The Influence of the Form of Autocatalysis on the Speed of Chemical Waves

P. Gray, S. K. Scott and K. Showalter

Email alerting service

The influence of the form of autocatalysis on the speed of chemical waves

By P. Gray[1], S. K. Scott[2] and K. Showalter[3]

[1] *Gonville and Caius College, Cambridge CB2 1TA, U.K.*
[2] *School of Chemistry, University of Leeds, Leeds LS2 9JT, U.K.*
[3] *Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045, U.S.A.*

When a travelling wave of chemical reaction is supported by isothermal autocatalysis, the speed of the wave depends on the way in which reaction rate depends on concentration as well as on the maximum rate attainable. For systems with quadratic and cubic autocatalytic processes mixed in the ratio $\nu : (1-\nu)$, the wave speed c is given by

$$c = 1/[2(1-\nu)]^{\frac{1}{2}}, \quad \text{for} \quad 0 \leqslant \nu \leqslant \tfrac{1}{2},$$
$$c = (2\nu)^{\frac{1}{2}}, \qquad \quad \text{for} \quad \tfrac{1}{2} \leqslant \nu \leqslant 1,$$

with a smooth change between these solutions at $\nu = \frac{1}{2}, c = 1$. Thus, there is a factor of 2 in the wave speed in going from pure cubic ($\nu = 0$) to pure quadratic ($\nu = 1$). The selection of the permanent form travelling wave is discussed in terms of the phase plane.

1. Introduction

The passage of relatively sharp reaction front, say, down a test tube of previously mixed reactants is a relatively familiar phenomenon (Showalter 1987). A common feature of all reactions showing such behaviour is that the chemistry displays some form of feedback, typically autocatalysis, so that the reaction intermediates or products increase the rate at which the initial species are consumed. In this paper we consider the propagation of a one-dimensional wave front in systems with combinations of quadratic and cubic autocatalysis, paying particular attention to the variation of the observed wave speed with the relative contributions of the two processes. The latter can be discussed in terms of the 'shape' of the autocatalytic function via suitable 'weighting' of the two contributing processes.

2. Autocatalysis

Autocatalytic processes are characterized by (overall) reaction rates that increase with increasing extent of reaction; at least over the earliest stages of the evolution (Gray & Scott 1990). This feature is most clearly revealed by plotting the reaction rate against the initial reactant concentration or the extent of reaction, as shown in figure 1. Empirically, two limiting forms typically arise: an approximately parabolic locus for which the reaction rate increases most quickly with the extent of reactant consumption in the earliest stages and a cubic-form curve for which the reaction rate
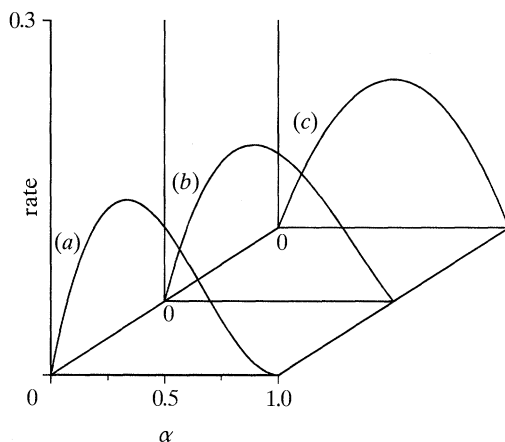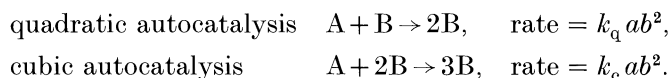
Figure 1. The variation of the shape of the autocatalytic function with the degree of mixing of cubic and quadratic processes: (a) $\nu = 0$, pure cubic; (b) $\nu = \frac{1}{2}$, equal mixing; (c) $\nu = 1$, pure quadratic.

increases only slowly at first but then rises more steeply at, say, 50% reaction. The former can often be successfully mimicked by a quadratic function: if the stoichiometric process is $A \to B$, then the rate at any stage can be represented as $k_q ab$, where a and b are the concentrations of the reactant and product species. The cubic form can similarly be fitted in this empirical sense by a rate law of the form $k_c ab^2$. These two autocatalytic representations have also often been 'visualized' in the mass-action form:

$$\text{quadratic autocatalysis} \quad A + B \to 2B, \quad \text{rate} = k_q ab^2,$$
$$\text{cubic autocatalysis} \quad A + 2B \to 3B, \quad \text{rate} = k_c ab^2.$$

In many 'real' systems, apparently more complex forms can be successfully represented as some linear combination or mixing of these two idealized extremes.

The shape of the rate function varies with the 'order' of the autocatalysis, and it is the influence of this changing shape on the reaction–diffusion wave properties of the system that we seek to examine in this paper. There is also another effect which we must first eliminate; that of changing area under the curve (i.e. of the average reaction rate). To allow for this, we first transform the equations to dimensionless form. For this we require a concentration and a chemical timescale. For the concentration base we take the initial concentration a_0 of the reactant A. Thus the dimensionless concentration $\alpha = a/a_0$ starts at unity and decreases to zero at complete conversion. Noting also that in the absence of subsequent reaction, the concentration of the autocatalyst at any time can be related immediately to the difference between the initial and instantaneous reactant concentration, $b = a_0 - a$ or, in dimensionless terms, by $(1-\alpha)$. For the chemical timescale t_{ch}, we consider first a purely cubic autocatalytic system. The dimensional equation has

$$-\,\mathrm{d}a/\mathrm{d}t = k_c a(a_0 - a)^2. \tag{1}$$

A natural timescale can be found based on the pseudo-first-order rate constant $t_{ch}^{-1} = k_c a_0^2$. With then $\tau = t/t_{ch}$, the equation becomes

$$-\,\mathrm{d}\alpha/\mathrm{d}\tau = \alpha(1-\alpha)^2. \tag{2}$$

Integrating this, the area under the curve between $\alpha = 0$ and 1 has the value $\frac{1}{12}$.

For pure quadratic autocatalysis, we can use the chemical timescale $t_{ch} = 2k_q a_0$ to obtain the dimensionless equation

$$-\,\mathrm{d}\alpha/\mathrm{d}\tau = \tfrac{1}{2}\alpha(1-\alpha). \tag{3}$$

This also gives an area under the rate against α curve of $\frac{1}{12}$. (It is for this reason that we introduce the factor 2 into t_{ch} and, hence, of $\frac{1}{2}$ into the rate function.)

With an arbitrary mixture of cubic and quadratic autocatalysis, the dimensionless rate equation can be written as

$$-\,\mathrm{d}\alpha/\mathrm{d}\tau = (1-\nu)\,\alpha(1-\alpha)^2 + \tfrac{1}{2}\nu\alpha(1-\alpha), \tag{4}$$

where $\nu = 2k_q/(k_c a_0 + 2k_q)$ is the 'mole fraction' of the quadratic contribution and $0 \leqslant \nu \leqslant 1$. The area under the curve is still the same as for the two limiting cases, irrespective of ν. This form reduces smoothly to the pure cubic and quadratic extremes in the limits $k_q \to 0, \nu = 0$ and $k_c \to 0, \nu = 1$ respectively.

3. Reaction–diffusion systems

We imagine an infinitely long, thin reaction domain extending in the limit from $x' = -\infty$ to $x' = +\infty$, where x' is the spatial coordinate. Reaction will be initiated by 'seeding' the system with some autocatalyst B at $x' = -\infty$ at $t = 0$. We seek now to establish the existence and form of any permanent form travelling waves that develop (typically after some initial transient evolution). The governing reaction–diffusion equations for the general combination of both autocatalytic processes can be written in the form

$$\partial a/\partial t = D\,\partial^2 a/\partial x'^2 - k_c\,ab^2 - k_q\,ab, \tag{5a}$$

$$\partial b/\partial t = D\,\partial^2 b/\partial x'^2 + k_c\,ab^2 + k_q\,ab. \tag{5b}$$

These can be combined after an initial transient phase using the relation $b = (a_0 - a)$ as described above. The boundary conditions ahead of the wave ($x' \to +\infty$) have $a = a_0, b = 0$ and $\partial a/\partial x' = \partial b/\partial x' = 0$; behind the wave ($x' \to -\infty$) is the fully reacted state $a = 0, b = a_0$ with, again, $\partial a/\partial x' = \partial b/\partial x' = 0$.

4. Purely cubic autocatalysis: $k_q = 0$

The reaction–diffusion equation for a system with only the cubic rate law can be written in the form

$$\partial\alpha/\partial\tau = \partial^2\alpha/\partial x^2 - \alpha(1-\alpha)^2, \tag{6a}$$

with

$$\alpha = 0, \partial\alpha/\partial x = 0 \quad \text{at} \quad x = -\infty \quad \text{and} \quad \alpha = 1, \partial\alpha/\partial x = 0 \quad \text{at} \quad x = +\infty, \tag{6b}$$

where the dimensionless time τ and distance x have been scaled with respect to the chemical timescale discussed in §2: $\tau = t/t_{ch}, x = x'(Dt_{ch})^{-\frac{1}{2}}$. If a permanent form travelling wave with velocity c exists, it is convenient to transform into travelling coordinate frame, introducing $z = x - c\tau$. Equation (6) then takes the ordinary differential form

$$\mathrm{d}^2\alpha/\mathrm{d}z^2 + c\,\mathrm{d}\alpha/\mathrm{d}z - \alpha(1-\alpha)^2 = 0, \tag{7a}$$

with

$$\alpha = \mathrm{d}\alpha/\mathrm{d}z = 0 \quad \text{at} \quad z = -\infty \quad \text{and} \quad \alpha = 1, \mathrm{d}\alpha/\mathrm{d}z = 0 \quad \text{at} \quad x = +\infty. \tag{7b}$$
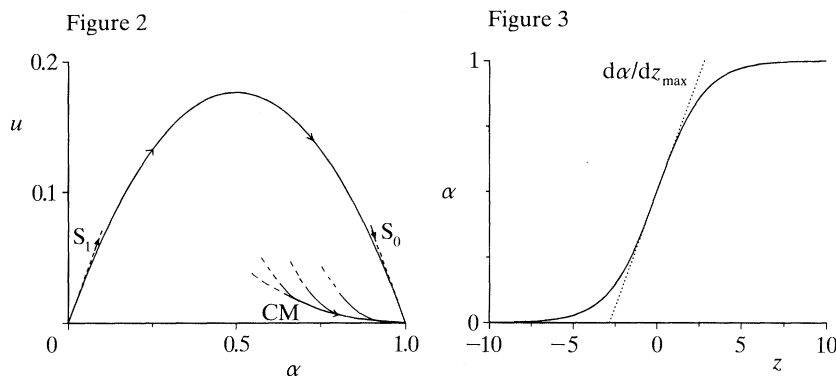
Figure 2. The gradient-concentration phase plane for pure cubic autocatalysis showing the outset S_1 from the saddle $(0,0)$ and the inset S_0 to the stable node at $(1,0)$: these join to form the solution path. Other trajectories approach $(1,0)$ along the centre manifold CM tangent to the α axis.

Figure 3. The cubic wave solution, showing the maximum gradient at $\alpha = \frac{1}{2}, z = 0$.

A suitable approach to solving this equation is to 'guess' that the concentration gradient $d\alpha/dz$ has a parabolic form $d\alpha/dz = k\alpha(1-\alpha)$, where k (like c) is some constant to be determined. Differentiating this assumed form gives $d^2\alpha/dz^2 = k(1-2\alpha)(d\alpha/dz) = k^2\alpha(1-\alpha)(1-2\alpha)$. If these two are now substituted into the governing equation, we obtain

$$k^2\alpha(1-\alpha)(1-2\alpha) + ck\alpha(1-\alpha) - \alpha(1-\alpha)^2 = 0. \tag{8}$$

After cancellation of the common factor $\alpha(1-\alpha)$, this leaves the condition

$$k(k+c) - 1 - (2k^2-1)\alpha = 0. \tag{9}$$

If this relation is to hold for all values of α, then we require $2k^2-1 = 0$ and $k(k+c)-1 = 0$, giving $k = c = 1/\sqrt{2}$. Figure 2 shows the appropriate $(\alpha, d\alpha/dz)$ phase-plane with the parabolic connection from $(0,0)$ to $(1,0)$ corresponding to the initial and final conditions. The wavefront itself is shown in figure 3 and is given, by integration of the gradient equation, as

$$(1-\alpha) = \exp(-z/\sqrt{2})/[1+\exp(-z/\sqrt{2})]. \tag{10}$$

The maximum gradient occurs exactly half way along the wave and has the value $(d\alpha/dz)_{max} = 1/\sqrt{32}$.

The permanent form travelling wave solution derived above is typically confirmed by numerical computation of the full initial-value problem, almost independent of the exact manner in which the wave is initiated in such studies. It is, however, not the only travelling wave solution. Billingham & Needham (1991a) have shown that even for this case there is another (infinite) family of waves that satisfy the above equation. These solutions and their origin are best discussed against the framework of the phase-plane mentioned above and shown in figure 2.

The phase plane shows how the concentration α and the gradient $d\alpha/dz$ vary with respect to each other along the wave. The governing equation (7) can be rewritten as two first-order ordinary differential equations:

$$d\alpha/dz = u, \tag{11a}$$

$$du/dz = -cu + \alpha(1-\alpha)^2. \tag{11b}$$

A 'solution' to the reaction–diffusion equation corresponds to a 'path' or 'trajectory' across the phase plane, starting from the initial point $(0,0)$ and entering the final point $(1,0)$ as z increases. These initial and final points are singularities of the phase plane, as both $d\alpha/dz$ and $du/dz\,(=d^2\alpha/dz^2)$ are zero together at these points. The 'local stability' of the singularities can be determined by examining the eigenvalues of the jacobian matrix corresponding to the phase plane equations. This shows that the 'starting point' $(0,0)$ is a saddle point, with an outset S_1 pointing in the direction $\alpha > 0, u = d\alpha/dz > 0$. The singularity at $(1,0)$ is a node, but has a degeneracy as one of the eigenvalues is zero. Examination of the trajectories close to the node shows that there is a unique invariant stable manifold S_0 that approaches $(1,0)$ from $\alpha < 1, u > 0$, whereas all other trajectories arrive at the singular point along a centre manifold that is tangent to the α axis.

The trajectory corresponding to the 'minimum' velocity solution derived above is the path that leaves $(0,0)$ along the outset S_1 and enters $(1,0)$ along the invariant stable manifold S_0 (this outset and inset do, in fact join to make the solution path). This is, in this sense, a special case. Other trajectories that also correspond to solutions enter $(1,0)$ along the centre manifold. There are an infinite number of these, and their velocities span the range $1/\sqrt{2} < c < \infty$. Billingham & Needham have discussed the question of which of these various solutions will actually be selected in a given case. They conjecture that the special case of the minimum velocity will be selected by any system for which the initial concentration of the autocatalyst decreases with x more quickly than the inverse form $\beta(x,0) \leqslant (1/\sqrt{2})\,x^{-1}$, but that if $\beta(x,0) = \sigma/x$ with $\sigma > 1/\sqrt{2}$, one of the faster waves, with velocity $c = \sigma$ will develop.

Finally, in this section, the case in which A and B diffuse with different coefficients has been considered by Billingham & Needham (1991b). They show that a similar overall structure to that described above arises for the special case $D = D_A = D_B$. With $D_A \neq D_B$, there is again a minimum velocity wave with speed c_{min} that depends on the ratio D_B/D_A. This minimum velocity can only be obtained numerically, but c_{min} tends to zero as $D_B/D_A \to 0$ and grows as D_B/D_A increases (growing as $c_{min} \sim 0.862\,\sqrt{(D_B/D_A)}$ for $D_B/D_A \gg 1$).

5. Purely quadratic autocatalysis: $k_c = 0$

For a system with simple quadratic autocatalysis, the dimensionless reaction–diffusion equation in travelling wave coordinates has the form

$$d^2\alpha/dz^2 + c\,d\alpha/dz - \tfrac{1}{2}\alpha(1-\alpha) = 0. \tag{12}$$

The method of assuming a parabolic gradient does not work in this case, and the system is most easily examined in the phase plane $u\alpha$ (where $u = d\alpha/dz$):

$$d\alpha/dz = u, \tag{13a}$$

$$du/dz = -cu + \tfrac{1}{2}\alpha(1-\alpha). \tag{13b}$$

There are again two singularities in the phase plane (figure 4): $(\alpha, u) = (0,0)$ and $(1,0)$. The origin is a saddle point, and the system will depart from this along the outset into the positive quadrant. The singularity at $(1,0)$, corresponding to the condition ahead of the wave, has eigenvalues determined by the roots of

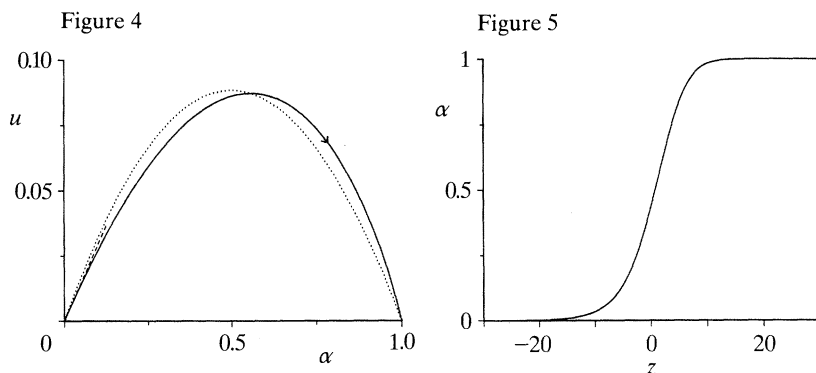$$\lambda^2 + c\lambda + \tfrac{1}{2} = 0, \tag{14}$$

Figure 4

Figure 5

Figure 4. The phase plane for the pure quadratic wave showing the minimum velocity solution. The dotted parabola gives the locus of maxima and minima.

Figure 5. The minimum velocity quadratic wave solution.

i.e.
$$\lambda^{\pm} = \tfrac{1}{2}\{-c \pm [c^2 - 2]^{\frac{1}{2}}\}. \tag{15}$$

For any wave speed $c \geqslant \sqrt{2}$, the eigenvalues are real and negative, so the singularity is a stable node. The important point here is that the trajectory approaches $(1, 0)$ from $u > 0$ and $\alpha < 1$, satisfying the physical requirement that $\alpha \leqslant 1$ (with $\alpha > 1$, the corresponding concentration of the autocatalyst will be negative). If $c < \sqrt{2}$, the singularity is a stable focus and trajectories approach $(1, 0)$ via damped oscillations during which $\alpha > 1$.

Thus, there is an infinite family of possible wave solutions, and a minimum velocity $c_{\min} = \sqrt{2}$. The minimum velocity has particular significance, and is that typically observed from direct numerical integration of an initial-value problem for the reaction–diffusion equations. For this solution with $c = c_{\min}$, the singularity at $(1, 0)$ is a degenerate stable node, with $\lambda^+ = \lambda^- = 1/\sqrt{2}$. Merkin & Needham (1989) have paid particular attention to the problem of selection of wave velocity from the infinite spectrum of solutions. They have shown, that for typical initial conditions (compact support), the wave speed is controlled by a small, weak diffusion region propagating ahead of the actual wavefront. It is this that selects the minimum velocity from the family above. The resulting wave profile (figure 5) is not symmetric but has its maximum slope ($u_{\max} = 0.0872$) at $\alpha = 0.5575$.

By considering the more general case in which that species A and B have unequal diffusion coefficients, Billingham & Needham (1991b) have shown that it is the diffusion of the autocatalyst that determines the wave speed. They obtained for the dimensionless minimum velocity $c_{\min} = \sqrt{(2D_B/D_A)}$, giving $\mathrm{d}x'/\mathrm{d}t = (2D_B k_q a_0)^{\frac{1}{2}}$.

6. Mixed cubic and quadratic autocatalysis

To consider the general case of mixed cubic and quadratic processes, we non-dimensionalize equation (5) following the arguments of §2:

$$\partial\alpha/\partial\tau = \partial^2\alpha/\partial x^2 - (1-\nu)\,\alpha(1-\alpha)^2 + \tfrac{1}{2}\nu\alpha(1-\alpha). \tag{16}$$

The governing equation can again be written in travelling wave coordinates:

$$\mathrm{d}^2\alpha/\mathrm{d}z^2 + c\,\mathrm{d}\alpha/\mathrm{d}z - (1-\nu)\,\alpha(1-\alpha)^2 + \tfrac{1}{2}\nu\alpha(1-\alpha) = 0 \tag{17}$$
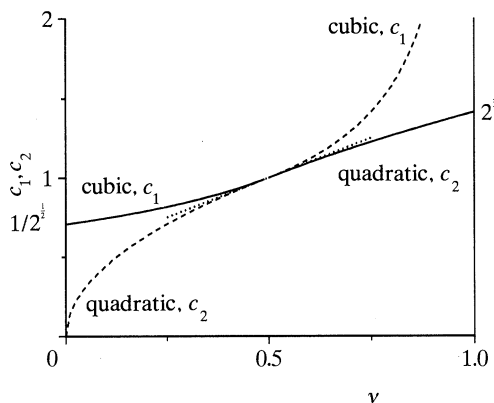
Figure 6. Dependence of the wave velocities c_1 and c_2 on the degree of mixing ν, showing the change in observed solution at $\nu = \frac{1}{2}$.

with, again, the phase-plane representation:

$$\mathrm{d}\alpha/\mathrm{d}z = u, \tag{18a}$$

$$\mathrm{d}u/\mathrm{d}z = -cu + (1-\nu)\,\alpha(1-\alpha)^2 + \tfrac{1}{2}\nu\alpha(1-\alpha). \tag{18b}$$

Both the 'cubic' method of assuming a parabolic gradient and the 'quadratic' approach of examining the nature of the stable singularity can be applied to these equations.

(a) Cubic method

We assume that the gradient $\mathrm{d}\alpha/\mathrm{d}z$ is related to the concentration by the parabolic form $\mathrm{d}\alpha/\mathrm{d}z = k\alpha(1-\alpha)$, where k has to be determined. Proceeding as before, we obtain for the wave speed

$$c_1(\nu) = 1/[2(1-\nu)]^{\frac{1}{2}}. \tag{19}$$

The wave profile for this solution is again the symmetric form (10).

(b) Quadratic method

Examining the phase plane singularity at $(1, 0)$, we find that the eigenvalues are given by $\lambda^{\pm} = \frac{1}{2}\{-c \pm [c^2 - 2\nu]^{\frac{1}{2}}\}$, so wave solutions may exist for all $c \geqslant c_2(\nu)$, where

$$c_2(\nu) = (2\nu)^{\frac{1}{2}}. \tag{20}$$

(c) Choice of solution

The dependence of c_1 and c_2 on ν is shown in figure 6. The two loci touch tangentially at $\nu = \frac{1}{2}$ (and with $c_1 = c_2 = 1$), with the cubic type wave speed lying above the quadratic type wave speed for all other ν. As ν tends to zero, we find $c_1 \rightarrow 1/\sqrt{2}$ and $c_2 \rightarrow 0$. The former accords with the behaviour determined in §6a above, so we expect the 'cubic' form solution to be dominant at this (pure cubic) limit. At the other extreme, with $\nu \rightarrow 1$, we have $c_1 \rightarrow \infty$ and $c_2 \rightarrow \sqrt{2}$. The latter is the minimum velocity solution for pure quadratic autocatalysis, so we expect the 'quadratic' type analysis to be appropriate at this end. Clearly then, the system is switching from one branch in figure 6 to the other as ν increases. This crossing can

only occur smoothly at the point of tangency at $\nu = \frac{1}{2}$, i.e. for the case in which cubic and quadratic processes make exactly equal contributions. Numerical computation confirms that the wave speed observed typically is given by

$$c_{\mathrm{obs}} = c_1 \quad \text{for} \quad 0 \leqslant \nu < \tfrac{1}{2}, \tag{21 a}$$

$$c_{\mathrm{obs}} = c_2 \quad \text{for} \quad \tfrac{1}{2} < \nu \leqslant 1. \tag{21 b}$$

Some further information concerning the changeover in the observed solution is given in the Appendix. This aspect has also been discussed by Hadeler & Rother (1975).

In dimensional terms, we can note a significant difference between the cubic type and quadratic type wave speeds. For $\nu < \frac{1}{2}$, the system chooses the cubic wave speed c_1, equivalent to

$$\mathrm{d}x'/\mathrm{d}t = (\tfrac{1}{2}Dk_{\mathrm{c}}a_0^2)^{\frac{1}{2}}(1 + 2k_{\mathrm{q}}/k_{\mathrm{c}}a_0), \tag{22}$$

whose numerical value depends on both autocatalytic processes. For $\nu > \frac{1}{2}$, the system chooses the quadratic wave with speed c_2, giving

$$\mathrm{d}x'/\mathrm{d}t = (2Dk_{\mathrm{q}}a_0)^{\frac{1}{2}} \tag{23}$$

for all values of k_{c} and k_{q}. Thus the quadratic wave travels essentially independent of the cubic contribution.

7. Discussion and conclusions

In the above sections we have examined the structure of reaction–diffusion wave propagation in isothermal autocatalytic systems. The 'classic cases' of pure cubic and pure quadratic processes support such waves, with dimensionless speeds of $1/\sqrt{2}$ and $\sqrt{2}$ respectively. 'Mixed' systems have a wave speed that varies smoothly between these values depending on the relative strengths of the two channels. The normalized weightings of the two autocatalytic processes used here thus show that the influence of the 'shape' of the autocatalytic function is to increase the natural propagation velocity by a factor of 2 as cubic is replaced by quadratic autocatalysis (but in such a way as to maintain a constant average reaction rate for the whole system). Thus, shifting more of the area under the rate against concentration curve to lower extents of reaction (higher α) allows a faster wave solution.

Other variations in the mixing of the two processes can be imagined. If a constant cubic contribution is taken and the quadratic channel increased from zero, so increasing the total overall chemical rate, ν will again increase from 0. The wave speed then, at first, increases linearly with the quadratic contribution; due to the factor $(1 + 2k_{\mathrm{q}}/k_{\mathrm{c}}a_0)$ in equation (22). Once the system with equal contributions ($\nu = \frac{1}{2}$) has been passed, the wave speed becomes independent of the cubic form and grows as the square root of the quadratic rate constant according to equation (23). On the other hand, if we maintain a fixed quadratic contribution and increase the cubic channel from zero, then there is no change in wave speed until ν has decreased to $\frac{1}{2}$. After that, the wave speed increases with the increasing value of k_{c}, again finally growing as the square root.

The variation in wave speed also is mirrored in the variation of the 'thickness' of the reaction wave front. We can represent the wave thickness by considering the maximum gradient $u_{\max}$ as a function of ν. For pure cubic autocatalysis, $u_{\max} = 1/\sqrt{32}$, with the maximum gradient occurring exactly at 50% consumption. The

position of the maximum slope stays at $\alpha = \frac{1}{2}$ for all of the symmetric 'cubic type' waves that are observed for $\nu \leqslant \frac{1}{2}$, with the maximum gradient decreasing as $u_{max} = \frac{1}{4}[\frac{1}{2}(1-\nu)]^{\frac{1}{2}}$. Thus the equal contribution case, with $\nu = \frac{1}{2}$, has a maximum slope of $\frac{1}{8}$, lower than that for pure cubic by a factor $1/\sqrt{2}$. We may note that this decrease in wave sharpness exactly offsets the increase in wave speed. This is generally the case. To a fixed observer, therefore, the wave takes the same time to pass for all systems. For $\nu > \frac{1}{2}$, there is no analytical solution for the wave profile. The maximum gradient now moves away from $\alpha = \frac{1}{2}$, to higher values of α, tending to the pure quadratic location $\alpha = 0.5575$ as $\nu \to 1$. The maximum gradient decreases smoothly from $\frac{1}{8}$ at $\nu = \frac{1}{2}$ to 0.0872 at $\nu = 1$.

The smooth dependence of wave speed on the degree of mixing of the two channels described above does, however, involve some intricate detail. Until recently, the pure cubic and pure quadratic cases were thought to have quite different structure. The classic quadratic 'Fisher–Kolmogorov' case was known to allow an infinite number of wave solutions (Luther 1906, 1987; Fisher 1937; Kolmogorov *et al.* 1937; Showalter & Tyson 1987), with a minimum speed solution emerging naturally in all computations, although no analytical solution could be (or has yet been) found. The pure cubic case allows an analytical solution for both the wavefront and its speed and this was thought to be a unique solution. A related analytical solution also exists for the mixed cases (Saul & Showalter 1985). However, in all these cases there is also an infinite family of waves, with velocities equal to or greater than some minimum, and there are similar problems of selection of a particular solution in a given case. As shown above, and in more technical detail in the appendix, 'normal' initial data lead to the selection of the 'cubic type' wave for systems in which the cubic route is dominant ($\nu \leqslant \frac{1}{2}$) and to the 'quadratic type' when $\nu > \frac{1}{2}$. These two solutions are equivalent for the case of equal mixing, $\nu = \frac{1}{2}$, at which the change-over occurs smoothly. With $\nu \leqslant \frac{1}{2}$, the system cannot select its minimum velocity solution (which would have a quadratic type form) because the concentration of the autocatalyst becomes negative for such low speeds: the cubic type wave has a wave speed that is equal to the lowest quadratic wave velocity such that β does not become negative, but has some qualitative differences (most notably with respect to the rate of exponential decay of small perturbations) from the quadratic type solutions. The pure cubic solution has an additional complexity in that its phase plane structure has a degenerate node with a zero eigenvalue, giving rise to a centre manifold along which all the allowable quadratic type solutions enter. This zero eigenvalue causes such solutions to change from exponential to an algebraic decay of perturbations (but this applies only in the case $\nu = 0$).

Appendix

Figure 7 sketches the important features of the phase-plane and how these develop with the wave speed for the three representative cases: $\nu > \frac{1}{2}$, $\nu = \frac{1}{2}$ and $\nu > \frac{1}{2}$. The most significant points are the saddle point at $(0,0)$ and the stable node/focus at $(1,0)$. When the latter is a stable node, the associated eigenvectors describe two paths
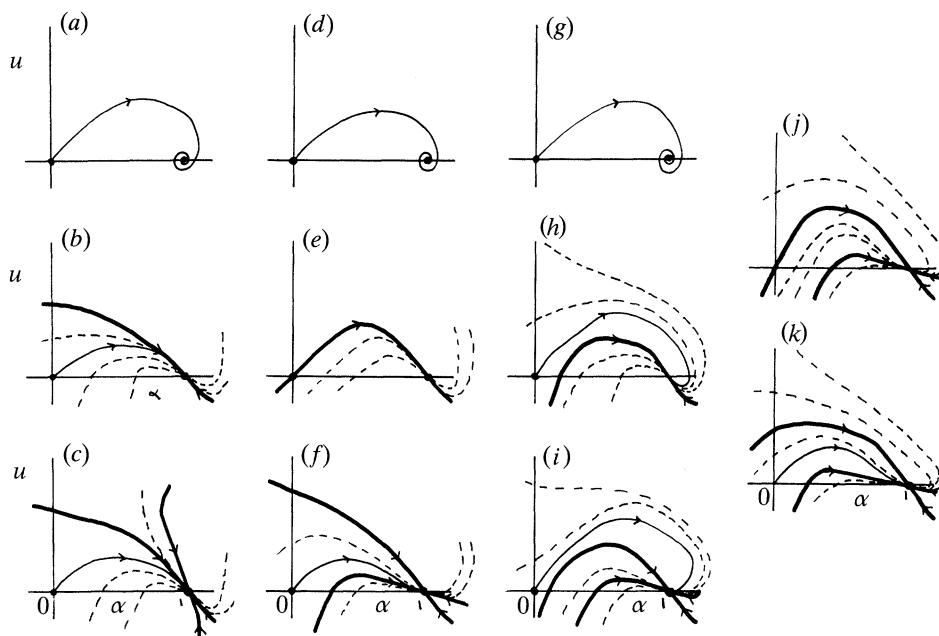
Figure 7. Evolution of the phase plane with wave speed for (a)–(c) $\nu > \frac{1}{2}$; (d)–(f) $\nu = \frac{1}{2}$; (g)–(k) $\nu < \frac{1}{2}$. (See text for details.) (a), (d), (g) $c < c_{\mathrm{sp}}$; (b), (e) $c = c_{\mathrm{sp}} = c_{\mathrm{min}}$; (h) $c = c_{\mathrm{sp}}$; (c) $c > c_{\mathrm{sp}}$; (i) $c_{\mathrm{sp}} < c < c_{\mathrm{min}}$; (j) $c = c_{\mathrm{min}}$; (k) $c > c_{\mathrm{min}}$.

or 'insets' that are straight lines locally to the node (but that then traverse across the phase plane). It is the relation of these insets to the connection from the origin to $(1, 0)$ that determines the nature of wave selected and the allowable speeds.

To begin, we examine the case with $\nu > \frac{1}{2}$. At the lowest wave speeds, figure 7a, the singularity at $(1, 0)$ is a stable focus. The local paths wind in to this point and so traverse regions of the phase plane for which α is greater than unity. Such dimensionless reactant concentrations would imply negative concentrations of the autocatalyst and so are not acceptable. As c is increased to some value c_{sp}, the spiral focus gives way to node. Exactly at c_{sp}, the node has two equal, real eigenvalues and so it is degenerate. There is a single local straight line path (heavy line) as shown in figure 7b. All other local paths approach the node along this eigenvector (dashed lines). The reaction wave trajectory originating from $(0, 0)$ also approaches along this path, and moves onto the node with α approaching unity from below. Thus, there is an allowable connection between the singular points as soon as the focus changes to a node. If the wave speed is increased further, the node becomes non-degenerate and the two eigenvectors split, figure 7c. All local paths, including the connection from the saddle at $(0, 0)$, approach the node along (and from underneath) the lower straight line path (that with the less negative eigenvalue) and hence α does not exceed unity at any point. The development of the eigenvalues associated with the stable node is shown in figure 8a. These are born as a real pair at $c = c_{\mathrm{sp}}$ and then separate. The exponential decay of small perturbations to the wave front is governed by the less negative root as described above.

For the special case $\nu = \frac{1}{2}$, we again have a spiral for $c < c_{\mathrm{sp}}$ and a degenerate node for $c = c_{\mathrm{sp}}$, as indicated in figure 7d, e. In this case, the local straight line path into the node corresponds exactly to the connection to the saddle at the origin. This still
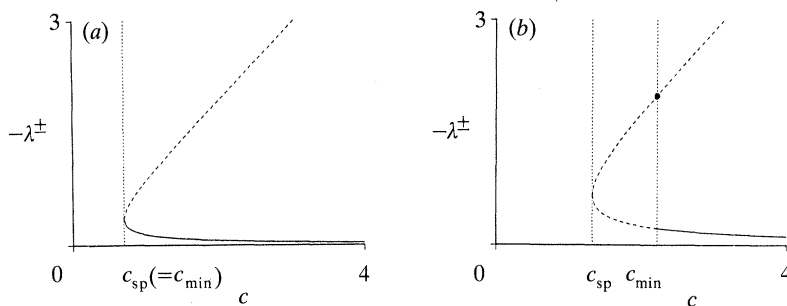
Figure 8. Variation of eigenvalue governing the exponential decay of perturbations ahead of the wave front with wave speed: (a) $\nu > \frac{1}{2}$, the wave solution emerges at $c_{sp} = c_{min}$ and evolves along the lower branch; (b) $\nu < \frac{1}{2}$, the eigenvalues become real at $c = c_{sp}$ but the wave solution is only acceptable for $c \geqslant c_{min}$, for $c = c_{min}$, the upper eigenvalue is appropriate but for all larger c the system evolves along the lower branch.

approaches the node with α remaining bounded by unity, so it is an allowable solution. With $c > c_{sp}$, figure 7f, the connection from $(0,0)$ to $(1,0)$ lies between the two local straight line paths, approaching along the lower of these (from above).

With $\nu < \frac{1}{2}$ there is a significant difference. Although the spiral for $c < c_{sp}$ (figure 7g) gives rise to a degenerate node at $c = c_{sp}$, the single local straight line path evolves back across the phase plane in such a way as to cut the α axis before the saddle at the origin. Thus any connection from the saddle is shepherded around the node and approaches 'from the other side', with α passing through unity (figure 7h). Thus there is still no physically acceptable solution. As c increases further, the degenerate eigenvector splits (figure 7i) but both local straight line paths evolve to intersect the α axis before the origin. Only at some higher wave speed, c_{min}, does an allowable connection emerge. This occurs when the eigenvector associated with the more negative eigenvalue passes through $(0,0)$ (figure 7j). For and speed $c > c_{min}$, the connection from the saddle to the node lies between the two local straight line paths, and so is bounded by these. An important point is that the final approach is now along the lower inset, that corresponding to the less negative eigenvalue (figure 7k). There is thus an abrupt change in the form of the exponential decay between the first connection ($c = c_{min}$) and those with higher velocities, as indicated in figure 8b. (Notice that the eigenvalues exist for all $c > c_{sp}$, but there are only allowable connections for $c > c_{min}$.) This indicates the difference between the special case of the cubic wave with $c = c_{min}$ ($= c_1$ in the main text), which involves one eigenvalue, and the family of faster waves $c = c_2$, which are related to the other eigenvalue and eigenvector.

As ν becomes zero, in the limit of pure cubic autocatalysis, the lower eigenvector becomes tangential to the α axis, as seen previously in figure 2. The associated eigenvalue becomes zero and hence the centre manifold with non-exponential decay arises for the solutions with $c > c_{min}$ in this case (only).

References

Billingham, J. & Needham, D. J. 1991a A note on the properties of a family of travelling-wave solutions arising in cubic autocatalysis. *Dynam. Stab. Syst.* **6**, 33–49.

Billingham, J. & Needham, D. J. 1991b The development of travelling waves in quadratic and cubic autocatalysis with unequal diffusion rates. I. Permanent form travelling waves. *Phil. Trans. R. Soc. Lond.* A **334**, 1–24.

Fisher, R. A. 1937 The advance of advantageous genes. *Ann. Eugen.* **7**, 355–369.

Gray, P. & Scott, S. K. 1990 *Chemical oscillations and instabilities.* Oxford University Press.

Gray, P., Merkin, J. H., Needham, D. J. & Scott, S. K. 1990 The development of travelling waves in a simple isothermal chemical system. III. Cubic and mixed autocatalysis. *Proc. R. Soc. Lond.* A **430**, 509–524.

Hadeler, K. P. & Rother, F. 1975 Travelling fronts in nonlinear diffusion equations. *J. math. Biol.* **2**, 251–263.

Kolmogorov, A., Petrovsky, I. & Piscounov, N. 1937 tude de l'équation de la diffusion avec croissance de la quantité de matiere et son application á un problème biologique. *Moscou Université Bull. Math.* **1**, 1–25.

Luther, R. 1906 Propagation of chemical reactions in space. *Z. Elektrochem.* **12**, 596.

Luther, R. 1987 Propagation of chemical reactions in space. *J. chem. Educ.* **64**, 740–742. (Translation by R. Arnold, K. Showalter & J. J. Tyson.)

Merkin, J. H. & Needham, D. J. 1989 Propagating reaction–diffusion waves in a simple isothermal quadratic autocatalytic chemical system. *J. engng Math.* **23**, 343–356.

Saul, A. & Showalter, K. 1985 Propagating reaction–diffusion fronts. In *Oscillations and traveling waves in chemical systems* (ed. R. J. Field & M. Burger), ch. 11, pp. 419–39. New York: Wiley.

Showalter, K. 1987 Chemical waves. In *Kinetics of nonhomogeneous processes* (ed. G. R. Freeman), ch. 14, pp. 769–820. New York: Wiley.