is experimentally observed (Hanna et al., 1981, 1982). For excess iodate solutions the model is limited to a qualitative description of the wave behavior. These waves are characterized by a truncated iodide front followed by a “sharp” iodine front. An analytic solution of an unusual type describes the sharp front as part of a “change of phase” through infinity. The propagation velocity of these waves, however, is determined by the leading iodide front.

11.7 APPENDIX: STABILITY OF THE ANALYTIC SOLUTION FOR IODIDE FRONTS WITH ARSENOUS ACID IN STOICHIOMETRIC EXCESS

We noted in Section 11.4 that the partial differential equation (11.1) admits a continuum of traveling wave-front solutions. We now indicate a proof that the analytic solution is stable under conditions holding for Eq. (11.24). Stability means here that a broad class of initial conditions will generate solutions of Eq. (11.24) that approach a translate of the stable solution asymptotically.

Each solution of Eq. (11.24) corresponds to a particular propagation velocity. As noted in Section 11.4, the stable solution is the steepest, slowest front, which is the limiting form of any initial conditions that are nonzero only in a bounded region. We will therefore show that the steepness and velocity given by Eqs. (11.28) and (11.30) must be maximal and minimal, respectively, so that no propagating front solutions of Eq. (11.24) exist that are steeper or slower.

Following Aronson and Weinberger (1975), we can define $v_{\text{min}}$ by a construction in the phase plane. Fix a velocity $v > 0$. We first take the limit as $\varepsilon \to 0$ of the trajectories passing through a point $(0, -\varepsilon)$. This extremal trajectory of Eq. (11.4), the steepest trajectory to the origin, will be denoted by $T_v$. Thus $T_v$ must approach the origin along the steeper of the two eigenvectors at the origin. All other trajectories approaching the origin must follow the shallow eigenvector (Aronson and Weinberger, 1975).

Now as we let $v$ increase, $T_v$ becomes steeper at the origin, since its slope there is $-1/(2D)[v + \sqrt{v^2 - 4Df_1'(0)}]$. In the region $\gamma < 0$ and $0 = u_1 < u \leq u_2$, the entire trajectory $T_v$ lies strictly below the trajectory $T_{v_1}$ if $v_1 > v_2$. Furthermore, for sufficiently large velocities $T_v$ will cross the line $u = u_2$ at a point $(u_2, -\eta)$ for some $\eta > 0$. We are therefore assured that the number $v_{\text{min}} = \inf\{v > 0: v^2 > 4Df_1'(0) \text{ and } \exists \eta > 0 \text{ for } (u_2, -\eta) \in T_v\}$ is well defined.
The proof that this number is the minimal speed is given by Aronson and Weinberger (1975).

Thus, if $v_{\text{min}}^2 > 4Df'(0)$, $T_{v_{\text{min}}}$ is the only trajectory connecting the steady states which approaches the origin along the steeper eigenvector. [If $v_{\text{min}}^2 = 4Df'(0)$, then $T_{v_{\text{min}}}$ does not necessarily hit the saddle at $(u_2, 0)$.] This property is satisfied by the analytic solution in our case: The parabolic trajectory Eq. (11.27) approaches the origin along $\gamma = -ku$ while all other trajectories approach along the nearly horizontal eigenvector $\gamma = (k - v/D)u$ (see Fig. 11.3).

For some cubic functions $f$ the analytic solution Eq. (11.20) approaches the origin along the shallower eigenvector; therefore this solution will be unstable [except when the velocity Eq. (11.16) is $2\sqrt{Df'(0)}$, and the two eigenvalues are the same]. Consider the generic cubic $f(u) = \alpha(u + a)(u - u^2)$, with $a > 0$. Take $D = 1$ for convenience. For $a \geq 1$, we have $f(u) \leq f'(0)u$ for $u \in [0, 1]$, the well-studied case where $v_{\text{min}} = 2\sqrt{f'(0)} = 2\sqrt{aa}$. In this case the analytic solution Eq. (11.20) with $v_0 = \sqrt{2\alpha}(\frac{1}{2} + a)$, is certainly unstable, since $v_0 > v_{\text{min}}$. Note that the eigenvalues at the origin corresponding to $v_0$ are $-\sqrt{\alpha/2}$ and $-\sqrt{\alpha/2(2a)}$. The slope of the parabolic trajectory Eq. (11.10) is $-k = -\sqrt{\alpha/2}$ at the origin, the shallower of the two for $a > \frac{1}{2}$. Thus the analytic solution is unstable as $a$ decreases to $\frac{1}{2}$, at which point the two eigenvectors merge [$v_0^2 = 4f'(0)$] and the analytic solution becomes the steepest, slowest front. For $0 < a < \frac{1}{2}$, the eigenvector with slope $-\sqrt{\alpha/2(2a)}$ becomes more horizontal, and the parabolic trajectory is quite stable. This is the case for the iodate–arsenous acid system.
REFERENCES


