

Chemical Clock Reactions: The Effect of Precursor Consumption

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During a clock reaction an initial induction period is observed before a significant change in concentration of one of the chemical species occurs. In this study we develop the results of Billingham and Needham [3] who studied a particular class of inhibited autocatalytic clock reactions. We obtain modified expressions for the length of the induction period and show that characteristic clock reaction behaviour is only observed within certain parameter limits.

Keywords: clock reaction, autocatalysis, induction, inhibition

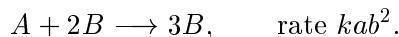
AMS Subject classification: 34Exx

1. Introduction

A clock reaction is a chemical reaction which gives rise to a significant induction period during which one of the chemical species, the clock chemical, has a very low concentration. The end of the induction period is marked by a rapid increase in concentration of the clock chemical. This rapid growth can produce remarkable effects experimentally such as sudden dramatic colour changes in solution phase reactions. One particular class of reaction even produces a flash of light [7]. Examples of clock reactions include the arsenic(III) sulfide clock reaction [13], the formaldehyde clock reaction [9], the iodine bisulphate clock [10] and the hydration of carbon dioxide [8].

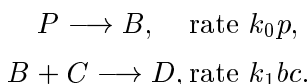
In this paper we consider a combination of two different mechanisms which give rise to clock reaction behaviour. The first is known as induction. In this case the rate of production of the clock chemical is small when its concentration is small and increases as the concentration increases, for example cubic autocatal-

ysis:



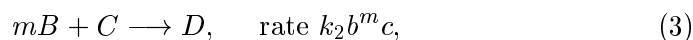
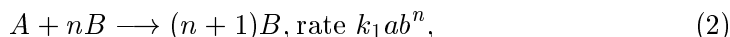
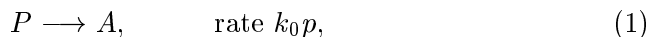
In this reaction species B catalyses its own production (see [2]). Reactions which are thought to be well modelled by autocatalysis include the oscillatory B-Z reaction [6] and the iodine-bisulphate clock reaction [5].

Another mechanism which can give rise to clock reaction behaviour is inhibition. In this case the clock chemical is supplied to the system via the decay of the precursor chemical. An inhibitor chemical reacts with the clock chemical limiting its concentration and a significant increase in concentration of the clock chemical is only possible once the inhibitor chemical has been consumed. For example (see [2]),



Examples of reactions which are thought to be well modelled by this mechanism are the photosynthesis of hydrogen chloride inhibited by ammonia and the polymerisation of vinyl acetate by benzoquinone [4].

Merkin *et al* [11] used part of the FKN mechanism, which involved an inhibition and an autocatalytic step, to model the bromate-ferroin clock reaction. Using asymptotic methods they were able to make predictions about the length of the induction period which agreed well with experimental results. Billingham and Needham [2] used a combination of autocatalysis and inhibition to model the iodate-arsenous acid reaction. They used phase plane techniques to classify the behaviour of the system for different parameter regimes and constructed asymptotic solutions in certain parameter limits. In a second paper [3] they considered the system,



for the cases $n, m = 1$ and $n, m = 2$. They developed an asymptotic solution when precursor decay was negligible during the induction period and were able to obtain expressions for the length of the induction period in each of the different cases. In this study we allow for the consumption of the precursor chemical and use the method of matched asymptotic expansions to obtain solutions which

describe the evolution of the chemical concentrations. We are thus able to obtain modified expressions for the length of the induction period. We examine the conjecture made by Billingham and Needham [3] which states that if precursor consumption is significant then clock reaction behaviour will only be observed within certain parameter limits. This conjecture turns out to be correct for the cases $n = m = 1$ and $n = m = 2$ but not for the case $n = 2, m = 1$. We note that in reaction scheme (1), (2) and (3) the autocatalyst plays the part of the clock chemical.

2. Mathematical formulation

The chemical concentrations p, a, b and c , satisfy the equations,

$$\frac{dp}{dt} = -k_0p, \quad (4)$$

$$\frac{da}{dt} = k_0p - k_1ab^n, \quad (5)$$

$$\frac{db}{dt} = k_1ab^n - mk_2b^m c, \quad (6)$$

$$\frac{dc}{dt} = -k_2b^m c, \quad (7)$$

and we impose the initial conditions,

$$p = p_0, \quad a = 0, \quad b = b_0, \quad c = c_0, \quad d = 0 \quad \text{at} \quad t = 0. \quad (8)$$

We note that the concentration of the inert product, D , can be determined by conservation of matter as, $d = c_0 - c$. Equation (4) can be integrated immediately to give,

$$p = p_0 e^{-k_0 t}. \quad (9)$$

By integrating the appropriate linear combinations of equations (5), (6) and (7) we find,

$$a + b - mc = p_0(1 - e^{-k_0 t}) + b_0 - mc_0. \quad (10)$$

We now eliminate c from equation (6) and the problem reduces to the system of two first order ordinary differential equations,

$$\frac{da}{dt} = k_0 p_0 e^{-k_0 t} - k_1 ab^n, \quad (11)$$

$$\frac{db}{dt} = k_1 ab^n - k_2 b^m [a + b - p_0(1 - e^{-k_0 t}) - b_0 + mc_0], \quad (12)$$

subject to the initial conditions,

$$a(0) = 0, \quad b(0) = b_0. \quad (13)$$

It is now convenient to define dimensionless variables as,

$$\alpha = a/b_0, \quad \beta = b/b_0, \quad \gamma = c/b_0, \quad \tau = k_1 b_0^n t. \quad (14)$$

In terms of the variables (14) equations (10), (11) and (12) become,

$$\frac{d\alpha}{d\tau} = \epsilon P_0 e^{-\epsilon\tau} - \alpha\beta^n, \quad (15)$$

$$\frac{d\beta}{d\tau} = \alpha\beta^n - \frac{\beta^m}{\delta} [\alpha + \beta - P_0(1 - e^{-\epsilon\tau}) + m\lambda - 1], \quad (16)$$

$$m\gamma = \alpha + \beta - P_0(1 - e^{-\epsilon\tau}) + m\lambda - 1, \quad (17)$$

where the dimensionless parameters P_0 , λ , ϵ , and δ are defined by,

$$P_0 = \frac{p_0}{b_0}, \quad \lambda = \frac{c_0}{b_0}, \quad \epsilon = \frac{k_0}{k_1 b_0^n}, \quad \delta = \frac{k_1}{k_2 b_0^{m-n}}, \quad (18)$$

and initial conditions (8) now take the form,

$$\alpha(0) = 0, \quad \beta(0) = 1, \quad \gamma(0) = \lambda. \quad (19)$$

The parameters P_0 and λ are the dimensionless initial concentrations of P and C , respectively. The parameter ϵ is a measure of the reaction rate of step (1) relative to the rate of the autocatalytic step (2) and the parameter δ is a measure of the rate of the autocatalytic step (2) relative to the rate of the inhibition reaction (3).

Billingham and Needham [3] assumed that the reactant P is initially in large excess over the autocatalyst B , and that reaction (1) proceeds much more slowly than the autocatalytic step (2). This is the pool chemical approximation and mathematically led them to consider the situation in which,

$$\epsilon \ll 1, \quad P_0 \gg 1 \quad \text{with} \quad \mu = \epsilon P_0 = O(1). \quad (20)$$

Under this assumption the leading order problem is given as,

$$\frac{d\alpha}{d\tau} = \mu - \alpha\beta^n, \quad (21)$$

$$\frac{d\beta}{d\tau} = \alpha\beta^n - \frac{1}{\delta}\beta^m[\alpha + \beta - \mu\tau + m\lambda - 1], \quad (22)$$

$$m\gamma = \alpha + \beta - \mu\tau + m\lambda - 1. \quad (23)$$

We note that Billingham and Needham [3] use the symbol K where $K = \delta^{-1}$. For the majority of their analysis they assumed that $K \gg 1$, that is $\delta \ll 1$. This assumption is valid when the inhibition reaction proceeds much faster than the autocatalytic reaction. They also made the assumption that $\lambda > 1/m$. This requires the initial concentration of the inhibitor chemical to be large enough to consume all the autocatalyst present initially.

Using the small parameter δ , asymptotic solutions were constructed for the cases $n = 1, 2$ and $m = 1, 2$. They found that a rapid growth in the autocatalyst concentration followed a significant induction period, in which the concentration of the autocatalyst was small, for all cases apart from $n = 2, m = 1$. Analytical expressions were given for the length of the induction period which was found to be of $O(\delta^{-1})$ for the cases $n = m = 1$ and $n = m = 2$. For the remaining case, $n = 1, m = 2$, it was found to be of $O(\delta^{-1/3})$.

Further analysis showed that for the case $n = 2, m = 1$ clock reaction behaviour could be observed for values of $\delta > \delta^*$. Numerical investigations suggested that for typical parameter values δ^* would be of $O(1)$. This led Billingham and Needham [3] to make the following conjecture: Clock reaction behaviour will only be observed for $\epsilon < \epsilon^*(\delta)$ with:

$$\epsilon^* = O(\delta) \quad \text{as } \delta \rightarrow 0 \quad \text{for } n = m = 1 \quad \text{and } n = m = 2, \quad (24)$$

$$\epsilon^* = O(\delta^{\frac{1}{3}}) \quad \text{as } \delta \rightarrow 0 \quad \text{for } n = 1, \quad m = 2. \quad (25)$$

This conjecture implies that if sufficient precursor chemical is consumed in the early stages of the reaction then clock reaction behaviour will not be observed.

We propose to study the effect of precursor consumption both on the length of the induction period and the existence of clock reaction behaviour. We make the same assumptions as Billingham and Needham [3] restricting our analysis to the parameter regime where $\delta \ll 1$ and $\lambda > 1/m$. As suggested by the above conjecture we define,

$$\epsilon = \epsilon_0 \delta, \quad \epsilon_0 = O(1) \quad \text{with} \quad \mu = \epsilon P_0 = O(1), \quad (26)$$

for the cases $n = m = 1$ and $n = m = 2$, and we define,

$$\epsilon = \epsilon_0 \delta^{\frac{1}{3}}, \quad \epsilon_0 = O(1) \quad \text{with} \quad \mu = \epsilon P_0 = O(1), \quad (27)$$

for the case $n = 1, m = 2$. By doing this we are choosing a value of ϵ which will en-

sure that the end of the induction period coincides with a significant consumption of the precursor chemical. Equations (15), (16) and (17) now become,

$$\frac{d\alpha}{d\tau} = \mu e^{-\epsilon_0 \delta^\sigma \tau} - \alpha \beta^n, \quad (28)$$

$$\frac{d\beta}{d\tau} = \alpha \beta^n - \frac{\beta^m}{\delta} \left[\alpha + \beta - \frac{\mu}{\epsilon_0 \delta^\sigma} (1 - e^{-\epsilon_0 \delta^\sigma \tau}) + m\lambda - 1 \right], \quad (29)$$

$$m\gamma = \alpha + \beta - \frac{\mu}{\epsilon_0 \delta^\sigma} (1 - e^{-\epsilon_0 \delta^\sigma \tau}) + m\lambda - 1, \quad (30)$$

subject to the initial conditions,

$$\alpha(0) = 0, \quad \beta(0) = 1, \quad \gamma(0) = \lambda, \quad (31)$$

where $\sigma = 1$, for the cases $n = m = 1, 2$ and $\sigma = 1/3$, for the case $n = 1, m = 2$. If we take the limit $\epsilon_0 \rightarrow 0$ then equations (28), (29) and (30) reduce to the system (21), (22) and (23) studied by Billingham and Needham [3]. This proves to be a useful check for the analysis carried out in the following sections.

We note that equations (28), (29) and (30) admit asymptotic solutions of the form,

$$\alpha \rightarrow \frac{\mu}{\epsilon_0 \delta^\sigma}, \quad \beta \rightarrow 0, \quad \gamma \rightarrow \lambda - \frac{1}{m} \quad \text{as } \tau \rightarrow \infty, \quad (32)$$

and,

$$\alpha \rightarrow 0, \quad \beta \rightarrow \frac{\mu}{\epsilon_0 \delta^\sigma} - (m\lambda - 1), \quad \gamma \rightarrow 0 \quad \text{as } \tau \rightarrow \infty. \quad (33)$$

If the large time solution takes the form (32) then reaction step (3) inhibits the autocatalyst so strongly that reaction (2) never proceeds fast enough to produce a significant concentration of B. Thus clock reaction behaviour does not occur. If the solution is of the form (33) then step (2) proceeds quickly enough to produce sufficient autocatalyst to consume all the inhibitor. Once the precursor has been totally consumed the concentration of B tends to a constant value. Solution (33) describes the behaviour in this limit.

For the cases $n = m = 1, 2$, with $\epsilon = \epsilon_0 \delta$, we show that our system is asymptotic to either solution (32) or (33) depending on the parameters μ , ϵ_0 and λ , verifying the first part of the conjecture made by Billingham and Needham [3]. For the case $n = 1, m = 2$, with $\epsilon = \epsilon_0 \delta^{1/3}$, we show that our system is always asymptotic to solution (33). This disproves the latter part of their conjecture.

To obtain a condition for clock reaction behaviour in this latter case we consider the situation in which,

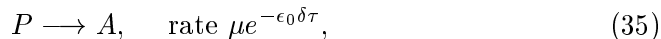
$$\epsilon = \epsilon_0 = O(1), \quad \text{with} \quad \mu = \epsilon P_0 = O(1). \quad (34)$$

By choosing $\epsilon = O(1)$ we ensure that the precursor has decayed to become negligibly small before the end of the induction period. This time we find that the final form of the solution is asymptotic to either (32) or (33), with $\sigma = 0$, depending on the parameters μ , ϵ_0 and λ .

In the following sections we present both numerical and asymptotic solutions to the cases discussed above. We utilise the small parameter δ to complete our asymptotic solutions and we assume that $\lambda > 1/m$.

3. Quadratic autocatalysis with linear inhibition ($n = m = 1$)

In this case the reaction scheme is,



where $\delta = k_1/k_2$ and $\epsilon_0 \delta = k_0/k_1 b_0$. We require a solution of,

$$\frac{d\alpha}{d\tau} = \mu e^{-\epsilon_0 \delta \tau} - \alpha \beta, \quad (38)$$

$$\frac{d\beta}{d\tau} = \alpha \beta - \frac{\beta}{\delta} \left[\alpha + \beta - \frac{\mu}{\epsilon_0 \delta} (1 - e^{-\epsilon_0 \delta \tau}) + \lambda - 1 \right], \quad (39)$$

$$\gamma = \alpha + \beta - \frac{\mu}{\epsilon_0 \delta} (1 - e^{-\epsilon_0 \delta \tau}) + \lambda - 1, \quad (40)$$

subject to the initial conditions,

$$\alpha(0) = 0, \quad \beta(0) = 1, \quad \gamma(0) = \lambda. \quad (41)$$

We use the technique of matched asymptotic expansions to solve equations (38) and (39) subject to (41). Six asymptotic regions are required to describe the full solution of the initial value problem. The analysis verifies conjecture (24) made by Billingham and Needham [3] by showing that a rapid growth in the autocatalyst concentration is only possible within certain parameter limits. We now give a brief outline of the main features of the asymptotic solution.

Region I:

After noting that initially $\beta = O(1)$ an examination of equations (38) and (39) shows appropriate scaled variables to be,

$$\hat{\alpha} = \delta^{-1}\alpha = O(1), \quad \hat{\beta} = \beta = O(1), \quad \hat{\tau} = \delta^{-1}\tau = O(1). \quad (42)$$

The governing equations (38) and (39) become,

$$\frac{d\hat{\alpha}}{d\hat{\tau}} = \mu e^{-\epsilon_0 \delta^2 \hat{\tau}} - \delta \hat{\alpha} \hat{\beta}, \quad (43)$$

$$\frac{d\hat{\beta}}{d\hat{\tau}} = \delta^2 \hat{\alpha} \hat{\beta} - \hat{\beta} \left[\delta \hat{\alpha} + \hat{\beta} - \frac{\mu}{\epsilon_0 \delta} (1 - e^{-\epsilon_0 \delta^2 \hat{\tau}}) + \lambda - 1 \right]. \quad (44)$$

and solving these equations subject to the initial conditions gives the expansions,

$$\hat{\alpha} \sim \mu \hat{\tau} + \delta \left[\hat{k}_1 + \frac{\mu \hat{\tau} e^{-(\lambda-1)\hat{\tau}}}{\lambda} \right] + \delta^2 \left[\hat{k}_2 + \frac{\hat{k}_1 e^{-(\lambda-1)\hat{\tau}}}{\lambda} - \frac{\mu \epsilon_0 \hat{\tau}^2}{2} \right] + o(\delta^2), \quad (45)$$

$$\hat{\beta} \sim \frac{(\lambda-1)e^{-(\lambda-1)\hat{\tau}}}{\lambda} + \delta^2 \left[\frac{\mu(\lambda-1)\hat{\tau}^2}{2\lambda} - \frac{\hat{k}_1 \hat{\tau}(\lambda-1)}{\lambda} + \frac{\hat{k}_3(\lambda-1)}{\lambda} \right] e^{-(\lambda-1)\hat{\tau}} + o(\delta^2), \quad (46)$$

for $\bar{\tau} \gg 1$, where \hat{k}_1, \hat{k}_2 and \hat{k}_3 are constants of integration. These expansions become non-uniform as $\hat{\tau} \rightarrow \infty$ in particular when $\hat{\tau} = O(\delta^{-1})$.

Region II:

In this region the autocatalyst has decayed to become exponentially small and appropriate scalings are,

$$\bar{\alpha} = \alpha = O(1), \quad \bar{\phi} = -\delta \log \beta = O(1), \quad \bar{\tau} = \tau = O(1). \quad (47)$$

Solving the rescaled governing equations subject to the appropriate matching conditions gives the expansions,

$$\bar{\alpha} = \mu \bar{\tau} - \delta \left[\frac{\mu \epsilon_0 \bar{\tau}^2}{2} \right] + \delta^2 \left[\hat{k}_1 + \frac{\mu \epsilon_0^2 \bar{\tau}^3}{6} \right] + O(\delta^3) + \bar{\alpha}_e, \quad (48)$$

$$\beta = \frac{\lambda-1}{\lambda} \exp \left\{ -\frac{(\lambda-1)\bar{\tau}}{\delta} + \frac{\mu \bar{\tau}^2}{2} - \delta \left(\hat{k}_1 \bar{\tau} - \frac{\mu \epsilon_0^2 \bar{\tau}^3}{6} \right) + o(\delta) \right\}, \quad (49)$$

where $\bar{\alpha}_e$ denotes an exponentially small correction. Non-uniformities occur as $\bar{\tau} \rightarrow \infty$ in particular when $\bar{\tau} = O(\delta^{-1})$.

Region III:

We now introduce a third asymptotic region in which appropriate scalings are,

$$\tilde{\alpha} = \delta\alpha = O(1), \quad \tilde{\phi} = -\delta^2 \log \beta = O(1), \quad \tilde{\tau} = \delta\tau = O(1). \quad (50)$$

Equations (38) and (39) become,

$$\frac{d\tilde{\alpha}}{d\tilde{\tau}} = \mu e^{-\epsilon_0 \tilde{\tau}} - \frac{\tilde{\alpha}}{\delta} e^{-\tilde{\phi}/\delta^2}, \quad (51)$$

$$\frac{d\tilde{\phi}}{d\tilde{\tau}} = \frac{\tilde{\alpha}}{\delta} - \frac{\mu}{\epsilon_0 \delta} (1 - e^{-\epsilon_0 \tilde{\tau}}) + \lambda - 1 - \tilde{\alpha} + e^{-\tilde{\phi}/\delta^2}, \quad (52)$$

we obtain the leading order solution for $\tilde{\alpha}$ as,

$$\tilde{\alpha} = \frac{\mu}{\epsilon_0} (1 - e^{-\epsilon_0 \tilde{\tau}}). \quad (53)$$

and an examination of equation (51) shows the remaining algebraic correction terms to be constant. We find that the autocatalyst concentration is given by,

$$\beta = \frac{\lambda - 1}{\lambda} \exp \left\{ -\frac{1}{\delta^2} \left[\left(\lambda - 1 - \frac{\mu}{\epsilon_0} \right) \tilde{\tau} + \frac{\mu}{\epsilon_0^2} (1 - e^{-\epsilon_0 \tilde{\tau}}) \right] - \hat{k}_1 \tilde{\tau} \right\} \times \{1 + O(\delta)\}. \quad (54)$$

The behaviour of equation (54) changes dramatically as $\tilde{\tau} \rightarrow \tilde{\tau}_0$ where, at leading order, $\tilde{\tau}_0$ satisfies,

$$\left(\lambda - 1 - \frac{\mu}{\epsilon_0} \right) \tilde{\tau}_0 = \frac{\mu}{\epsilon_0^2} (e^{-\epsilon_0 \tilde{\tau}_0} - 1). \quad (55)$$

For there to be a rapid growth in autocatalyst concentration, and hence for clock reaction behaviour to occur, there must exist a real solution of equation (55). It is straightforward to show that for such a solution to exist the condition,

$$0 < \lambda - 1 < \mu/\epsilon_0, \quad (56)$$

must be satisfied. If condition (56) is not fulfilled then the large time solution of equations (38) and (39) will be of the form (32) and hence the autocatalyst concentration will decay to zero for large time. We have assumed for the purpose of our analysis that $\lambda > 1$. The other condition requires there to be sufficient precursor chemical initially to produce enough chemical A so that the rate of the autocatalytic reaction can increase to a point where it can overcome the inhibition reaction. An estimate of $\tilde{\tau}_0$ can be obtained using an iterative numerical scheme such as the Newton-Raphson method and we give some typical results at the end of this section in table 1.

To continue the asymptotic solution we must construct expansions for $\tilde{\alpha}$ and $\tilde{\phi}$ as $\tilde{\tau} \rightarrow \tilde{\tau}_0$. We note that the exponentially small correction to $\tilde{\alpha}$ satisfies,

$$\begin{aligned} \frac{d\tilde{\alpha}_e}{d\tilde{\tau}} &= -\frac{1}{\delta} \frac{\mu}{\epsilon_0} \left(1 - e^{-\epsilon_0 \tilde{\tau}}\right) \frac{(\lambda - 1)}{\lambda} \\ &\times \exp \left\{ -\frac{1}{\delta^2} \left[\left(\lambda - 1 - \frac{\mu}{\epsilon_0} \right) \tilde{\tau} + \frac{\mu}{\epsilon_0^2} \left(1 - e^{-\epsilon_0 \tilde{\tau}}\right) \right] - \hat{k}_1 \tilde{\tau} \right\} \times \{1 + O(\delta)\}. \end{aligned} \quad (57)$$

and appropriate expansions are,

$$\begin{aligned} \tilde{\alpha} &\sim a - \mu e^{\epsilon_0 \tilde{\tau}_0} (\tilde{\tau}_0 - \tilde{\tau}) \\ &+ \delta \frac{a(\lambda - 1)}{\lambda(\lambda - 1 - a)} \exp \left\{ (\lambda - 1 - a) \frac{(\tilde{\tau}_0 - \tilde{\tau})}{\delta^2} + \hat{k}_1 (\tilde{\tau}_0 - \tilde{\tau}) \right\} \times \{1 + O(\delta)\}, \end{aligned} \quad (58)$$

$$\tilde{\phi} \sim -(\lambda - 1 - a)(\tilde{\tau}_0 - \tilde{\tau}) - \delta^2 \left[\hat{k}_1 (\tilde{\tau}_0 - \tilde{\tau}) + \log \left(\frac{\lambda - 1}{\lambda} \right) \right] + O(\delta^3). \quad (59)$$

The constant a represents the leading order concentration $\tilde{\alpha}_0$ at $\tilde{\tau}_0$ and is given as,

$$a = \frac{\mu}{\epsilon_0} \left(1 - e^{-\epsilon_0 \tilde{\tau}_0}\right). \quad (60)$$

We note that it is necessary to include the exponentially small correction term in expansion (58) as this gives the matching condition for the next region. Expansion (59) becomes non-uniform as $\tilde{\tau} \rightarrow \tilde{\tau}_0$ in particular when $\tilde{\tau} - \tilde{\tau}_0 = O(\delta^2)$.

Region IV:

We introduce another asymptotic region centred on $\tilde{\tau}_0/\delta$ and of width $O(\delta^2)$. Appropriate scalings are,

$$A = \alpha - \frac{a}{\delta} = O(1), \quad B = \beta = O(1), \quad T = \frac{\tau}{\delta} - \frac{\tilde{\tau}_0}{\delta^2} = O(1). \quad (61)$$

The leading order equations are given as,

$$\frac{dA}{dT} = -aB, \quad \frac{dB}{dT} = -B(\lambda - 1 - a + A + B), \quad (62)$$

and these are solved subject to the matching conditions,

$$A \sim \frac{a(\lambda - 1)}{\lambda(\lambda - 1 - a)} \exp \{T[a - (\lambda - 1)]\}, \quad (63)$$

$$B \sim \frac{(\lambda - 1)}{\lambda} \exp \{T[a - (\lambda - 1)]\}. \quad (64)$$

as $T \rightarrow -\infty$. By dividing equation (62)₂ by equation (62)₁ and applying the above matching conditions we obtain the relation,

$$A + B = (\lambda - 1)(e^{A/a} - 1). \quad (65)$$

It is thus possible to obtain implicit expressions for A and B which we find remain bounded for finite T . Solving for the correction terms gives the expansions,

$$A \sim [-(\lambda - 1) - k_4 e^{aT}] + \delta \left[\frac{k_4^2}{a} e^{2aT} + k_4(\lambda - 1)T e^{aT} + \mu T e^{-\epsilon_0 \tilde{\tau}_0} \right] + o(\delta), \quad (66)$$

$$B \sim [k_4 e^{aT}] - \delta \left[\frac{k_4^2}{a} e^{2aT} + k_4(\lambda - 1)T e^{aT} \right] + o(\delta), \quad (67)$$

for $T \gg 1$. Non-uniformities occur as $T \rightarrow -\frac{1}{a} \log \delta$ and in order to obtain asymptotic expansions which remain uniform in the neighbourhood of this point we introduce another asymptotic region.

Region V:

Appropriate scalings for this region are,

$$\bar{A} = \delta \alpha = O(1), \quad \bar{B} = \delta \beta = O(1), \quad \bar{T} = \frac{\tau}{\delta} - \frac{\tilde{\tau}_0}{\delta^2} + \frac{\log \delta}{a} = O(1), \quad (68)$$

and rewriting the previous regions expansions in terms of this region's variables leads us to pose five term expansions. It is possible to solve exactly for all but the final term in each expansion and we find that all terms remain bounded for finite \bar{T} . Approximating for $\bar{T} \gg 1$ gives the asymptotic expansions,

$$\begin{aligned} \bar{A} \sim & \left[\frac{a^3}{k_4} e^{-a\bar{T}} \right] + \delta \log \delta \left[\frac{(\lambda - 1)a}{k_4} e^{-a\bar{T}} \right] + \delta \left[\frac{(\lambda - 1)a^2}{k_4} \bar{T} e^{-a\bar{T}} \right] \\ & + \delta^2 (\log \delta)^2 \left[\frac{(\lambda - 1)^2}{k_4} e^{-a\bar{T}} \right] + \delta^2 \log \delta \left[\frac{a\bar{T}(\mu e^{-\epsilon_0 \tilde{\tau}_0} - (\lambda - 1)^2)}{k_4} e^{-a\bar{T}} \right] \\ & + \delta^2 \left[\frac{\mu e^{-\epsilon_0 \tilde{\tau}_0}}{a} \right] + o(\delta^2), \end{aligned} \quad (69)$$

$$\begin{aligned} \bar{B} \sim & \left[a - \frac{a^3}{k_4} e^{-a\bar{T}} \right] - \delta \log \delta \left[\frac{(\lambda - 1)a}{k_4} e^{-a\bar{T}} \right] - \delta \left[(\lambda - 1) - \frac{(\lambda - 1)a^2}{k_4} \bar{T} e^{-a\bar{T}} \right] \\ & - \delta^2 (\log \delta)^2 \left[\frac{(\lambda - 1)^2}{k_4} e^{-a\bar{T}} \right] \end{aligned}$$

$$\begin{aligned}
& -\delta^2 \log \delta \left[\frac{\mu e^{-\epsilon_0 \tilde{\tau}_0}}{a} - \frac{a \bar{T} (\mu e^{-\epsilon_0 \tilde{\tau}_0} - (\lambda - 1)^2)}{k_4} e^{-a \bar{T}} \right] \\
& + \delta^2 \left[\mu \bar{T} e^{-\epsilon_0 \tilde{\tau}_0} - \frac{\mu e^{-\epsilon_0 \tilde{\tau}_0}}{a} \right] + o(\delta^2). \tag{70}
\end{aligned}$$

Non-uniformities occur as $\bar{T} \rightarrow \infty$ in particular when $\bar{T} = O(\delta^{-2})$ and so we rescale to form the final asymptotic region.

Region VI:

The scalings for this final region are,

$$\check{\alpha} = \frac{\alpha}{\delta} = O(1), \quad \check{\beta} = \delta \beta = O(1), \quad \check{\tau} = \delta \tau = O(1), \tag{71}$$

under which equations (38) and (39) become,

$$\delta^2 \frac{d\check{\alpha}}{d\check{\tau}} = \mu e^{-\epsilon_0 \check{\tau}} - \check{\alpha} \check{\beta}, \tag{72}$$

$$\frac{d\check{\beta}}{d\check{\tau}} = \check{\alpha} \check{\beta} - \frac{\check{\beta}^2}{\delta^2} \left[\delta \check{\alpha} + \frac{\check{\beta}}{\delta} - \frac{\mu}{\epsilon_0 \delta} (1 - e^{-\epsilon_0 \check{\tau}}) + \lambda - 1 \right]. \tag{73}$$

By posing suitable expansions for $\check{\alpha}$ and $\check{\beta}$ we obtain, in terms of the unscaled variables, final expansions of the form,

$$\alpha = \frac{\epsilon_0 \delta e^{-\epsilon_0 \tau}}{(1 - e^{-\epsilon_0 \delta \tau})} \left[1 + \delta \frac{\epsilon_0 (\lambda - 1)}{\mu (1 - e^{-\epsilon_0 \delta \tau})} \right] + o(\delta^2), \tag{74}$$

$$\beta = \frac{\mu}{\epsilon_0 \delta} (1 - e^{-\epsilon_0 \check{\tau}}) - (\lambda - 1) + o(1). \tag{75}$$

It is clear that as $\tau \rightarrow \infty$ then $\alpha \rightarrow 0$ and $\beta \rightarrow \mu/\epsilon_0 \delta - (\lambda - 1)$, hence the solution now takes on the asymptotic form (33). This completes the asymptotic solution of the initial value problem for $\lambda > 1$ and $\delta \ll 1$. Further details of the asymptotic solution are given in [12].

We now summarise the structure of the asymptotic solution. Region I is an initial transient region in which β decays to become exponentially small and γ is reduced to approximately $(\lambda - 1)$. The concentration α continues to grow linearly through the first and second region and β remains exponentially small and γ close to $(\lambda - 1)$ in region II. The rate of growth of α is slowed in region III and as $\tau \rightarrow \tilde{\tau}_0/\delta$ the concentration β starts to increase very rapidly. To resolve this sharp increase we construct a thin asymptotic region, region IV, which is centred on $\tau = \tilde{\tau}_0/\delta$. Expansions show that a further logarithmic shift is required

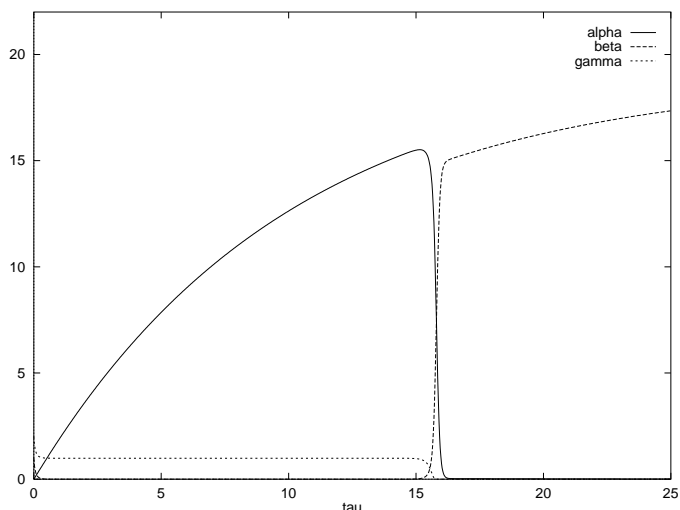


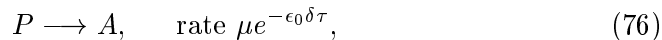
Figure 1. Numerical solution of the initial value problem for the case $n = m = 1$ with $\lambda = 2$, $\epsilon_0 = 1$, $\mu = 2$ and $\delta = 0.1$

to form a further asymptotic region, region V. The concentration α now decays to become exponentially small and we obtain the scalings for the final asymptotic region. In region VI the solution has the large time form (33).

The NAG D02BBF fourth order Runge Kutta scheme was used to solve the initial value problem (38), (39) and (40) subject to (41). Figure 1 shows the results for parameter values $\lambda = 2$, $\epsilon_0 = 1$, $\mu = 2$ and $\delta = 0.1$. The numerical solution verifies the asymptotic structure described above. Figure 2 shows plots of the concentration β for varying values of δ . This shows that clock reaction behaviour is displayed, even for moderately small values of δ and that it becomes more sharply defined as δ decreases. Table 1 compares the asymptotic value of τ_0 , calculated by solving equation (55) using a Newton-Raphson technique, with the approximate value found in the numerical solution. This was taken to be the point at which the concentrations α and β became equal. Good agreement is observed between the numerical and asymptotic results.

4. Cubic autocatalysis with quadratic inhibition ($n = m = 2$)

In this case the reaction scheme is,



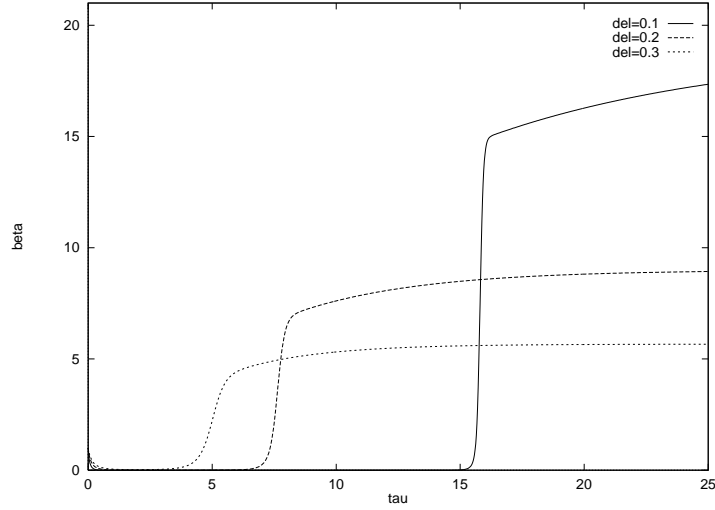
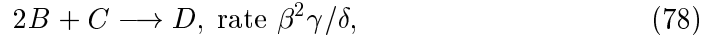


Figure 2. Numerical solution of the initial value problem for the case $n = m = 1$ with $\lambda = 2$, $\epsilon_0 = 1$, $\mu = 2$ and $\delta = 0.1, 0.2, 0.3$

δ	asymptotic estimate of τ_0	numerical estimate of τ_0
0.1	15.93	15.80
0.2	7.96	7.62
0.3	5.31	5.02

Table 1

Comparison of numerical and asymptotic estimates of the length of the induction period for the case $n = m = 1$ with $\lambda = 2$, $\epsilon_0 = 1$ and $\mu = 2$



where $\delta = k_1/k_2$ and $\epsilon_0\delta = k_0/k_1b_0^2$. We require a solution of,

$$\frac{d\alpha}{d\tau} = \mu e^{-\epsilon_0\delta\tau} - \alpha\beta^2, \quad (79)$$

$$\frac{d\beta}{d\tau} = \alpha\beta^2 - \frac{\beta^2}{\delta} \left[\alpha + \beta - \frac{\mu}{\epsilon_0\delta} (1 - e^{-\epsilon_0\delta\tau}) + 2\lambda - 1 \right], \quad (80)$$

$$\gamma = \frac{1}{2} \left[\alpha + \beta - \frac{\mu}{\epsilon_0\delta} (1 - e^{-\epsilon_0\delta\tau}) + 2\lambda - 1 \right], \quad (81)$$

subject to the initial conditions,

$$\alpha(0) = 0, \quad \beta(0) = 1, \quad \gamma(0) = \lambda. \quad (82)$$

We construct an asymptotic solution in the same way as the previous section and find that five asymptotic regions are required to describe the full solution of the initial value problem. Our analysis again confirms conjecture (24) by showing that clock reaction behaviour is only observed within certain parameter limits. We now summarise the scalings and the leading order solutions in each of the regions.

$$\mathbf{Region I:} \quad \hat{\tau} = \delta^{-1}\tau = O(1), \quad \hat{\alpha} = \delta^{-1}\alpha = O(1), \quad \hat{\beta} = \beta = O(1).$$

$$\hat{\alpha} = \mu\hat{\tau}, \quad \log\left(\frac{\hat{\beta} + 2\lambda - 1}{2\lambda\hat{\beta}}\right) - \frac{2\lambda - 1}{\hat{\beta}} = -(2\lambda - 1)^2\hat{\tau} - (2\lambda - 1). \quad (83)$$

We note that as $\hat{\tau} \rightarrow \infty$ the latter expression becomes,

$$\hat{\beta} \sim \frac{1}{(2\lambda - 1)\hat{\tau}}. \quad (84)$$

$$\mathbf{Region II:} \quad \bar{\tau} = \delta\tau = O(1), \quad \bar{\alpha} = \delta\alpha = O(1), \quad \bar{\beta} = \delta^{-2}\beta = O(1).$$

$$\bar{\alpha} = \frac{\mu}{\epsilon_0}(1 - e^{-\epsilon_0\bar{\tau}}), \quad \bar{\beta} = \frac{1}{[(2\lambda - 1) - \mu/\epsilon_0]\bar{\tau} + \mu/\epsilon_0^2[1 - e^{-\epsilon_0\bar{\tau}}]}. \quad (85)$$

The equation for $\bar{\beta}$ is singular provided there exists a $\bar{\tau}_0$ such that,

$$\left(2\lambda - 1 - \frac{\mu}{\epsilon_0}\right)\bar{\tau}_0 = \frac{\mu}{\epsilon_0^2}(1 - e^{-\epsilon_0\bar{\tau}_0}). \quad (86)$$

It is straightforward to show that a necessary condition is,

$$0 < 2\lambda - 1 < \mu/\epsilon_0. \quad (87)$$

This inequality gives the parameter range in which clock reaction behaviour will be observed. If condition (87) is not satisfied then the solution will take on the form (32) and clock reaction behaviour will not be observed. This inequality has the same physical implications as condition (56) in the previous section.

$$\mathbf{Region III:} \quad T = \frac{\tau}{\delta} - \frac{\bar{\tau}_0}{\delta^2} - \frac{\phi}{\delta^2} = O(1), \quad A = \alpha - \frac{a}{\delta} = O(1), \quad B = \beta = O(1).$$

We note that a/δ represents the concentration α when $\bar{\tau} = \bar{\tau}_0$ and ϕ is a small shift from $\bar{\tau}_0$ which can be obtained implicitly in terms of δ , λ , a and $\bar{\tau}_0$. Both A

and B are found to develop singularities as $T \rightarrow T_0$ and appropriate coordinate expansions are given as,

$$A \sim \frac{-1}{a(T_0 - T)} - (2\lambda - 1), \quad B \sim \frac{1}{a(T_0 - T)}, \quad \text{as } T \rightarrow T_0. \quad (88)$$

To determine T_0 it is necessary to match to region II at higher order.

Region IV:

$$\bar{T} = \frac{\tau}{\delta^2} - \frac{\bar{\tau}_0}{\delta^3} - \frac{\phi}{\delta^3} - \frac{T_0}{\delta} = O(1), \quad \bar{A} = \delta\alpha = O(1), \quad \bar{B} = \delta\beta = O(1).$$

We find that \bar{A} and \bar{B} remain bounded for finite \bar{T} and approximating for $\bar{T} \gg 1$ gives,

$$\bar{A} \sim ae^{-a^2(\bar{T}-\bar{T}_0)}, \quad \bar{B} \sim a(1 - e^{-a^2(\bar{T}-\bar{T}_0)}), \quad (89)$$

where the constant \bar{T}_0 must be determined by matching at higher order to the previous region. When we construct full expansions for \bar{A} and \bar{B} we find that non-uniformities do not occur until $\bar{T} = O(\delta^{-3})$.

Region V: $\tilde{\tau} = \delta\tau = O(1), \quad \tilde{\alpha} = \delta^{-2}\alpha = O(1), \quad \tilde{\beta} = \delta\beta = O(1).$

$$\tilde{\alpha} = \frac{\epsilon_0^2 e^{-\epsilon_0 \tilde{\tau}}}{\mu(1 - e^{-\epsilon_0 \tilde{\tau}})^2}, \quad \tilde{\beta} = \frac{\mu}{\epsilon_0} (1 - e^{-\epsilon_0 \tilde{\tau}}) - \delta(2\lambda - 1). \quad (90)$$

As $\tau \rightarrow \infty$ then $\alpha \rightarrow 0$ and $\beta \rightarrow \mu/\epsilon_0\delta - (2\lambda - 1)$ hence the solution now takes on the asymptotic form (33). This completes the asymptotic solution of the initial value problem for $\lambda > 1/2$ and $\delta \ll 1$. Further details of the asymptotic solution are given in [12].

The asymptotic solution has a very similar structure to that of the case $n = m = 1$. The main differences being that the autocatalyst decays to become algebraically small during the induction period and that the rapid growth in autocatalyst concentration occurs at the end of the second asymptotic region.

The NAG D02BBF fourth order Runge Kutta scheme was used to solve the initial value problem (79), (80) and (81) subject to (82). Figure 3 shows the results for parameter values $\lambda = 1$, $\epsilon_0 = 1$, $\mu = 3$ and $\delta = 0.1$. The dominant features of the numerical solution verify the asymptotic analysis.

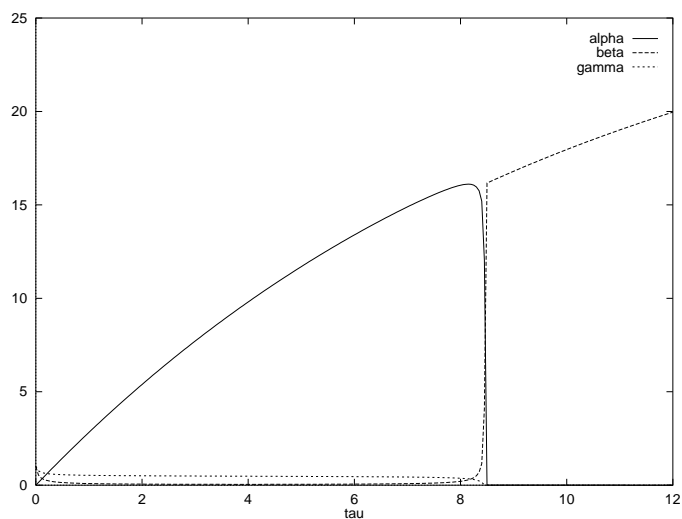


Figure 3. Numerical solution of the initial value problem for the case $n = m = 2$ with $\lambda = 1$, $\epsilon_0 = 1$, $\mu = 3$ and $\delta = 0.1$

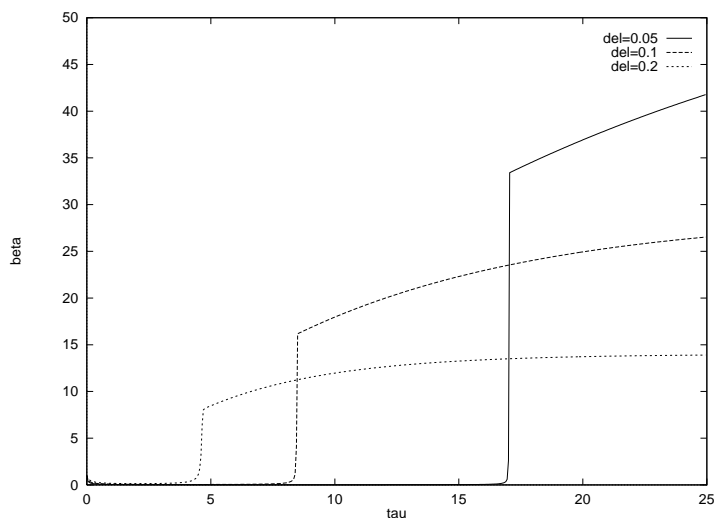


Figure 4. Numerical solution of the initial value problem for the case $n = m = 2$ with $\lambda = 1$, $\epsilon_0 = 1$, $\mu = 3$ and $\delta = 0.05, 0.1, 0.2$

Figure 4 shows plots of the concentration of β for varying values of δ . As predicted by the asymptotic theory the transition region becomes thinner as δ decreases and hence clock reaction behaviour becomes more sharply defined.

Table 2 compares the asymptotic value of τ_0 , calculated by solving equation (86) using a Newton-Raphson technique, with the approximate value found from

δ	asymptotic estimate of τ_0	numerical estimate of τ_0
0.05	17.48	17.03
0.1	8.74	8.49
0.2	4.37	4.61

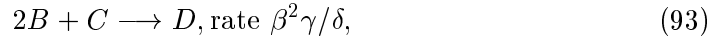
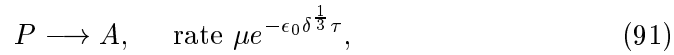
Table 2

Comparison of numerical and asymptotic estimates of the length of the induction period for the case $n = m = 2$ with $\lambda = 1$, $\epsilon_0 = 1$ and $\mu = 3$

the numerical solution. This was taken to be the point at which the concentrations α and β became equal.

5. Quadratic autocatalysis with quadratic inhibition ($n = 1$, $m = 2$, $\epsilon = O(\delta^{\frac{1}{3}})$)

In this case the reaction scheme is,



where $\delta = k_1/k_2 b_0$ and $k_0/k_2 b_0$. We require a solution of,

$$\frac{d\alpha}{d\tau} = \mu e^{-\epsilon_0 \delta^{\frac{1}{3}} \tau} - \alpha\beta, \quad (94)$$

$$\frac{d\beta}{d\tau} = \alpha\beta - \frac{1}{\delta} \beta^2 \left[\alpha + \beta - \frac{\mu}{\epsilon_0 \delta^{\frac{1}{3}}} (1 - e^{-\epsilon_0 \delta^{\frac{1}{3}} \tau}) + 2\lambda - 1 \right], \quad (95)$$

$$\gamma = \frac{1}{2} \left[\alpha + \beta - \frac{\mu}{\epsilon_0 \delta^{\frac{1}{3}}} (1 - e^{-\epsilon_0 \delta^{\frac{1}{3}} \tau}) + 2\lambda - 1 \right], \quad (96)$$

subject to the initial conditions,

$$\alpha(0) = 0, \quad \beta(0) = 1, \quad \gamma(0) = \lambda. \quad (97)$$

Seven regions are required to describe the solution of the full initial value problem. The analysis disproves the conjecture made by Billingham and Needham by showing that clock reaction behaviour is observed for all parameter values. We now give details of the scalings and the leading order solutions in each of the regions.

Region I: $\hat{\alpha} = \delta^{-1}\alpha = O(1)$, $\hat{\beta} = \beta = O(1)$, $\hat{\tau} = \delta^{-1}\tau = O(1)$.

$$\hat{\alpha} = \mu\hat{\tau}, \quad \hat{\beta} \sim \frac{1}{(2\lambda - 1)\hat{\tau}}, \quad \hat{\tau} \gg 1. \quad (98)$$

Region II: $\bar{\alpha} = \alpha = O(1)$, $\bar{\beta} = \delta^{-1}\beta = O(1)$, $\bar{\tau} = \tau = O(1)$.

$$\bar{\alpha} = \mu\bar{\tau}, \quad \bar{\beta} = \frac{\mu\bar{\tau}}{2\lambda - 1}. \quad (99)$$

Region III: $\tilde{\alpha} = \delta^{\frac{1}{3}}\alpha = O(1)$, $\tilde{\beta} = \delta^{-\frac{2}{3}}\beta = O(1)$, $\tilde{\tau} = \delta^{\frac{1}{3}}\tau = O(1)$.

The leading order solutions are given as,

$$\tilde{\alpha} = \frac{\mu}{\epsilon_0} \left(1 - e^{-\epsilon_0\tilde{\tau}}\right). \quad (100)$$

$$\tilde{\beta} = \frac{\frac{\mu}{\epsilon_0} \left(1 - e^{-\epsilon_0\tilde{\tau}}\right)}{\left\{ (2\lambda - 1)^2 - \frac{2\mu^2}{\epsilon_0^2} \left[\tilde{\tau} - \frac{2}{\epsilon_0} \left(1 - e^{-\epsilon_0\tilde{\tau}}\right) - \frac{1}{2\epsilon_0} \left(1 - e^{-2\epsilon_0\tilde{\tau}}\right) \right] \right\}^{\frac{1}{2}}}, \quad (101)$$

For a singularity to occur in equation (101) and hence for clock reaction behaviour to occur there must exist a $\tilde{\tau}_0$ such that,

$$(2\lambda - 1)^2 = \frac{2\mu^2}{\epsilon_0^2} \left[\tilde{\tau}_0 - \frac{2}{\epsilon_0} \left(1 - e^{-\epsilon_0\tilde{\tau}_0}\right) - \frac{1}{2\epsilon_0} \left(1 - e^{-2\epsilon_0\tilde{\tau}_0}\right) \right], \quad (102)$$

It is straightforward to show that this equation has a real solution for all non-negative parameter values. Thus the final solution for the case $n = 1$, $m = 2$ with $\epsilon = O(\delta^{\frac{1}{3}})$ always takes the asymptotic form (33) and clock reaction behaviour is always observed.

Region IV: $A = \alpha - \frac{a}{\delta^{\frac{1}{3}}} = O(1)$, $B = \delta^{-\frac{1}{2}}\beta = O(1)$, $T = \tau - \frac{\tilde{\tau}_0}{\delta^{\frac{1}{3}}} = O(1)$.

We note that a denotes the scaled concentration $\tilde{\alpha}$ at $\tilde{\tau} = \tilde{\tau}_0$.

$$A = \mu e^{-\epsilon_0\tilde{\tau}_0}T - (2\lambda - 1), \quad B = \frac{1}{\sqrt{2}(T_0 - T)^{\frac{1}{2}}}, \quad (103)$$

where the constant T_0 can be fixed by matching to region III.

Region V:

$$\bar{A} = \alpha - \frac{a}{\delta^{\frac{1}{3}}} = O(1), \quad B = \delta^{-\frac{1}{3}}\beta = O(1), \quad \bar{T} = \frac{\tau}{\delta^{\frac{1}{3}}} - \frac{\tilde{\tau}_0}{\delta^{\frac{2}{3}}} - \frac{T_0}{\delta^{\frac{1}{3}}} = O(1).$$

We obtain the expansions,

$$\bar{A} \sim \mu T_0 e^{-\epsilon_0 \tilde{\tau}_0} - (2\lambda - 1) + \delta^{\frac{1}{3}} \left[\mu \bar{T} e^{-\epsilon_0 \tilde{\tau}_0} - \tilde{k}_4 e^{a\bar{T}} \right] + o(\delta^{\frac{1}{3}}), \quad (104)$$

$$\bar{B} \sim \tilde{k}_4 e^{a\bar{T}} + O(\delta^{\frac{1}{3}}). \quad (105)$$

where \tilde{k}_4 is a constant which can be determined by matching to region IV. We base the scalings for the next region on the non-uniformity which occurs as $\bar{T} \rightarrow -\frac{2}{3a} \log \delta$.

Region VI:

$$\hat{A} = \delta^{\frac{1}{3}}\alpha = O(1), \quad \hat{B} = \delta^{\frac{1}{3}}\beta = O(1), \quad \hat{T} = \frac{\tau}{\delta^{\frac{1}{3}}} - \frac{\tilde{\tau}_0}{\delta^{\frac{2}{3}}} - \frac{T_0}{\delta^{\frac{1}{3}}} + \frac{2}{3a} \log \delta = O(1).$$

$$\hat{A} = \frac{a^2}{a + \tilde{k}_4 e^{a\hat{T}}}, \quad \hat{B} = \frac{\tilde{k}_4 a}{a e^{-a\hat{T}} + \tilde{k}_4}. \quad (106)$$

If we develop appropriate expansions we find that non-uniformities occur as $\hat{T} \rightarrow \infty$ in particular when $\hat{T} = O(\delta^{-\frac{1}{3}})$. This gives us the scalings for the final asymptotic region.

Region VII: $\check{\alpha} = \delta^{-\frac{1}{3}}\alpha = O(1), \quad \check{\beta} = \delta^{\frac{1}{3}}\beta = O(1), \quad \check{\tau} = \delta^{\frac{1}{3}}\tau = O(1).$

In terms of the unscaled variables the final expansions are,

$$\alpha = \frac{\epsilon_0 \delta^{\frac{1}{3}} e^{-\epsilon_0 \delta^{\frac{1}{3}} \tau}}{(1 - e^{-\epsilon_0 \delta^{\frac{1}{3}} \tau})} \left[1 + \delta^{\frac{1}{3}} \frac{\epsilon_0 (2\lambda - 1)}{\mu (1 - e^{-\epsilon_0 \delta^{\frac{1}{3}} \tau})} \right] + o(\delta^{\frac{2}{3}}), \quad (107)$$

$$\beta = \frac{\mu}{\epsilon_0 \delta^{\frac{1}{3}}} \left(1 - e^{-\epsilon_0 \delta^{\frac{1}{3}} \tau} \right) - (2\lambda - 1) + o(1). \quad (108)$$

As $\tau \rightarrow \infty$ then $\alpha \rightarrow 0$ and $\beta \rightarrow \mu/\epsilon_0 \delta^{\frac{1}{3}} - (2\lambda - 1)$ hence the solution now takes on the asymptotic form (33). This completes the asymptotic solution for $\lambda > 1/2$ and $\delta \ll 1$. Further details of the asymptotic solution are given in [12].

We now summarise the structure of the asymptotic solution. In region I β decays to become small and γ decays to become approximately $(\lambda - 1/2)$. and region II is a transient region in which both α and β grow linearly. In the next

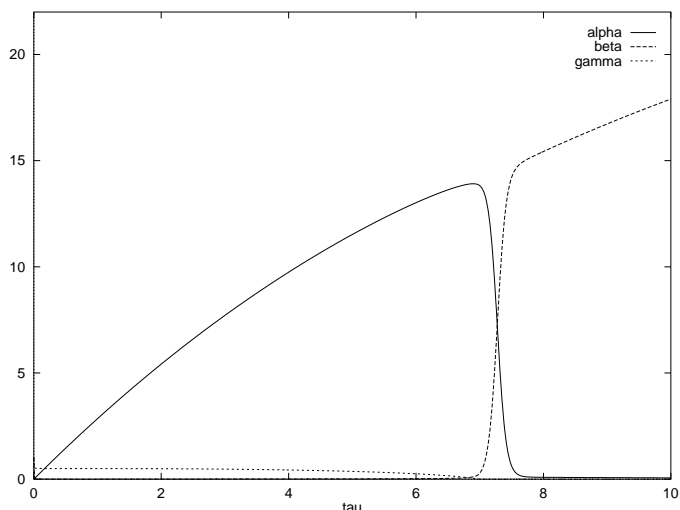


Figure 5. Numerical solution of the initial value problem for the case $n = 1$ $m = 2$ with $\epsilon_0 = 1$, $\mu = 3$, $\lambda = 1$ and $\delta = 10^{-3}$

region the rate of growth of α decreases and as $\tau \rightarrow \tilde{\tau}_0/\delta^{\frac{1}{3}}$ there is a rapid growth in the autocatalyst concentration. We resolve this sharp increase by scaling into a thin region, region IV, centred on $\tau = \tilde{\tau}_0/\delta^{\frac{1}{3}}$. In regions IV and V the concentration of the autocatalyst continues to increase while the concentration α remains constant at leading order. It is not until region VI that the concentration of the autocatalyst stops growing and the concentration α becomes small. In the final region the solution takes on the form (33) and the autocatalyst concentration is observed to tend to a constant.

Again the NAG D02BBF fourth order Runge Kutta scheme was used to solve the initial value problem (94), (95) and (96) subject to (97). Figure 5 shows the results for parameter values $\epsilon_0 = 1$, $\mu = 3$, $\lambda = 1$. The numerical solution verifies the asymptotic structure described above and displays similar characteristics to the cases $n = m = 1$ and $n = m = 2$. We note that the width of the transition region is $O(\delta^{\frac{1}{3}})$ which is larger than in the previous cases. This is illustrated more clearly by figure 6 which shows the concentration β for different values of δ .

Figure 3 gives a comparison between the asymptotic time of blow up and the numerical time of blow up. The latter was taken to be the point at which the concentrations α and β became equal and the asymptotic estimate calculated using a Newton-Raphson method to solve equation (102). As δ decreases the

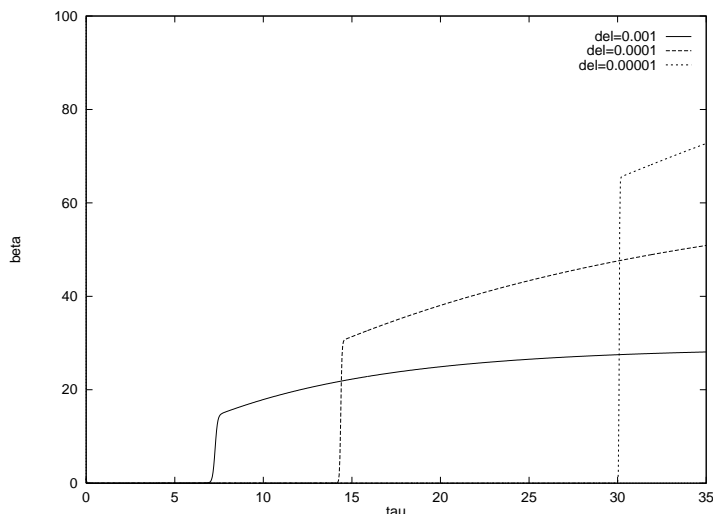


Figure 6. Numerical solution of the initial value problem for the case $n = 1$ $m = 2$ with $\epsilon_0 = 1$, $\mu = 3$, $\lambda = 1$ and $\delta = 10^{-3}, 10^{-4}, 10^{-5}$

δ	asymptotic estimate of τ_0	numerical estimate of τ_0
10^{-3}	6.4	7.3
10^{-4}	13.7	14.3
10^{-5}	29.7	30.1

Table 3

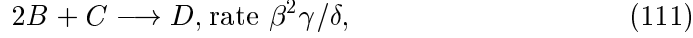
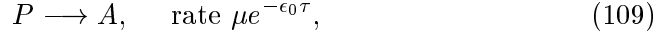
Comparison of numerical and asymptotic estimates of the length of the induction period for the case $n = 1$ $m = 2$ with $\epsilon_0 = 1$, $\mu = 3$ and $\lambda = 1$

asymptotic results agree more closely with the numerical estimate which we would expect.

6. Quadratic autocatalysis with quadratic inhibition ($n = 1$, $m = 2$, $\epsilon = O(1)$)

The analysis in section 5 showed that clock reaction behaviour always occurred when $\epsilon = O(\delta^{\frac{1}{3}})$. We now consider the case when $\epsilon = O(1)$ which ensures that the precursor chemical has fully decayed before the end of the induction period. We show that clock reaction behaviour is only exhibited within certain

parameter limits. The reaction scheme is,



where $\delta = k_1/k_2 b_0$ and $\epsilon_0 = k_0/k_1 b_0$. We require a solution of,

$$\frac{d\alpha}{d\tau} = \mu e^{-\epsilon_0 \tau} - \alpha\beta, \quad (112)$$

$$\frac{d\beta}{d\tau} = \alpha\beta - \frac{1}{\delta} \beta^2 \left[\alpha + \beta - \frac{\mu}{\epsilon_0} (1 - e^{-\epsilon_0 \tau}) + 2\lambda - 1 \right], \quad (113)$$

$$\gamma = \frac{1}{2} \left[\alpha + \beta - \frac{\mu}{\epsilon_0} (1 - e^{-\epsilon_0 \tau}) + 2\lambda - 1 \right], \quad (114)$$

subject to the initial conditions,

$$\alpha(0) = 0, \quad \beta(0) = 1, \quad \gamma(0) = \lambda. \quad (115)$$

To describe the full solution of (112) and (113) subject to initial conditions (115) requires five asymptotic regions. We now give a brief outline of the main features of the asymptotic solution.

Region I:

As in the previous sections the initial scalings are,

$$\hat{\alpha} = \delta^{-1} \alpha = O(1), \quad \hat{\beta} = \beta = O(1), \quad \hat{\tau} = \delta^{-1} \tau = O(1). \quad (116)$$

Solving subject to the initial conditions gives the expansions,

$$\hat{\alpha} \sim \mu \hat{\tau} - \delta \left[\frac{\mu \hat{\tau}}{2\lambda - 1} - \frac{\mu \epsilon_0 \hat{\tau}^2}{2} \right] + \delta^2 \left[\frac{\mu \epsilon_0^2 \hat{\tau}^3}{6} + \frac{\mu \hat{\tau}}{(2\lambda - 1)^2} \right] + o(\delta^2), \quad (117)$$

$$\hat{\beta} \sim \left[\frac{1}{(2\lambda - 1) \hat{\tau}} - \frac{\log \hat{\tau}}{(2\lambda - 1)^3 \hat{\tau}^2} - \frac{\eta}{(2\lambda - 1)^3 \hat{\tau}^2} \right] + \delta^2 \left[\frac{\mu \hat{\tau}}{3(2\lambda - 1)} \right] + o(\delta^2), \quad (118)$$

for $\hat{\tau} \gg 1$. Both expansions become non-uniform as $\hat{\tau} \rightarrow \infty$ in particular when $\hat{\tau} = O(\delta^{-1})$.

Region II:

Appropriate scalings are,

$$\bar{\alpha} = \alpha = O(1), \quad \bar{\beta} = \delta^{-1} \beta = O(1), \quad \bar{\tau} = \tau = O(1), \quad (119)$$

and we find that at leading order $\bar{\alpha}$ is given as,

$$\bar{\alpha} = \frac{\mu}{\epsilon_0} (1 - e^{-\epsilon_0 \bar{\tau}}), \quad (120)$$

and that the leading order expression for $\bar{\beta}$ satisfies,

$$\frac{d\bar{\beta}}{d\bar{\tau}} = \frac{\mu}{\epsilon_0} (1 - e^{-\epsilon_0 \bar{\tau}}) \bar{\beta} - \bar{\beta}^2 (2\lambda - 1). \quad (121)$$

As $\bar{\tau} \rightarrow \infty$ then $\bar{\alpha}$ and $\bar{\beta}$ become,

$$\bar{\alpha} \sim \frac{\mu}{\epsilon_0} + \text{e.s.t.}, \quad \bar{\beta} \sim \frac{\mu}{\epsilon_0(2\lambda - 1)} + \text{e.s.t.} \quad (122)$$

where e.s.t. stands for exponentially small terms. We note that we can now assume that the precursor chemical has fully decayed to all algebraic orders. If we develop expansions valid for $\bar{\tau} \gg 1$ then we find that non-uniformities occur as $\bar{\tau} \rightarrow \infty$ in particular when $\bar{\tau} = O(\delta^{-1})$.

Region III:

Appropriate scalings are,

$$\tilde{\alpha} = \alpha = O(1), \quad \tilde{\beta} = \delta^{-1}\beta = O(1), \quad \tilde{\tau} = \delta\tau = O(1). \quad (123)$$

By solving the leading order equations subject to the appropriate matching conditions we can show $\tilde{\alpha}$ and $\tilde{\beta}$ to satisfy,

$$\log\left(\frac{\tilde{\beta}}{\tilde{\beta} - 1}\right) - \frac{1}{\tilde{\beta}} = (\tilde{\tau}_0 - \tilde{\tau}), \quad \log\left(\frac{\tilde{\alpha}}{a}\right) + \frac{a}{\tilde{\alpha}} - 1 = (\tilde{\tau}_0 - \tilde{\tau}), \quad (124)$$

where $a = \mu/\epsilon_0 - (2\lambda - 1)$ and $\tilde{\tau}_0$ is given by,

$$\tilde{\tau}_0 = -\log\left[1 - \frac{\epsilon_0(2\lambda - 1)}{\mu}\right] - \frac{\epsilon_0(2\lambda - 1)}{\mu}. \quad (125)$$

Equation (125) gives the length of the induction period, that is the point when there is a rapid growth in the concentration of $\tilde{\beta}$. For $\tilde{\tau}_0$ to be real we require,

$$\frac{\mu}{\epsilon_0} > 2\lambda - 1. \quad (126)$$

This condition states that there must be enough precursor chemical initially to produce sufficient chemical A to consume all the inhibitor chemical via the auto-catalytic reaction.

Expanding for $(\tilde{\tau}_0 - \tilde{\tau}) \ll 1$ and $\tilde{\beta} \gg 1$ gives the coordinate expansions,

$$\tilde{\alpha} \sim a + \sqrt{2(\tilde{\tau}_0 - \tilde{\tau})} + O(\tilde{\tau}_0 - \tilde{\tau}), \quad \tilde{\beta} \sim \frac{1}{\sqrt{2(\tilde{\tau}_0 - \tilde{\tau})}}, \quad (127)$$

and if further terms are developed in the asymptotic expansion then non-uniformities are seen to occur as $\tilde{\tau} \rightarrow \tilde{\tau}_0$ in particular when, $\tilde{\tau}_0 - \tilde{\tau} = O(\delta)$.

Region IV:

Appropriate scalings are,

$$A = \frac{(\alpha - a)}{\delta^{\frac{1}{2}}} = O(1), \quad B = \delta^{-\frac{1}{2}}\beta = O(1), \quad T = \tau - \frac{\tilde{\tau}_0}{\delta} = O(1), \quad (128)$$

and we obtain the leading order rescaled equations,

$$\frac{dA}{dT} = -aB, \quad \frac{dB}{dT} = aB - B^2(A + B). \quad (129)$$

If we divide equation (129)₂ by (129)₁ then we obtain a Bernoulli type equation which can be solved subject to the appropriate conditions to give,

$$A + B = \frac{a \exp(-A^2/2a)}{\int_A^\infty \exp(-u^2/2a) du}. \quad (130)$$

Examination of this integral shows that $A \rightarrow -\infty$ and $B \rightarrow \infty$ as $T \rightarrow \infty$. In this limit equations (129)₁ and (129)₂ simplify to linear ordinary differential equations which have the exponential solutions,

$$A \sim -\bar{k}_3 e^{aT}, \quad B \sim \bar{k}_3 e^{aT}, \quad (131)$$

as $T \rightarrow \infty$, where \bar{k}_3 is a non zero constant which can be determined by matching to region III. Consideration of the scalings (128) shows that a non-uniformity occurs as $T \rightarrow \frac{1}{a} \log\left(\frac{1}{\delta^{\frac{1}{2}}}\right)$.

Region V:

The scalings for this final region are,

$$\bar{A} = \alpha = O(1), \quad \bar{B} = \beta = O(1), \quad \bar{T} = \tau - \frac{\tilde{\tau}_0}{\delta} - \frac{1}{a} \log\left(\frac{1}{\delta^{\frac{1}{2}}}\right) = O(1), \quad (132)$$

and, in terms of the unscaled variables, the final expressions for \bar{A} and \bar{B} are,

$$\alpha = \frac{a^2}{a + \bar{k}_3 e^{a\bar{T}}}, \quad \beta = \frac{a\bar{k}_3 e^{a\bar{T}}}{a + \bar{k}_3 e^{a\bar{T}}}. \quad (133)$$

As $\tau \rightarrow \infty$ then $\alpha \rightarrow 0$ and $\beta \rightarrow a$, thus the solution takes on asymptotic form (33). We note that a non-uniformity will occur when $\bar{T} = O(\delta^{-1})$ but if we construct a further region based on appropriate rescalings then it is found to be passive as it reproduces the large time behaviour of this region. This completes

the asymptotic solution for $\lambda > 1/2$ and $\delta \ll 1$. Further details of the asymptotic solution are given in [12].

We now summarise the structure of the asymptotic solution. In the initial region β decays rapidly to become small and the inhibitor chemical decreases to become approximately $(\lambda - 1/2)$. In region II both the concentrations α and β become constant at leading order and γ starts to decrease. The concentration of chemical A begins to fall in region III as the precursor chemical has been consumed. We also observe a decrease in γ as the reaction scheme is consuming chemical A at the expense of the inhibitor. At some well defined time $\tau = \tilde{\tau}_0/\delta$ the inhibitor chemical is completely consumed and this produces a rapid increase in the autocatalyst concentration and a corresponding decrease in α . This signifies the end of the induction period and we find we must scale into a thin region centred on $\tau = \tilde{\tau}_0/\delta$. In this region both α and β are still large of $O(\delta^{-\frac{1}{2}})$ and when appropriate expansions are developed we find that a logarithmic shift in the temporal variable is required. We now obtain the scalings for the final region, in which both α and β are of $O(1)$. The solutions in this region show that α decays to become small and the autocatalyst concentration increases until it attains its large time value of $a = \mu/\epsilon_0 - (2\lambda - 1)$.

The NAG D02BBF fourth order Runge Kutta scheme was used to solve the initial value problem (112), (113), (114) and (115). Figure 7 shows the numerical solution for the parameter values $\epsilon_0 = 1$, $\mu = 3$, $\lambda = 1$ and $\delta = 0.005$. Although the autocatalyst concentration seems to display similar trends to the other cases there is a marked difference in the behaviour of α and γ which we have described above. The condition for clock reaction behaviour to be displayed is well illustrated by figure 7. In physical terms enough chemical A must be fed into the system by the precursor to consume all the inhibitor via the autocatalytic reaction. Thus clock reaction behaviour will not occur if $\alpha \rightarrow 0$ before $\gamma \rightarrow 0$.

Figure 8 shows the concentration of the autocatalyst for different values of δ . As predicted by the asymptotic solution the width of the transition region decreases as δ becomes smaller and hence clock reaction behaviour becomes more sharply defined.

Table 4 compares the asymptotic and the numerical length of the induction period. The asymptotic value was calculated using the expression,

$$\tau_0 = \frac{\tilde{\tau}_0}{\delta} + \frac{1}{a} \log \left(\frac{1}{\delta^{\frac{1}{2}}} \right), \quad (134)$$

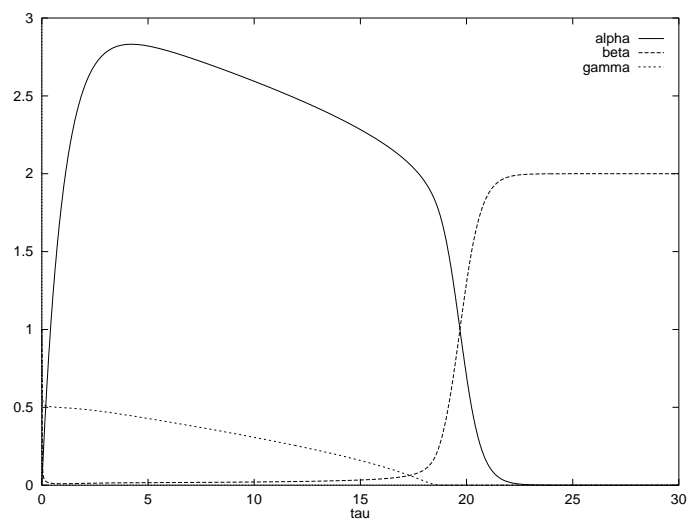


Figure 7. Numerical solution of the initial value problem for the case $n = 1$ $m = 2$ $\epsilon_0 = O(1)$ with $\epsilon_0 = 1$, $\mu = 3$, $\lambda = 1$ and $\delta = 0.005$

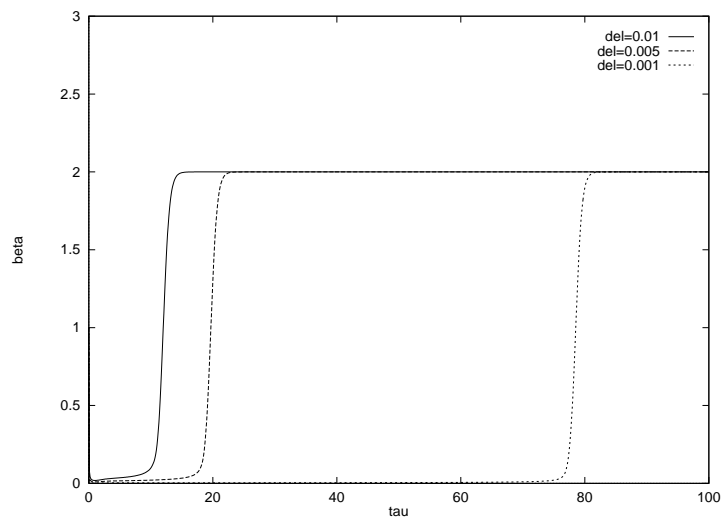


Figure 8. Numerical solution of the initial value problem for the case $n = 1$ $m = 2$ $\epsilon = O(1)$ with $\epsilon_0 = 1$, $\mu = 3$, $\lambda = 1$ and $\delta = 0.01, 0.005, 0.001$

where $\tilde{\tau}_0$ is given by equation (125). The numerical estimate was taken to be when the concentrations α and β became equal. As expected the asymptotic prediction becomes closer to the numerical estimate as δ becomes smaller.

δ	asymptotic estimate of τ_0	numerical estimate of τ_0
0.01	8.4	12.0
0.005	15.7	19.7
0.001	74.0	78.5

Table 4

Comparison of numerical and asymptotic estimates of the length of the induction period for the case $n = 1$ $m = 2$ $\epsilon = O(1)$ with $\epsilon_0 = 1$, $\mu = 3$ and $\lambda = 1$

	$n = m = 1$	$n = m = 2$	$n = 1$ $m = 2$	$n = 1$ $m = 2$
ϵ	$\epsilon_0 \delta$	$\epsilon_0 \delta$	$\epsilon_0 \delta^{\frac{1}{3}}$	ϵ_0
δ	k_1/k_2	k_1/k_2	$k_1/k_2 b_0$	$k_1/k_2 b_0$
τ_0	$O(\delta^{-1})$	$O(\delta^{-1})$	$O(\delta^{-\frac{1}{3}})$	$O(\delta^{-1})$
Condition	$\frac{\mu}{\epsilon_0} > \lambda - 1$	$\frac{\mu}{\epsilon_0} > 2\lambda - 1$	no condition	$\frac{\mu}{\epsilon_0} > 2\lambda - 1$

Table 5

Properties of the initial values problem for $\delta \ll 1$

7. Comparison of the reaction schemes

Initially we consider the cases of quadratic autocatalysis with linear inhibition ($n = m = 1$) and cubic autocatalysis with quadratic inhibition ($n = m = 2$). These two schemes display quite similar characteristics and the main points are summarised in table 5. We found that, for $\delta \ll 1$ ($k_1 \ll k_2$) and $\lambda > 1/m$ ($c_0 > b_0/m$), clock reaction behaviour is only exhibited within certain parameter limits. In terms of the dimensional parameters this condition is given as,

$$p_0 > \frac{k_2}{k_1} (m c_0 - b_0). \quad (135)$$

We note that this verifies part of the conjecture made by Billingham and Needham [3]. Condition (135) states that the initial precursor concentration must be sufficiently large to produce enough chemical A to enable the rate of the autocatalytic reaction to increase to a point where it can overcome the inhibition reaction. We note that in both cases the rapid growth of the autocatalyst occurs when $\tau = O(\delta^{-1})$, the main difference between the two schemes being during the induction period when the concentration of the autocatalyst becomes exponentially small in the case $n = m = 1$, but only algebraically small in the case $n = m = 2$.

In the case of quadratic autocatalysis with quadratic inhibition ($n = 1$, $m = 2$) with $\epsilon = \epsilon_0 \delta^{\frac{1}{3}}$, our analysis showed that, for $\delta \ll 1$ ($k_1 \ll k_2 b_0$) and $\lambda > 1/2$ ($c_0 > b_0/2$), clock reaction behaviour is always exhibited. This disproves the latter part of the conjecture made by Billingham and Needham [3]. We note that the mechanism for rapid growth of the autocatalyst is the same as in the previous two cases but this time it occurs when $\tau = O(\delta^{-\frac{1}{3}})$.

For the case of quadratic autocatalysis with quadratic inhibition ($n = 1$, $m = 2$) with $\epsilon = O(1)$. For $\delta \ll 1$ ($k_1 \ll k_2 b_0$) and $\lambda > 1/2$ ($c_0 > b_0/2$), clock reaction behaviour is only exhibited within certain parameter limits. In terms of the dimensional parameters this condition is given as,

$$p_0 > 2c_0 - b_0. \quad (136)$$

Condition (136) is not physically equivalent to condition (135) as it contains no stipulation on the reaction rate constants. It states that the initial precursor concentration must be sufficiently large to produce enough chemical A to consume all the inhibitor via the autocatalytic reaction. Once this has happened a rapid growth in the autocatalyst is observed.

Finally we note that, for the case of cubic autocatalysis with linear inhibition with $\delta \ll 1$ and $\lambda < 1$, Billingham and Needham [3] showed that clock reaction behaviour can not be exhibited. This is because the rate of the autocatalytic reaction can never become large enough to overcome the inhibition reaction.

8. Conclusion

In this study we have looked at four model reaction schemes based on reaction steps (1), (2) and (3). We have extended the work of Billingham and Needham [3] by allowing for the decay of the precursor chemical and showed that all reaction schemes can display characteristic clock reaction behaviour. By using asymptotic methods we have been able to construct a full solution of the initial value problem in each of the different cases. This has enabled us investigate the conjecture made by Billingham and Needham [3] which states that when precursor chemical consumption is significant then clock reaction behaviour will only be observed within certain parameter limits. We find that this conjecture is correct for the cases $n = m = 1$ and $n = m = 2$ but not for the case $n = 1$, $m = 2$. We have determined appropriate parameter limits and also obtained expressions

for the length of the induction period which, when compared with the numerical results, give good agreement.

We note finally that the schemes considered are examples of inhibited autocatalytic reactions and can be used to model nucleation crystal growth. An example of such a model has been proposed by Billingham and Coveney [1]. They used reactions (1), (2) and (3) to represent the rate determining steps of cement hydration in the presence of a retarder. Their model describes the transition of the surface coating of the cement grain from an impermeable gel to a permeable crystal. At the end of the induction period there is a very rapid growth of the crystalline phase which allows for renewed reaction and thus thickening of the cement. Their model is in qualitative agreement with experimental observations.

References

- [1] J. Billingham and P.V. Coveney, Simple chemical clock reactions - Application to cement hydration, *J. Chem. Soc. Faraday Trans.* 89 (1993), 3021-3028.
- [2] J. Billingham and D.J. Needham, Mathematical-modeling of chemical clock reactions I. Induction, inhibition and the iodate arsenous-acid reaction, *Proc. R. Soc. Lond. A* 340 (1992), 569-591.
- [3] J. Billingham and D.J. Needham, Mathematical-modeling of chemical clock reactions II. A class of autocatalytic clock reaction schemes, *J. Engineering Mathematics* 27 (1993), 113-145.
- [4] G.W. Burnet and H.W. Melville, Determination of velocity coefficients for polymerisation processes, *Proc. R. Soc. Lond A* 189 (1947), 456-480.
- [5] D. O. Cooke, *Inorganic Reaction Mechanisms*, London : The Chemical Society, 1979.
- [6] R.J. Field and R. M. Noyes, Oscillations in chemical systems. IV. Limit cycle behaviour in a model of a real chemical reaction, *J. Chem. Phys* 60 (1974), 1877-1884.
- [7] P. Jones, J.E. Frew and N. Scowen, Inorganic fireflies - A chemiluminescent clock reaction, *J. Chem. Education* 64 (1987), 70-71.
- [8] P. Jones, M.L. Haggett and J.L. Longridge, The hydration of carbon dioxide - A double clock experiment, *J. Chem. Education* 41 (1964), 610-612.
- [9] P. Jones and K.B. Oldham, The theory of the formaldehyde clock reaction, *J. Chem. Education* 40 (1963), 366-368.
- [10] J.L. Lambert and G.T. Fina, Iodine clock reaction-mechanisms, *J. Chem. Education* 61 (1984), 1037-1038.
- [11] J.H. Merkin, A.J. Poole, J.D.B. Smith and B.W. Thompson, Analysis of the bromate-ferroin clock reaction, *J. Mathematical Chem.* 19 (1996), 15-32.
- [12] S.J. Preece, Mathematical modelling of chemical clock reactions and cement hydration, University of Birmingham, PhD thesis (1999).

- [13] K.W. Watkins and R. Distefano, The arsenic(iii) sulfide clock reaction, *J. Chem. Education* 64 (1987), 255-257.