

Mathematical modelling of chemical clock reactions

II. A class of autocatalytic clock reaction schemes

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Abstract. A clock reaction is a chemical reaction which gives rise to an initial induction period before a significant concentration of one of the chemical species involved is produced. We study four closely related isothermal model reaction schemes which can exhibit clock reaction behaviour in a well-stirred situation. These reaction schemes represent a combination of quadratic or cubic autocatalysis with linear or quadratic inhibition.

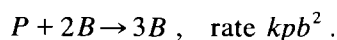
1. Introduction

During a chemical clock reaction the concentration of one of the chemical species involved (the clock chemical) has the following distinguishing features:

- (a) After the initial mixing of the reactants there is an induction period during which the concentration of the clock chemical is low.
- (b) At the end of the induction period the concentration of the clock chemical increases, often very rapidly.

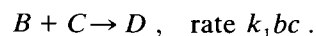
In part I, [1], we described two simple, isothermal reaction mechanisms that can lead to clock reaction behaviour. We also gave canonical examples of each in a closed, well-stirred reaction vessel.

(i) *Induction:* The rate of production of the clock chemical is small when its concentration is small. The concentration of the clock chemical is small initially. For example, cubic autocatalysis:



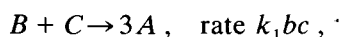
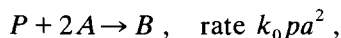
Here, P is a precursor chemical and B is the clock chemical with concentrations p and b , respectively. k is a reaction rate constant. Examples of solution phase reactions which are thought to be well modelled by cubic autocatalysis include the iodate-arsenous acid reaction [2], and the iodine-bisulphate clock reaction [3].

(ii) *Inhibition:* The clock chemical is supplied to the closed system by the decay of a precursor chemical. An inhibitor chemical reacts with the clock chemical, limiting its concentration. The concentration of the clock chemical increases once the inhibitor chemical is consumed. For example:



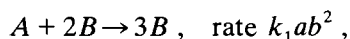
Here, C is the inhibitor chemical with concentration c and D is an inert product. k_0 and k_1 are reaction rate constants. Examples of reactions which are thought to be well modelled by this mechanism are the photosynthesis of hydrogen chloride inhibited by ammonia and the photopolymerization of vinyl acetate inhibited by benzoquinone [4]. Further examples of clock reactions, for which the underlying mechanism is less clear, are the formaldehyde clock [5], the hydration of carbon dioxide [6] and the oxidation of luminol by hydrogen peroxide [67].

We also studied the reaction scheme:

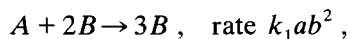


where A is an intermediate chemical species with concentration, a . This is a combination of the previous two reaction schemes and, overall, is cubic autocatalytic ($P + 2A \rightarrow 3A$). As we described in [1], this scheme is closely related to a two-step model for the iodate-arsenous acid and iodine-bisulphate clock reactions.

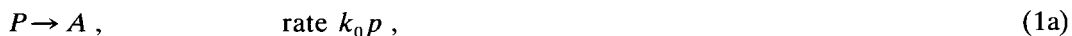
The other obvious combination of our two canonical schemes is:



This provides a model for a modified iodate-arsenous acid reaction where iodate ions, $A = \text{IO}_3^-$, are supplied to the system and an inhibitor chemical, C , reacts with iodine ions, $B = \text{I}^-$. A similar reaction scheme which has received some attention recently is:



Here the species B decays spontaneously rather than in combination with an inhibitor. It can be shown that this scheme exhibits oscillatory behaviour for certain ranges of parameter values [8]. In this paper we study four members of the class of reaction schemes,



with $n = 1, 2$ and $m = 1, 2$. Schemes based around a quadratic or cubic autocatalytic step have received much recent attention (for example [9], [10]). Particular attention has been

paid to the development of sustained oscillations, travelling waves, multistability and routes to chaos. However, the possibility of clock reaction behaviour has not been examined, and is not at all clear from the kinetics (1a, b, c) alone. It is this which we discuss in the present paper.

We note in passing that clock reaction behaviour has been much studied and is well understood in strongly exothermic reactions. In such reactions a clock reaction is equivalent to a long induction period followed by an explosion. Explosions can be purely thermal [11], or may be driven by branched chain propagation via a temperature dependent step similar to (1b) above [12]. In [11] and [12] the exothermic reaction schemes of interest are analysed using the method of matched asymptotic expansions – the technique which we use below to study the behaviour of reaction scheme (1).

2. Asymptotic analysis of the reaction scheme (1a–c)

The reaction rate equations for the concentrations p , a , b and c , are,

$$\frac{dp}{dt} = -k_0p, \quad \frac{da}{dt} = k_0p - k_1ab^n, \quad (2a, b)$$

$$\frac{db}{dt} = k_1ab^n - mk_2b^m c, \quad \frac{dc}{dt} = -k_2b^m c. \quad (2c, d)$$

The concentration of the inert product, D , is determined by conservation of matter as, $d = c_0 - c$, and we impose the initial conditions,

$$p = p_0, \quad a = 0, \quad b = b_0, \quad c = c_0, \quad d = 0 \quad \text{at } t = 0. \quad (2e)$$

Equation (2a) can be integrated immediately to give,

$$p = p_0 e^{-k_0 t}. \quad (3a)$$

By integrating the appropriate linear combination of equations (2b, c, d) we find that,

$$a + b - mc = p_0(1 - e^{-k_0 t}) + b_0 - mc_0. \quad (3b)$$

We then obtain the rate equations in terms of a and b above, by substituting from (3a, b) into (2b, c), as

$$\frac{da}{dt} = k_0 p_0 e^{-k_0 t} - k_1 ab^n, \quad (4a)$$

$$\frac{db}{dt} = k_1 ab^n - k_2 b^m (a + b - p_0(1 - e^{k_0 t}) - b_0 + mc_0). \quad (4b)$$

It is now convenient to define dimensionless variables by,

$$\alpha = a/b_0, \quad \beta = b/b_0, \quad \gamma = c/b_0, \quad \tau = k_1 b_0^n t. \quad (5)$$

In terms of the variables (5) equations (3b), (4a, b) and initial conditions (2e) become,

$$m\gamma = \alpha + \beta - P_0(1 - e^{-\varepsilon\tau}) + m\lambda - 1, \quad (6)$$

$$\frac{d\alpha}{d\tau} = \varepsilon P_0 e^{-\varepsilon\tau} - \alpha\beta^n, \quad (7a)$$

$$\frac{d\beta}{d\tau} = \alpha\beta^n - K\beta^m(\alpha + \beta - P_0(1 - e^{-\varepsilon\tau}) + m\lambda - 1), \quad (7b)$$

$$\alpha(0) = 0, \quad \beta(0) = 1, \quad \gamma(0) = \lambda, \quad (7c)$$

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

$$P_0 = \frac{P_0}{b_0}, \quad \lambda = \frac{c_0}{b_0}, \quad \varepsilon = \frac{k_0}{k_1 b_0^n}, \quad K = \frac{k_2 b_0^{m-n}}{k_1}, \quad (8)$$

The parameters P_0 and λ are the dimensionless initial concentrations of P and C , respectively. The parameters ε and K are measures of the reaction rate of steps (1a) and (1c) respectively, relative to the rate of the autocatalytic step (1b). We now make the further assumptions that the reactant P is initially in large excess over the clock chemical, B , and that the reaction step (1a) typically proceeds much more slowly than the step (1b). This is known as the pool chemical approximation [13]. Mathematically this assumption leads us to consider the situation in which,

$$\varepsilon \ll 1, \quad P_0 \gg 1 \quad \text{with} \quad \mu = \varepsilon P_0 = O(1). \quad (9)$$

If, instead of the decay step (1a), $P \rightarrow A$, we had specified that the species A is supplied to the system at a constant rate, k_{in} , we would have obtained the same equations, (12) at leading order, with $\mu = k_{in}/k_1 b_0^{n+1}$. This is the way that the pool chemical approximation is often invoked when a chemical species is produced at an almost constant rate. We note the effect of the slow consumption of P in §7.

We now examine the solution of the initial value problem (7) under conditions (9). Firstly, we expand α , β and γ as,

$$\alpha(\tau; \varepsilon, K) = \alpha_I(\tau; K) + o(1), \quad \beta(\tau; \varepsilon, K) = \beta_I(\tau; K) + o(1), \quad (10a, b, c)$$

$$\gamma(\tau; \varepsilon, K) = \gamma_I(\tau; K) + o(1), \quad \text{as } \varepsilon \rightarrow 0, \text{ with } \tau = O(1).$$

After substituting these expansions into equations (6) and (7a, b) we obtain the leading order problem,

$$m\gamma_I = \alpha_I + \beta_I - \mu\tau + m\lambda - 1, \quad (11)$$

$$\frac{d\alpha_I}{d\tau} = \mu - \alpha_I\beta_I^n, \quad \frac{d\beta_I}{d\tau} = \alpha_I\beta_I^n - K\beta_I^m(\alpha_I + \beta_I - \mu\tau + m\lambda - 1), \quad (12a, b)$$

$$\alpha_I(0) = 0, \quad \beta_I(0) = 1, \quad \gamma_I(0) = \lambda. \quad (12c)$$

Equations (11) and (12a, b) admit exact solutions of the form,

$$\alpha_I = \mu\tau - \tilde{c}, \quad \beta_I \equiv 0, \quad \gamma_I = \lambda + \frac{(\tilde{c} - 1)}{m}, \quad (13a)$$

where \tilde{c} is a constant, and also solutions of the asymptotic form,

$$\gamma_I \rightarrow 0, \quad \alpha_I + \beta_I \sim \mu\tau - (m\lambda - 1), \quad \alpha_I \sim 1/\mu^{n-1}\tau^n \quad \text{as } \tau \rightarrow \infty. \quad (13b)$$

We show below that the solution of the initial value problem (12) is asymptotic to a solution of the form (13a) or (13b) as $\tau \rightarrow \infty$, depending upon the values of the parameters K , λ and μ , and the reaction rate orders n and m . If the long time asymptotic solution is of the form (13a), the reaction step (1c) inhibits the clock chemical, B , so strongly that the autocatalytic step (1b) never proceeds rapidly enough to produce a significant concentration of B . However, if the long time asymptotic solution has the form (13b), the inhibitor, C , is completely consumed and the reactant, A , produced by the decay of the precursor, P , is rapidly converted to the clock chemical, B , via step (1b). In each case, one of the concentrations α_I or β_I becomes unbounded as $\tau \rightarrow \infty$. This indicates that the expansions (10) develop a nonuniformity as $\tau \rightarrow \infty$ and the form of the full equations (7) shows that this occurs when $\tau = O(\varepsilon^{-1})$ as $\varepsilon \rightarrow 0$. We can regard the expansions (10) as the inner solution and now construct an outer solution valid when $\tau = O(\varepsilon^{-1})$ as $\varepsilon \rightarrow 0$ in each of the two cases described by (13a, b).

$$(a) \quad \alpha_I \sim \mu\tau - \tilde{c}, \quad \beta_I \rightarrow 0, \quad \gamma_I \sim \lambda + \frac{(\tilde{c} - 1)}{m}, \quad \text{as } \tau \rightarrow \infty$$

We show below that, when this case arises, β_I decays exponentially as $\tau \rightarrow \infty$, which leads us to assume that $\beta_I = o(\varepsilon^p) \forall p > 0$ as $\varepsilon \rightarrow 0$. When $\tau = O(\varepsilon^{-1})$, $\alpha_I = O(\varepsilon^{-1})$ and appropriate scaled variables for the outer solution are therefore, $\bar{\tau} = \varepsilon\tau$, $\bar{\alpha} = \varepsilon\alpha$, $\beta = o(\varepsilon^n) \forall n > 0$, $\gamma = O(1)$, as $\varepsilon \rightarrow 0$. In terms of these variables, equation (7a) becomes, up to terms exponentially small in ε ,

$$\frac{d\bar{\alpha}}{d\bar{\tau}} = \mu e^{-\bar{\tau}}, \quad (14a)$$

which is to be solved subject to matching with the inner expansion (10) as $\bar{\tau} \rightarrow 0$. We expand $\bar{\alpha}$ as,

$$\bar{\alpha}(\bar{\tau}; \varepsilon; K) = \bar{\alpha}_{\text{out}0}(\bar{\tau}; K) + \varepsilon \bar{\alpha}_{\text{out}1}(\bar{\tau}, K) + o(\varepsilon), \quad (14b)$$

as $\varepsilon \rightarrow 0$, with $\bar{\tau} = O(1)$, and substitute into equation (14a). The resulting equations for $\bar{\alpha}_{\text{out}0}$ and $\bar{\alpha}_{\text{out}1}$ are readily solved subject to matching with the inner solution (13a) as $\bar{\tau} \rightarrow 0$, to give,

$$\bar{\alpha}(\bar{\tau}; \varepsilon; K) = \mu(1 - e^{-\bar{\tau}}) - \varepsilon\tilde{c} + o(\varepsilon), \quad \text{as } \varepsilon \rightarrow 0, \quad \text{with } \bar{\tau} = O(1). \quad (14c)$$

Thus $\bar{\alpha} \rightarrow \mu - \varepsilon\tilde{c}$ and hence $\alpha \rightarrow P_0 - \tilde{c}$, $\beta \rightarrow 0$, $\gamma \rightarrow \lambda + (\tilde{c} - 1)/m$, as $\bar{\tau} \rightarrow \infty$, which corresponds to an equilibrium state of the full equations (7a, b) following the total consumption of the precursor, P . This completes the solution of the initial value problem (7) for $0 < \varepsilon \ll 1$, in this case.

(b) $\alpha_I \sim 1/\mu^{n-1}\tau^n$, $\beta_I \sim \mu\tau$, $\gamma_I \rightarrow 0$, as $\tau \rightarrow \infty$

Equations (6) and (7a, b) indicate that γ_I decays exponentially as $\tau \rightarrow \infty$ in this case, which leads us to assume that $\gamma_I = o(\varepsilon^p) \forall p > 0$ as $\varepsilon \rightarrow 0$. When $\tau = O(\varepsilon^{-1})$, $\alpha_I = O(\varepsilon^n)$, $\beta_I = O(\varepsilon^{-1})$ and appropriate scaled variables for the outer solution are, $\bar{\tau} = \varepsilon\tau$, $\bar{\alpha} = \varepsilon^{-n}\alpha$, $\bar{\beta} = \varepsilon\beta$, $\gamma = o(\varepsilon^p) \forall p > 0$ as $\varepsilon \rightarrow 0$. In terms of these variables, equations (7a, b) become,

$$\varepsilon^{n+1} \frac{d\bar{\alpha}}{d\bar{\tau}} = \mu e^{-\bar{\tau}} - \bar{\alpha}\bar{\beta}^n \quad (15a)$$

$$\varepsilon^{m+1} \frac{d\bar{\beta}}{d\bar{\tau}} = \varepsilon^{m+1}\bar{\alpha}\bar{\beta}^n - K\varepsilon^{n+1}\bar{\alpha}\bar{\beta}^m + \bar{\beta} - \mu(1 - e^{-\bar{\tau}}) + \varepsilon(m\lambda - 1), \quad (15b)$$

which are to be solved subject to matching with the inner expansion (10) as $\bar{\tau} \rightarrow 0$. We expand $\bar{\alpha}$ and $\bar{\beta}$ as,

$$\bar{\alpha}(\bar{\tau}; \varepsilon, K) = \bar{\alpha}_{\text{out}0}(\bar{\tau}; K) + \varepsilon\bar{\alpha}_{\text{out}1}(\bar{\tau}, K) + o(\varepsilon), \quad (15c)$$

$$\bar{\beta}(\bar{\tau}; \varepsilon, K) = \bar{\beta}_{\text{out}0}(\bar{\tau}; K) + \varepsilon\bar{\beta}_{\text{out}1}(\bar{\tau}, K) + o(\varepsilon), \quad \text{as } \varepsilon \rightarrow 0, \text{ with } \bar{\tau} = O(1),$$

and substitute into equations (15a, b). We can easily solve the resulting equations for $\bar{\alpha}_{\text{out}0}$, $\bar{\alpha}_{\text{out}1}$, $\bar{\beta}_{\text{out}0}$ and $\bar{\beta}_{\text{out}1}$ to obtain, after matching with the inner solution (13b) as $\bar{\tau} \rightarrow 0$,

$$\bar{\alpha}(\bar{\tau}; \varepsilon, K) = \frac{\bar{e}^{\bar{\tau}}}{\mu^{n-1}(1 - e^{-\bar{\tau}})^n} + \frac{\varepsilon n(m\lambda - 1)e^{-\bar{\tau}}}{\mu^n(1 - e^{-\bar{\tau}})^{n+1}} + o(\varepsilon), \quad (16)$$

$$\bar{\beta}(\bar{\tau}; \varepsilon, K) = \mu(1 - e^{-\bar{\tau}}) - \varepsilon(m\lambda - 1) + o(\varepsilon), \quad \text{as } \varepsilon \rightarrow 0, \text{ with } \bar{\tau} = O(1).$$

Thus $\bar{\alpha} \rightarrow 0$, $\bar{\beta} \rightarrow \mu - \varepsilon(m\lambda - 1)$, and hence $\alpha \rightarrow 0$, $\beta \rightarrow P_0 - (m\lambda - 1)$, $\gamma \rightarrow 0$ as $\bar{\tau} \rightarrow \infty$, which corresponds to an equilibrium state of the full equations (7a, b) following the total consumption of the precursor, P . This completes the asymptotic solution of the initial value problem (7) for $0 < \varepsilon \ll 1$ in this case.

We now present a detailed analysis of the inner problem (12) and show that the inner solution can display clock behaviour via a rapid transition from a solution of the form (13a) to a solution of the form (13b). In terms of the reaction schemes (1) this represents a sudden, rapid increase in the concentration of the clock chemical, B . In terms of the real clock reactions described in §1, such a sudden rapid increase in the concentration of the clock chemical often results in a sudden, dramatic colour change in solution phase reactions. As a consequence such reactions are often used as demonstrations for undergraduates ([14], [15]). Some clock reactions even produce a flash of light ([17]).

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

In this case, the reaction scheme (1) is, in the inner limit,





where $K = k_2/k_1$, $\mu = k_0 p_0/k_1 b_0^2$, and we require a solution of the initial value problem,

$$\gamma_I = \alpha_I + \beta_I - \mu\tau + \lambda - 1, \quad (18a)$$

$$\frac{d\alpha_I}{d\tau} = \mu - \alpha_I \beta_I, \quad \frac{d\beta_I}{d\tau} = \alpha_I \beta_I - K\beta_I(\alpha_I + \beta_I - \mu\tau + \lambda - 1), \quad (18b, c)$$

$$\alpha_I(0) = 0, \quad \beta_I(0) = 1, \quad \gamma_I(0) = \lambda. \quad (18d)$$

In order to proceed we make the further assumptions that $\lambda > 1$ and $K \gg 1$. The condition $\lambda > 1$ requires that the initial concentration of the inhibitor, C , is large enough to consume all of the clock chemical, B , present initially, whilst for $K \gg 1$ the reaction step (17c) typically proceeds much more rapidly than the autocatalytic step (17b). At first glance, we might expect that these conditions would lead to complete inhibition of the production of the clock chemical, B , so that the solution is asymptotic to (13a) as $\tau \rightarrow \infty$. However, by integrating equation (18c), making use of (18a) and initial condition (18d), we obtain, $\beta_I = \exp\{(\langle \alpha_I \rangle - K \langle \gamma_I \rangle)\tau\}$, where,

$$\langle X \rangle = \frac{1}{\tau} \int_0^\tau X(s) ds, \quad (19)$$

denotes the time-averaged value of $X(s)$ over the interval $0 \leq s \leq \tau$. In addition, we expect for $K \gg 1$ and $\lambda > 1$ that, after a short initial transient period, the solution lies close to (13a) so that $\langle \alpha_I \rangle \sim \frac{1}{2} \mu \tau^2$, $\langle \gamma_I \rangle \sim (\lambda - 1)$, and hence, $\beta_I \sim \exp[\{\frac{1}{2} \mu \tau - K(\lambda - 1)\}\tau]$, as $K \rightarrow \infty$, with $\tau = O(1)$. This suggests that β_I is exponentially small until τ approaches $\tau_0 = K\tilde{\tau}_0$, with $\tilde{\tau}_0 \sim 2(\lambda - 1)/\mu$ as $K \rightarrow \infty$, after which that β_I increases rapidly.

We now construct an asymptotic solution which confirms that, after a short initial transient period, β_I is exponentially small until τ approaches τ_0 , when the solution undergoes a rapid transition and takes on the asymptotic form (13b). After noting that the concentration β_I is initially of $O(1)$, an examination of equations (18b, c) shows that appropriate scaled variables are, $\hat{\alpha} = K\alpha_I$, $\hat{\tau} = K\tau$, β_I , in terms of which equations (18b, c) and initial conditions (18d) become,

$$\frac{d\hat{\alpha}}{d\hat{\tau}} = \mu - K^{-1}\hat{\alpha}\beta_I, \quad (20a)$$

$$\frac{d\beta_I}{d\hat{\tau}} = -\beta_I(\beta_I + \lambda - 1) - K^{-1}\beta_I(\hat{\alpha} - \mu\hat{\tau}) + K^{-2}\hat{\alpha}\beta_I, \quad (20b)$$

$$\hat{\alpha}(0) = 0, \quad \beta_I(0) = 1. \quad (20c)$$

We label the region where $\hat{\tau} = O(1)$ as region I and expand $\hat{\alpha}$ and β_I as,

$$\hat{\alpha} \sim \sum_{n=0}^{\infty} K^{-n} \hat{\alpha}_n, \quad \beta_I \sim \sum_{n=0}^{\infty} K^{-n} \beta_n, \quad \text{as } K \rightarrow \infty, \text{ with } \hat{\tau} = O(1). \quad (20d)$$

After substituting expansions (20d) into equations (20a, b) and solving in turn the resulting equations for $\hat{\alpha}_0, \hat{\alpha}_1, \hat{\alpha}_2, \beta_0, \beta_1$ and β_2 we obtain,

$$\hat{\alpha}_0 = \mu \hat{\tau}, \quad \beta_0 = \frac{\lambda - 1}{\lambda e^{(\lambda-1)\hat{\tau}} - 1}, \quad (21a, b)$$

with the expressions for $\hat{\alpha}_1, \hat{\alpha}_2, \hat{\beta}_1, \hat{\beta}_2$ omitted for brevity (see [16]). We can now use the solution (21) to obtain the behaviour of $\hat{\alpha}$ and β_l for $\hat{\tau} \gg 1$ as,

$$\hat{\alpha} \sim \mu \hat{\tau} + K^{-1} \left\{ a_1 + \frac{\mu \hat{\tau} e^{-(\lambda-1)\hat{\tau}}}{\lambda} \right\} + K^{-2} \left\{ a_2 + \frac{a_1 e^{-(\lambda-1)\hat{\tau}}}{\lambda} \right\} + \dots \quad (22a)$$

$$\beta_l \sim \frac{(\lambda - 1) e^{-(\lambda-1)\hat{\tau}}}{\lambda} + K^{-2} \left\{ \frac{\mu(\lambda - 1)\hat{\tau}^2}{2\lambda} - \frac{a_1(\lambda - 1)\hat{\tau}}{\lambda} + \frac{b_1(\lambda - 1)}{\lambda} \right\} e^{-(\lambda-1)\hat{\tau}} + \dots, \quad (22b)$$

as $K \rightarrow \infty$,

where the constants a_1, a_2 and b_1 are given in [16]. In addition, it is easy to show by induction that $\beta_n \rightarrow 0$ and $\hat{\alpha}_n \rightarrow a_n$ via exponentially small terms as $\hat{\tau} \rightarrow \infty$, where a_n are fixed constants for $n = 1, 2, \dots$.

Approximations (22a, b) become non-uniform as $\hat{\tau} \rightarrow \infty$, in particular when $\hat{\tau} = O(K)$, $\hat{\alpha} = O(K)$ and $\log \beta_l = O(K)$. To obtain uniform asymptotic expansions for α_l and β_l when $\hat{\tau} = O(K)$ we introduce region II in which the appropriate variables are $\tau = K^{-1}\hat{\tau}$, $\alpha_l, \beta_l = e^{-K\phi(\tau)}$, where $\phi > 0$ in region II. In terms of these new variables, equations (18b, c) become,

$$\frac{d\alpha_l}{d\tau} = \mu - \alpha_l e^{-K\phi}, \quad \frac{d\phi}{d\tau} = \alpha_l - \mu\tau + \lambda - 1 - K^{-1}\alpha_l + e^{-K\phi}, \quad (23a, b)$$

which are to be solved subject to matching with expansions (20d) in region I as $\tau \rightarrow 0$. The solution of equation (23a) which matches with the solution in region I to all algebraic orders of K as $\tau \rightarrow 0$ is,

$$\alpha_l \sim \mu\tau + \sum_{n=1}^{\infty} K^{-(n+1)} a_n + \alpha_e, \quad (24a)$$

where $\alpha_e = O(e^{-K\phi})$ as $K \rightarrow \infty$ with $\tau = O(1)$. We can now determine the solution of equation (23b) which matches with the solution in region I to all algebraic orders of K as $\tau \rightarrow 0$ as,

$$\begin{aligned} \phi \sim & (\lambda - 1)\tau - K^{-1} \left(\frac{1}{2} \mu \tau^2 + \log\{(\lambda - 1)/\lambda\} \right) + K^{-2} a_1 \tau \\ & + \sum_{n=1}^{\infty} K^{-(n+2)} ((a_{n+1} - a_n)\tau - b_n) + \phi_e, \end{aligned} \quad (24b)$$

where $\phi_e = O(e^{-K(\lambda-1)\tau})$ as $K \rightarrow \infty$ with $\tau = O(1)$, and the constants $b_n, n = 1, 2, \dots$, are determined by the form of the solutions $\beta_n, n = 2, 3, \dots$, in region I. It is also of interest to determine the behaviour of α_e , the exponentially small correction to the asymptotic form of α_l . By substituting from (24a) into equation (23a) we obtain the equation for α_e as,

$$\frac{d\alpha_e}{d\tau} = -\frac{\mu(\lambda - 1)}{\lambda} \tau e^{-K(\lambda-1)\tau} \exp\left(\frac{1}{2} \mu \tau^2\right) (1 + O(K^{-1})), \quad (25a)$$

which is to be solved subject to matching with expansion (20d) in region I as $\tau \rightarrow 0$. After an integration of (25a), we can estimate α_e using Laplace's method which, on matching to region I, leads to,

$$\alpha_e = K^{-1} \frac{\mu\tau}{\lambda} e^{-K(\lambda-1)\tau} \exp(\frac{1}{2}\mu\tau^2)(1 + O(K^{-1})), \quad \text{as } K \rightarrow \infty \text{ with } \tau = O(1). \quad (25b)$$

Finally, from (24) and (25) we have,

$$\alpha_l \sim \mu\tau + \sum_{n=1}^{\infty} K^{-(n+1)} a_n + K^{-1} \frac{\mu\tau}{\lambda} e^{-K(\lambda-1)\tau} \exp(\frac{1}{2}\mu\tau^2)(1 + O(K^{-1})), \quad (26a)$$

$$\beta_l \sim \frac{(\lambda-1)}{\lambda} e^{-K(\lambda-1)\tau} \exp\left[\frac{1}{2}\mu\tau^2 - K^{-1}a_1\tau - \sum_{n=1}^{\infty} K^{-(n+1)}((a_{n+1} - a_n)\tau - b_n)\right] \\ \times \{1 + O(e^{-K(\lambda-1)\tau})\}, \quad (26b)$$

as $K \rightarrow \infty$ with $\tau = O(1)$.

These expansions become non-uniform as $\tau \rightarrow K\tilde{\tau}_0$, where,

$$\tilde{\tau}_0 = \frac{2(\lambda-1)}{\mu} + \frac{2a_1K^{-2}}{\mu} + \frac{2(a_2 - a_1)K^{-3}}{\mu} + O(K^{-4}) \quad \text{as } K \rightarrow \infty. \quad (27)$$

In order to obtain uniform asymptotic expansions for α_l and β_l as $\tau \rightarrow K\tilde{\tau}_0$ we introduce region III, where appropriate scaled variables are, $\alpha_l = 2(\lambda-1)K + A$, $\beta_l = B$, $\tau = K\tilde{\tau}_0 + K^{-1}T$. In terms of these variables equations (18b, c) become,

$$\frac{dA}{dT} = -2(\lambda-1)B + K^{-1}(\mu - AB), \quad (28a)$$

$$\frac{dB}{dT} = (\lambda-1 - A - B)B + K^{-1}(\mu T + A + 2a_1)B + K^{-2}2(a_2 - a_1)B + O(K^{-3}B), \quad (28b)$$

which are to be solved subject to matching with the expansion (26) in region II as $T \rightarrow -\infty$. We now expand A and B as,

$$A = A_0 + K^{-1}A_1 + O(K^{-2}), \quad B = B_0 + K^{-1}B_1 + O(K^{-2}) \quad \text{as } K \rightarrow \infty, \quad (28c)$$

with $T = O(1)$. On substituting these expansions into equations (28a, b) we obtain, at leading order,

$$\frac{dA_0}{dT} = -2(\lambda-1)B_0, \quad \frac{dB_0}{dT} = (\lambda-1 - A_0 - B_0)B_0, \quad (29a, b)$$

which are to be solved subject to the matching conditions,

$$A_0 \sim -\frac{2(\lambda-1)e^{(\lambda-1)T}}{\lambda}, \quad B_0 \sim \frac{(\lambda-1)e^{(\lambda-1)T}}{\lambda}, \quad \text{as } T \rightarrow -\infty. \quad (29c)$$

This problem is readily solved in implicit form, and the details are given in [16], in which it is shown that $A_0(T)$, $B_0(T)$ remain bounded for all finite T . At $O(K^{-1})$ the problem can be

similarly solved subject to matching with (26), after which substitution into expansions (28c) and then approximating for $T \gg 1$ leads to,

$$A \sim \{-k_0 e^{2(\lambda-1)T} - (\lambda-1)\} + K^{-1} \left\{ \frac{k_0^2 e^{4(\lambda-1)T}}{2(\lambda-1)} + k_0(\lambda-1)T e^{2(\lambda-1)T} + \mu T + 2a_1 \right\} + \dots, \quad (30)$$

$$B \sim k_0 e^{2(\lambda-1)T} - K^{-1} \left\{ \frac{k_0^2 e^{4(\lambda-1)T}}{2(\lambda-1)} + k_0(\lambda-1)T e^{2(\lambda-1)T} \right\} + \dots, \quad \text{as } K \rightarrow \infty \text{ for } T \gg 1, \quad (31)$$

where the constant k_0 is given in [16]. Via (30, 31) we see that expansions (28c) become non-uniform as $T \rightarrow \log(K)/2(\lambda-1)$ and in order to obtain uniform asymptotic expansions for α_l and β_l in the neighbourhood of this point we introduce region IV. The appropriate scaled variables for region IV are,

$$\alpha_l = K\bar{A}, \quad \beta_l = K\bar{B}, \quad \tau = K\bar{\tau}_0 + \frac{1}{2(\lambda-1)} K^{-1} \log K + K^{-1}\bar{T}, \quad (32)$$

and equations (18b, c) become,

$$\frac{d\bar{A}}{d\bar{T}} = -\bar{A}\bar{B} + K^{-2}\mu, \quad (33)$$

$$K^{-1} \frac{d\bar{B}}{d\bar{T}} = -\bar{B}\{\bar{A} + \bar{B} - 2(\lambda-1)\} + K^{-1}\bar{B}\{\bar{A} - (\lambda-1)\} + K^{-2}(\mu\bar{T} + 2a_1)\bar{B} + \frac{K^{-2} \log K \mu \bar{B}}{2(\lambda-1)} + 2(a_2 - a_1)K^{-3} + O(K^{-4}\bar{B}), \quad (34)$$

which are to be solved subject to matching with expansions (28c) in region III as $\bar{T} \rightarrow -\infty$. We expand \bar{A} and \bar{B} as,

$$\bar{A} = \bar{A}_0 + K^{-1}(\log K)\bar{A}_1 + K^{-1}\bar{A}_2 + K^{-2}(\log K)^2\bar{A}_3 + K^{-2}(\log K)\bar{A}_4 + K^{-2}\bar{A}_5 + o(K^{-2}), \quad (35)$$

$$\bar{B} = \bar{B}_0 + K^{-1}(\log K)\bar{B}_1 + K^{-1}\bar{B}_2 + K^{-2}(\log K)^2\bar{B}_3 + K^{-2}(\log K)\bar{B}_4 + K^{-2}\bar{B}_5 + o(K^{-2}),$$

as $K \rightarrow \infty$, with $\bar{T} = O(1)$, and substitute into equations (33, 34) to obtain 12 equations for \bar{A}_i and \bar{B}_i , $i = 0, 1, \dots, 5$. These equations are easily solved, and the leading order solutions which match with expansions (28c) in region III as $\bar{T} \rightarrow -\infty$ are,

$$\bar{A}_0 = \frac{4(\lambda-1)^2}{2(\lambda-1) + k_0 e^{2(\lambda-1)\bar{T}}} = 2(\lambda-1) - \bar{B}_0. \quad (36)$$

For brevity the solutions at higher order are not presented (see [16]). By substituting these and higher order solutions into expansions (35) and approximating for $\bar{T} \gg 1$, we find that,

$$\begin{aligned}
 \bar{A} \sim & \frac{4(\lambda-1)^3}{k_0} e^{-2(\lambda-1)\bar{T}} + K^{-1} \{ \log K + 2(\lambda-1)\bar{T} \} \frac{2(\lambda-1)^2}{k_0} e^{-2(\lambda-1)\bar{T}} \\
 & + K^{-2} \left\{ \frac{(\lambda-1)^2 e^{-2(\lambda-1)\bar{T}}}{k_0} (\log K)^2 + \frac{2(\lambda-1)((\lambda-1)^2 - \mu)\bar{T} e^{-2(\lambda-1)\bar{T}}}{k_0} \log K \right. \\
 & \left. + \frac{\mu}{2(\lambda-1)} \right\} + \dots, \tag{37a}
 \end{aligned}$$

$$\begin{aligned}
 \bar{B} \sim & 2(\lambda-1) - \frac{4(\lambda-1)^2 e^{-2(\lambda-1)\bar{T}}}{k_0} - K^{-1} \left\{ \frac{2(\lambda-1)^2 e^{-2(\lambda-1)\bar{T}}}{k_0} \log K \right. \\
 & \left. + \frac{4(\lambda-1)^3 \bar{T} e^{-2(\lambda-1)\bar{T}}}{k_0} + \lambda - 1 \right\} - K^{-2} \left\{ \frac{(\lambda-1)^2}{k_0} e^{-2(\lambda-1)\bar{T}} (\log K)^2 \right. \\
 & \left. + \left[\frac{2(\lambda-1)((\lambda-1)^2 - \mu)\bar{T} e^{-2(\lambda-1)\bar{T}}}{k_0} - \frac{\mu}{2(\lambda-1)} \right] \log K - \mu \bar{T} - 2a_1 + \frac{\mu}{2(\lambda-1)} \right\} \\
 & + \dots, \text{ as } K \rightarrow \infty \text{ with } \bar{T} \gg 1. \tag{37b}
 \end{aligned}$$

These expansions become non-uniform when $\bar{T} = O(K^2)$. Therefore, to complete the asymptotic solution we introduce region V, where the appropriate scaled variables are $\alpha_l = K^{-1}\tilde{\alpha}$, $\beta_l = K\tilde{\beta}$, $\tau = K\tilde{\tau}$. After writing equations (18b, c) in terms of these variables we expand $\tilde{\alpha}$ and $\tilde{\beta}$ as,

$$\begin{aligned}
 \tilde{\alpha} &= \tilde{\alpha}_0 + K^{-1}\tilde{\alpha}_1 + K^{-2}\tilde{\alpha}_2 + O(K^{-3}), \quad \tilde{\beta} = \tilde{\beta}_0 + K^{-1}\tilde{\beta}_1 + K^{-2}\tilde{\beta}_2 + O(K^{-3}), \\
 \text{as } K \rightarrow \infty, \text{ for } \tilde{\tau} > \tilde{\tau}_0 + \frac{1}{2(\lambda-1)} K^{-2} \log K. \tag{38}
 \end{aligned}$$

On substituting these expansions into the scaled equations we obtain the solution at each order immediately and hence find that,

$$\tilde{\alpha} = \frac{1}{\tilde{\tau}} + \frac{K^{-1}(\lambda-1)}{\mu\tilde{\tau}^2} + \frac{K^{-2}(\lambda-1)^2}{\mu^2\tilde{\tau}^3} + O(K^{-3}), \tag{39a}$$

$$\tilde{\beta} = \mu\tilde{\tau} - K^{-1}(\lambda-1) - \frac{K^{-2}}{\tilde{\tau}} + O(K^{-3}), \text{ as } K \rightarrow \infty, \text{ for } \tilde{\tau} > \tilde{\tau}_0 + \frac{1}{2(\lambda-1)} K^{-2} \log K.$$

The expansions (39a) match with expansions (35) in region IV as $\tilde{\tau} \rightarrow \tilde{\tau}_0 + 1/(2(\lambda-1))K^{-2} \log K$ and remain uniform as $\tilde{\tau} \rightarrow \infty$. In terms of the original variables, α_l , β_l and τ , expansions (39a) show that

$$\begin{aligned}
 \alpha_l \sim & \frac{1}{\tau} + \frac{\lambda-1}{\mu\tau^2} + \frac{(\lambda-1)^2}{\mu^2\tau^3} + \dots, \quad \beta_l \sim \mu\tau - (\lambda-1) - \frac{1}{\tau} + \dots, \\
 \text{for } \tau > & K\tilde{\tau}_0 + \frac{K^{-1} \log K}{2(\lambda-1)} \gg 1, \tag{39b}
 \end{aligned}$$

and hence the solution finally takes on the asymptotic form (13b) as $\tau \rightarrow \infty$. This completes

the asymptotic solution of the initial value problem (18) for $\lambda > 1$ and $K \gg 1$. We can summarize the behaviour of α_I , β_I and γ_I at leading order as:

$$\begin{aligned} \text{Region I: } \tau = O(K^{-1}), \quad \alpha_I \sim K^{-1} \mu \hat{\tau}, \quad \beta_I \sim \frac{(\lambda - 1)}{\lambda e^{(\lambda-1)\hat{\tau}} - 1}, \\ \gamma_I \sim \frac{\lambda(\lambda - 1) e^{(\lambda-1)\hat{\tau}}}{\lambda e^{(\lambda-1)\hat{\tau}} - 1}, \quad \text{with } \hat{\tau} = K\tau = O(1), \text{ as } K \rightarrow \infty. \end{aligned} \quad (40a)$$

$$\begin{aligned} \text{Region II: } O(K^{-1}) < \tau < K\tilde{\tau}_0 - O(K^{-1}), \quad \alpha_I \sim \mu\tau, \\ \beta_I \sim \frac{(\lambda - 1)}{\lambda} e^{-(\lambda-1)K\tau + \frac{1}{2}\mu\tau^2}, \quad \gamma_I \sim (\lambda - 1), \quad \text{as } K \rightarrow \infty, \end{aligned} \quad (40b)$$

$$\begin{aligned} \text{Region III: } |\tau - K\tilde{\tau}_0| = O(K^{-1}), \quad \alpha_I = 2(\lambda - 1)K + O(1), \quad \beta_I = O(1), \\ \gamma_I = O(1), \quad \text{as } K \rightarrow \infty. \end{aligned} \quad (40c)$$

$$\begin{aligned} \text{Region IV: } \left| \tau - K\tilde{\tau}_0 - \frac{1}{2(\lambda - 1)} K^{-1} \log K \right| = O(K^{-1}), \\ \alpha_I \sim \frac{4(\lambda - 1)^2 K}{2(\lambda - 1) + k_0 e^{2(\lambda-1)\bar{T}}}, \quad \beta_I \sim \frac{k_0 2(\lambda - 1)K e^{2(\lambda-1)\bar{T}}}{2(\lambda - 1) + k_0 e^{2(\lambda-1)\bar{T}}}, \\ \gamma_I = o(K^{-p}) \forall p > 0, \quad \text{with } \bar{T} = K \left(\tau - K\tilde{\tau}_0 - \frac{1}{2(\lambda - 1)} K^{-1} \log K \right) = O(1), \\ \text{as } K \rightarrow \infty, \end{aligned} \quad (40d)$$

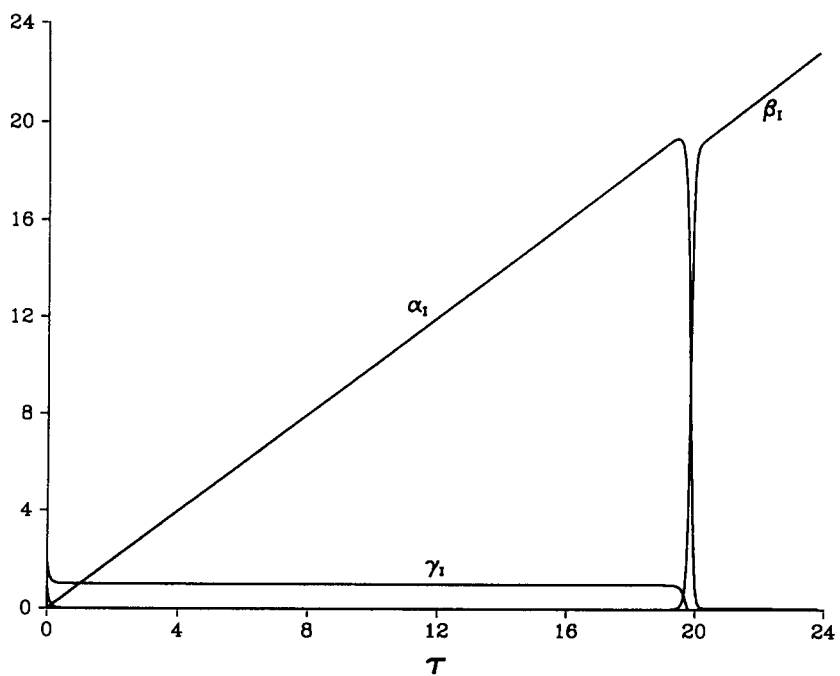
$$\begin{aligned} \text{Region V: } \tau > K\tilde{\tau}_0 + \frac{1}{2(\lambda - 1)} K^{-1} \log K + O(K^{-1}), \quad \alpha_I \sim 1/\tau, \\ \beta_I \sim \mu\tau - (\lambda - 1), \quad \gamma_I = o(K^{-p}) \forall p > 0, \quad \text{as } K \rightarrow \infty. \end{aligned} \quad (40e)$$

Region I is a thin initial transient region where β_I becomes exponentially small and γ_I is reduced to $\lambda - 1$. In region II, β_I attains its minimum value, β_{\min} , when $\tau = \frac{1}{2}K\tilde{\tau}_0 \sim (\lambda - 1)K/\mu$ and then increases slowly. The solution (26b) shows that,

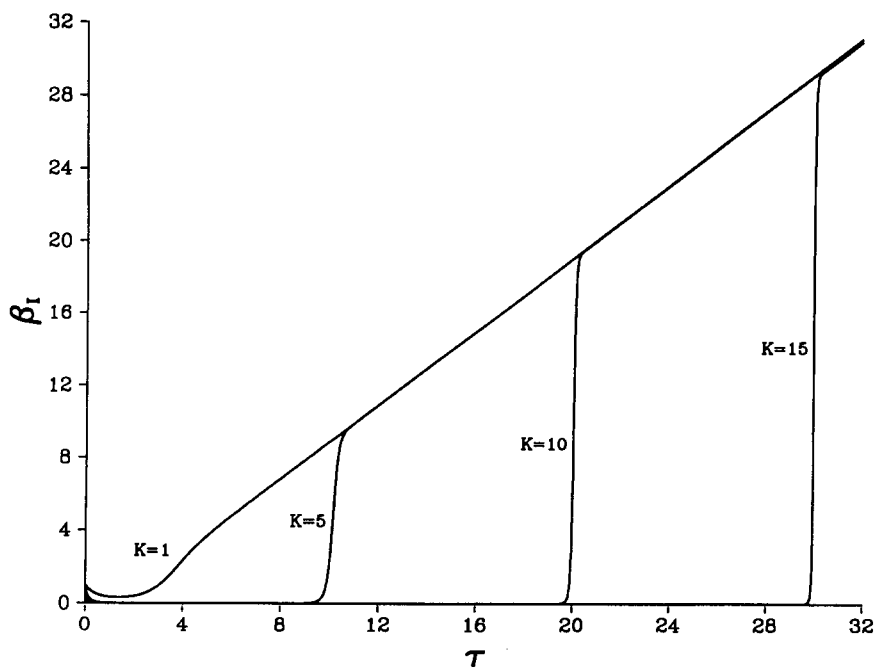
$$\beta_{\min} \sim \frac{(\lambda - 1)}{\lambda} e^{-(\lambda-1)^2 K^2 / 2\mu}, \quad \text{as } K \rightarrow \infty. \quad (40f)$$

Meanwhile, α_I increases linearly and γ_I remains close to $\lambda - 1$ until the solution changes dramatically as $\tau \rightarrow \tau_0 = K\tilde{\tau}_0$. In region III, which is a centred, transition region, β_I begins to increase much more rapidly, whilst the growth of α_I is halted and α_I and γ_I start to decrease. This process continues in region IV, where α_I decreases to $\mu/2(\lambda - 1)K$, β_I increases to $2(\lambda - 1)K$, and γ_I becomes exponentially small, so that the solution takes on the asymptotic form (13b) in region V.

The solution of the initial value problem (18) which we obtained numerically using a fourth order Runge–Kutta technique, is shown in Fig. 1(a) for $K = 10$, $\lambda = 2$, $\mu = 1$, and clearly displays the asymptotic structure described above. In this case the asymptotic theory predicts that transition occurs when $\tau \sim K\tilde{\tau}_0 + K^{-1} \log(K)/2(\lambda - 1) = 20.08 \dots$ in region IV, which is in good agreement with the behaviour of the numerical solution.



(a)



(b)

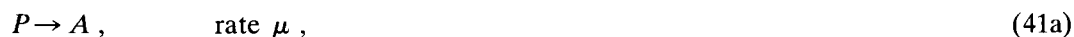
Fig. 1. The solution of the initial value problem (18) for $\lambda = 2$, $\mu = 1$ and: (a) $K = 10$, (b) $K = 1, 5, 10, 15$.

In Fig. 1(b), the behaviour of the concentration β_I is illustrated for $\lambda = 2$, $\mu = 1$, and a range of values of K . This shows that clock reaction behaviour occurs, even for moderate values of K , and becomes more sharply defined as K increases. However, the inner solution becomes non-uniform as $\tau \rightarrow \infty$, in particular when $\tau = O(\varepsilon^{-1})$ and matches with the appropriate outer solution given by (14c) or (16). Clearly, for the asymptotic structure of the inner solution outlined in (40) to be appropriate we require $1 \ll K \ll \varepsilon^{-1}$, when the outer solution is of the form (16). When $K = O(\varepsilon^{-1})$ it is possible to develop an asymptotic solution of the full initial value problem (7), valid for $0 < \varepsilon \ll 1$, which we expect may also display clock behaviour. For brevity, the details in this case are not pursued here but discussed at the end of the paper.

By considering the solution in terms of the physical variables, a , b , c and t we can now determine the behaviour of the chemical system (17) when $1 \ll K \ll \varepsilon^{-1}$ or, equivalently, $k_1^2 b_0 \gg k_0 k_2 \gg k_0 k_1$. In other words reaction step (17c) typically proceeds much faster than step (17b), which typically proceeds much faster than step (17a) with this difference in reaction rates much larger between steps (17a) and (17b) than between steps (17b) and (17c). After an initial transient period, with duration of $O(1/k_2 b_0)$, the concentration of the clock chemical, B , becomes exponentially small, of $O(b_0 \exp(-(c_0 - b_0)k_2 t))$, whilst the concentration of the inhibitor, C , is reduced to $c_0 - b_0$ via reaction step (17c). There then follows a long induction period during which the concentration of the reactant A is given by $a \approx k_0 p_0 t$, the concentration of C remains at $c_0 - b_0$ and the concentration of B reaches a minimum of $b_0(c_0 - b_0) \exp(-(c_0 - b_0)^2 k_2^2 / 2k_1 k_0 p_0) / c_0$, from expansion (40f). The induction period ends as $t \rightarrow t_0$, where $t_0 \approx 2(c_0 - b_0)k_2 / k_1 k_0 p_0$, and the concentration of B rapidly grows to $2(c_0 - b_0)k_1 / k_2$, whilst the concentration of A falls to $k_0 p_0 / 2(c_0 - b_0)k_2$ and C is effectively completely consumed. We note, that the induction period ends when $k_1 \langle a \rangle = k_2 \langle c \rangle$. For $t > t_0$ the concentration of the clock chemical, B , increases due to the decay of the reactant, P , via the autocatalytic step (17b) and $a \rightarrow 0$, $b \rightarrow p_0 + b_0 - c_0$, $c \rightarrow 0$ as $t \rightarrow \infty$. Finally, we note that the clock reaction behaviour of the system (17) is due to an inhibition mechanism alone and no induction mechanism exists (see [1]). This is also true of the reaction scheme (1) in the remaining three cases, which we analyse below.

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

In this case, the reaction scheme (1) is, in the inner limit,



where $K = k_2 / k_1$, $\mu = k_0 p_0 / k_1 b_0^3$. We require a solution of the initial value problem,

$$\gamma_I = \frac{1}{2}(\alpha_I + \beta_I - \mu\tau + 2\lambda - 1), \quad (42a)$$

$$\frac{d\alpha_I}{d\tau} = \mu - \alpha_I \beta_I^2, \quad \frac{d\beta_I}{d\tau} = \alpha_I \beta_I^2 - K \beta_I^2 (\alpha_I + \beta_I - \mu\tau + 2\lambda - 1), \quad (42b, c)$$

$$\alpha_I(0) = 0, \quad \beta_I(0) = 1, \quad \gamma_I(0) = \lambda, \quad (42d)$$

and, as for the case $n = m = 1$, for clock reaction behaviour we require $\lambda > \frac{1}{2}$ and $K \gg 1$.

On integrating equation (42c) after making use of (42a) and the initial conditions (42d), we obtain, $\beta_I = (1 - (\langle \alpha_I \rangle - 2K \langle \gamma_I \rangle) \tau)^{-1}$. With $K \gg 1$ and $\lambda > \frac{1}{2}$ we expect that the solution lies close to (13a) after a short initial transient period, so that,

$$\beta_I \sim \frac{1}{1 - \frac{1}{2} \mu \tau^2 + (2\lambda - 1)K\tau}, \quad \text{as } K \rightarrow \infty, \text{ with } \tau = O(1). \quad (43)$$

The approximate form (43) gives an indication of the structure of β_I as $K \rightarrow \infty$. There is an initial transient region with $\tau = O(K^{-1})$ in which $\beta_I = O(1)$, followed by an induction period with $\beta_I = O(K^{-1})$ and $\tau = O(1)$. This induction period ends as $\tau \rightarrow K\tilde{\tau}_0$, where $\tilde{\tau}_0 \sim 2(2\lambda - 1)/\mu$ as $K \rightarrow \infty$. For $\tau \sim K\tilde{\tau}_0$, β_I increases rapidly.

We can construct the detailed asymptotic solution of the initial value problem (42) for $\lambda > \frac{1}{2}$ and $K \gg 1$, which has a very similar structure to the solution of the initial value problem (18) that we described in detail in the previous section. The leading order solution again has five asymptotic regions.

Region I: $\hat{\tau} = K\tau = O(1)$, $\alpha_I = K^{-1}\hat{\alpha} + o(K^{-1})$, $\beta_I = \beta + o(1)$, as $K \rightarrow \infty$, where

$$\hat{\alpha} = \mu\hat{\tau}, \quad \log\left(\frac{\beta + 2\lambda - 1}{2\lambda\beta}\right) - \frac{2\lambda - 1}{\beta} = -(2\lambda - 1)^2\hat{\tau} - (2\lambda - 1). \quad (44a, b)$$

We note that, from the solution (44b),

$$\beta \sim \frac{1}{(2\lambda - 1)\hat{\tau}}, \quad \text{as } \hat{\tau} \rightarrow \infty. \quad (45)$$

Region II: $\bar{\tau} = K^{-1}\tau = O(1)$, $\alpha_I = K\bar{\alpha} + o(K)$, $\beta_I = K^{-2}\bar{\beta} + o(K^{-2})$, as $K \rightarrow \infty$, where

$$\bar{\alpha} = \mu\bar{\tau}, \quad \bar{\beta} = \frac{1}{(2\lambda - 1)\bar{\tau} - \frac{1}{2}\mu\bar{\tau}^2}. \quad (46a, b)$$

Region III: $\tau = 2(2\lambda - 1)K/\mu + K^{-1}T$, $\alpha_I = 2(2\lambda - 1)K + A + o(1)$,

$$\beta_I = B + o(1), \quad \text{as } K \rightarrow \infty,$$

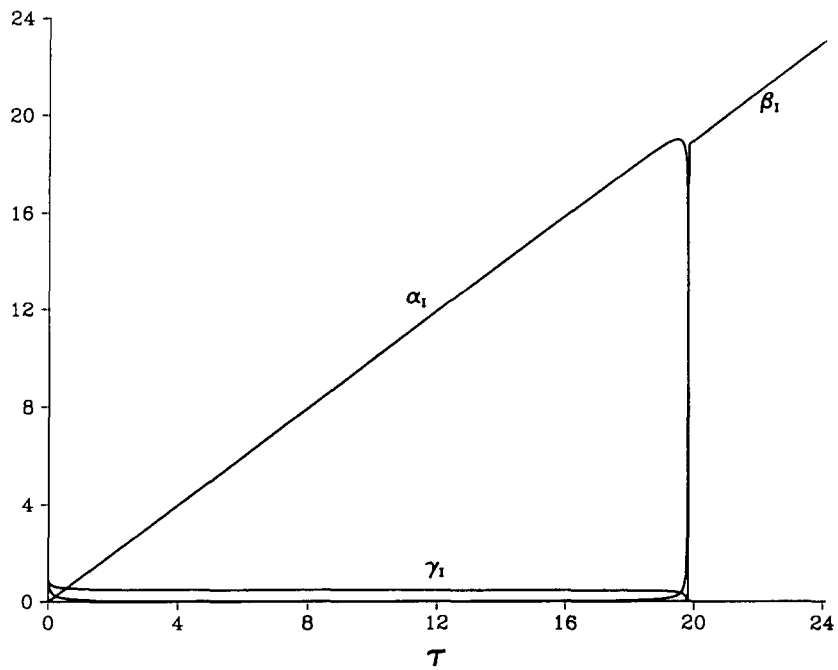
Here $A(T)$ and $B(T)$ are readily obtained in implicit form and given in [16]. Both develop a singularity as $T \rightarrow T_0$ (where the constant T_0 is determined by matching with the solution in region II at higher order) when,

$$A \sim \frac{-1}{2(2\lambda - 1)(T_0 - T)}, \quad B \sim \frac{1}{2(2\lambda - 1)(T_0 - T)}, \quad \text{as } T \rightarrow T_0. \quad (47)$$

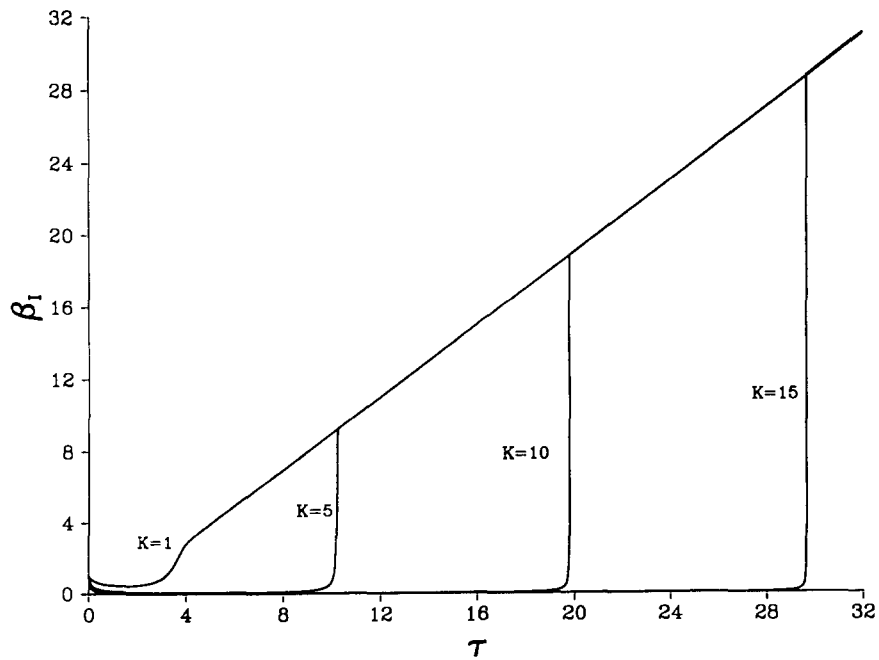
Region IV: $\tau = 2(2\lambda - 1)K/\mu + K^{-1}T_0 + K^{-2}\bar{T}$, $\alpha_I = K\bar{A} + o(K)$,

$$\beta_I = K\bar{B} + o(K), \quad \text{as } K \rightarrow \infty,$$

Both $\bar{A}(\bar{T})$ and $\bar{B}(\bar{T})$ are again obtained implicitly in [16]. In particular \bar{A} and \bar{B} remain bounded for all finite \bar{T} , with



(a)



(b)

Fig. 2. The solution of the initial value problem (42) for $\lambda = 1$, $\mu = 1$ and: (a) $K = 10$, (b) $K = 1, 5, 10, 15$.

$$\begin{aligned}\bar{A} &\sim 2(2\lambda - 1) e^{-4(2\lambda - 1)^2(\bar{T} - \bar{T}_0) - 1}, \\ \bar{B} &\sim 2(2\lambda - 1)(1 - e^{-4(2\lambda - 1)^2(\bar{T} - \bar{T}_0) - 1}) \quad \text{as } \bar{T} \rightarrow \infty.\end{aligned}\quad (48)$$

where \bar{T}_0 is a constant determined by matching with higher order terms in region III. The generation of further terms in this region (up to $O(K^{-3})$) shows that a nonuniformity occurs when $\bar{T} = O(K^3)$, $\bar{A} = O(K^{-3})$ and $\bar{B} = O(1)$.

$$\begin{aligned}\text{Region V: } \tilde{\tau} &= K^{-1}\tau = O(1), & \alpha_I &= K^{-2}\tilde{\alpha} + o(K^{-2}), & \beta_I &= K\tilde{\beta} + o(K), \quad \text{as } K \rightarrow \infty, \\ & \text{where } \tilde{\alpha} &= 1/\mu\tilde{\tau}^2, & \tilde{\beta} &= \mu\tilde{\tau}, & & (49a, b)\end{aligned}$$

and the solution has the asymptotic form (13b).

This completes the leading order asymptotic solution of the initial value problem (42) for $\lambda > \frac{1}{2}$ and $K \gg 1$. The qualitative form of the solution is similar to that of the solution for $n = m = 1$ which we outlined in §3. Region I is an initial transient region where β_I becomes of $O(K^{-1})$ and γ_I is reduced to $\lambda - \frac{1}{2}$. In region II β_I attains its minimum value, β_{\min} , when $\tau = \frac{1}{2}K\tilde{\tau}_0 \sim (2\lambda - 1)K/\mu$, and,

$$\beta_{\min} \sim \frac{2\mu K^{-2}}{(2\lambda - 1)^2}, \quad \text{as } K \rightarrow \infty. \quad (50)$$

Meanwhile, α_I increases linearly and γ_I remains close to $\lambda - \frac{1}{2}$ until the solution changes dramatically as $\tau \rightarrow \tau_0 = K\tilde{\tau}_0$. In the centred, transition region III, β_I begins to increase more rapidly, whilst the growth of α_I is halted and α_I and γ_I start to decrease. This process continues in the main transition region IV, where α_I decreases to $\mu/4(2\lambda - 1)^2K^2$, β_I increases to $(2(2\lambda - 1)K)$ and γ_I becomes exponentially small. Finally, the solution takes on the asymptotic form (13b) in region V. This asymptotic solution clearly represents clock reaction behaviour. The solution of the initial value problem (42) is shown in Fig. 2(a) for $K = 10$, $\lambda = 1$, $\mu = 1$. This was obtained numerically and clearly has the asymptotic structure outlined above. This solution suffers some numerical inaccuracy since $d\alpha_I/dt_I$ and $d\beta_I/dt_I$ are of $O(K^3)$ in region IV, but displays the expected qualitative behaviour. In Fig. 2(b) the concentration β_I is illustrated for $\mu = 1$, $\lambda = 1$ and a range of values of K . Clock reaction behaviour again occurs, even for moderate values of K , and becomes more sharply defined as K increases. A close examination of Figs 1(b) and 2(b) also shows that during the rapid transition in the neighbourhood of $\tau = K\tilde{\tau}_0$, β_I changes more sharply for $n = m = 2$ than for $n = m = 1$. This is as predicted by our asymptotic analysis since $d\alpha_I/d\tau$ and $d\beta_I/d\tau$ are of $O(K^3)$ in the transition region for $n = m = 2$ but only of $O(K^2)$ for $n = m = 1$. Finally, we note that we require $1 \ll K \ll \varepsilon^{-1}$ for the above asymptotic structure to be appropriate, as explained for the case $n = m = 1$ in §3. Similar considerations apply to the case $K = O(\varepsilon^{-1})$ as described in §3.

5. Quadratic autocatalysis with quadratic inhibition $n = 1$, $m = 2$

When $n = 1$ and $m = 2$ the reaction scheme (1) is, in the inner limit,





where $K = k_2 b_0 / k_1$ and $\mu = k_0 p_0 / k_1 b_0^2$. We require a solution of the initial value problem,

$$\gamma_I = \frac{1}{2}(\alpha_I + \beta_I - \mu\tau + 2\lambda - 1), \quad (52a)$$

$$\frac{d\alpha_I}{d\tau} = \mu - \alpha_I \beta_I, \quad \frac{d\beta_I}{d\tau} = \alpha_I \beta_I - K\beta_I^2(\alpha_I + \beta_I - \mu\tau + 2\lambda - 1), \quad (52b, c)$$

subject to the initial conditions,

$$\alpha_I(0) = 0, \quad \beta_I(0) = 1, \quad \gamma_I(0) = \lambda. \quad (52d)$$

As in the previous case, we examine the initial value problem (52) when $\lambda > \frac{1}{2}$ and $K \gg 1$. On integrating equation (52c), making use of (52a) and the initial conditions (52d), we obtain,

$$\beta_I = \frac{\exp(\langle \alpha_I \rangle \tau)}{1 + 2K \int_0^\tau \gamma_I(s) \exp(\langle \alpha_I \rangle s) ds}. \quad (53a)$$

In addition, with $\lambda > \frac{1}{2}$ and $K \gg 1$, we expect that the solution lies close to (13a) after a short initial transient period, and hence, via (53a),

$$\beta_I \sim \frac{e^{1/2\mu\tau^2}}{1 + K(2\lambda - 1) \int_0^\tau e^{1/2\mu s^2} ds}, \quad \text{as } K \rightarrow \infty \text{ with } \tau = O(1). \quad (53b)$$

The form of (53b) suggests that there is an initial transient region when $\tau = O(K^{-1})$ and $\beta_I = O(1)$, after which $\beta_I = O(K^{-1})$ when $\tau = O(1)$. However, for $\tau \gg 1$ we have, via (53b),

$$\beta_I \sim \frac{K^{-1}\mu\tau}{2\lambda - 1}, \quad \text{as } K \rightarrow \infty \text{ for } \tau \gg 1. \quad (53c)$$

This suggests that the solution does not remain close to the solution (13a) as $\tau \rightarrow \infty$, but it is not clear whether there is a rapid transition to a solution of the asymptotic form (13b).

We can now construct the detailed asymptotic solution of the initial value problem (52) for $\lambda > \frac{1}{2}$, $K \gg 1$ which shows that, after a short initial transient period, β_I remains of $O(K^{-1})$ until τ approaches $\tau_0 = K^{1/3} \tilde{\tau}_0$, where $\tilde{\tau}_0 = O(1)$ as $K \rightarrow \infty$, when the solution undergoes a rapid transition and takes on the asymptotic form (13b). The leading order solution has seven asymptotic regions, which are outlined below.

Region I: $\hat{\tau} = K\tau = O(1)$, $\alpha_I = K^{-1}\hat{\alpha} + o(K^{-1})$, $\beta_I = \beta + o(1)$ as $K \rightarrow \infty$, where

$$\hat{\alpha} = \mu\hat{\tau}, \quad \log\left(\frac{\beta + 2\lambda - 1}{\beta}\right) - \frac{(2\lambda - 1)}{\beta} = -(2\lambda - 1)^2\hat{\tau} - (2\lambda - 1), \quad (54a, b)$$

with $\beta \sim 1/(2\lambda - 1)\tilde{\tau}$ as $\tilde{\tau} \rightarrow \infty$.

Region II: $\tau = O(1)$, $\alpha_I = \alpha + o(1)$, $\beta_I = K^{-1}\check{\beta} + o(K^{-1})$, as $K \rightarrow \infty$, where

$$\alpha = \mu\tau, \quad \check{\beta} = \frac{e^{1/2\mu\tau^2}}{(2\lambda - 1) \int_0^\tau e^{1/2\mu s^2} ds}. \quad (55a, b)$$

We also note that,

$$\check{\beta} \sim \frac{\mu\tau}{(2\lambda - 1)}, \quad \text{as } \tau \rightarrow \infty, \quad (55c)$$

which is the asymptotic behaviour predicted by (53b) in (53c). In order to determine the structure of the next asymptotic region it is necessary to obtain the next term in the expansion for β . We find that, up to $O(K^{-1})$,

$$\check{\beta} \sim \frac{\mu\tau}{(2\lambda - 1)} - \frac{K^{-1}\mu^3\tau^4}{3(2\lambda - 1)^2}, \quad \text{as } K \rightarrow \infty \text{ with } \tau \gg 1, \quad (55d)$$

and therefore a further non-uniformity arises when $\tau = O(K^{1/3})$.

Region III: $\bar{\tau} = K^{-1/3}\tau = O(1)$, $\alpha_I = K^{1/3}\bar{\alpha}_0 + \bar{\alpha}_1 + o(1)$,
 $\beta_I = K^{-2/3}\bar{\beta} + o(K^{-2/3})$, as $K \rightarrow \infty$,

where

$$\bar{\alpha}_1 = ((2\lambda - 1)^2 - \frac{2}{3}\mu^2\bar{\tau}^3)^{1/2} - (2\lambda - 1), \quad \bar{\beta} = -\frac{\mu\bar{\tau}}{((2\lambda - 1)^2 - \frac{2}{3}\mu^2\bar{\tau}^3)^{1/2}}. \quad (56a, b)$$

Region IV: $\tau = K^{1/3}\tilde{\tau}_0 + T$, $\alpha_I = K^{1/3}\mu\tilde{\tau}_0 + A_0 + K^{-1/6}A_1 + o(K^{-1/6})$,
 $\beta_I = K^{-1/2}B + o(K^{-1/2})$, as $K \rightarrow \infty$,

where

$$\tilde{\tau}_0 = (3(2\lambda - 1)^2/2\mu^2)^{1/3}, \quad (57)$$

and

$$A_1 = \{2\tilde{\tau}_0^2\mu^2(T_0 - T)\}^{1/2}, \quad B = \frac{\mu\tilde{\tau}_0}{\{2\tilde{\tau}_0^2\mu^2(T_0 - T)\}^{1/2}}, \quad A_0 = \mu T - (2\lambda - 1). \quad (58a, b, c)$$

Here the constant T_0 is determined by matching with the solution in region III at higher order.

Region V: $\tau = K^{1/3}\tilde{\tau}_0 + T_0 + K^{-1/3}\bar{T}$,

$$\alpha_I = K^{1/3}\mu\tilde{\tau}_0 + (\mu T_0 - (2\lambda - 1)) + K^{-1/3}\bar{A} + o(K^{-1/3}),$$

$$\beta_I = K^{-1/3}\bar{B}, \quad \text{as } K \rightarrow \infty.$$

Here $\bar{A}(\bar{T})$ and $\bar{B}(\bar{T})$ are obtained implicitly in [16], where it is shown that, \bar{A} and \bar{B} are bounded for all finite \bar{T} . As $\bar{T} \rightarrow \infty$ we have,

$$\bar{A} \sim \mu \bar{T} - (\mu \tilde{\tau}_0)^{1/2} \exp(\mu \tilde{\tau}_0 \bar{T} - (\mu \tilde{\tau}_0)^{1/2} \hat{c} + \frac{1}{2}), \quad (59)$$

$$\bar{B} \sim (\mu \tilde{\tau}_0)^{1/2} \exp(\mu \tilde{\tau}_0 \bar{T} - (\mu \tilde{\tau}_0)^{1/2} \hat{c} + \frac{1}{2}), \quad (60)$$

where the constant \hat{c} is determined by higher order matching to region IV.

$$\text{Region VI: } \tau = K^{1/3} \tilde{\tau}_0 + T_0 + \frac{2}{3\mu \tilde{\tau}_0} K^{-1/3} \log K + K^{-1/3} \hat{T}, \quad \alpha_I = K^{1/3} \hat{A} + o(K^{1/3}),$$

$$\beta_I = K^{1/3} \hat{B} + o(K^{1/3}), \quad \text{as } K \rightarrow \infty,$$

where

$$\hat{A} = \frac{(\mu \tilde{\tau}_0)^{3/2} e^{-\mu \tilde{\tau}_0 \hat{T}}}{\tilde{k}_0 + (\mu \tilde{\tau}_0)^{1/2} e^{-\mu \tilde{\tau}_0 \hat{T}}}, \quad \hat{B} = \frac{\tilde{k}_0 \mu \tilde{\tau}_0}{\tilde{k}_0 + (\mu \tilde{\tau}_0)^{1/2} e^{-\mu \tilde{\tau}_0 \hat{T}}}, \quad (61a, b)$$

with $\tilde{k}_0 = \exp(\frac{1}{2} - (\mu \tilde{\tau}_0)^{1/2} \hat{c})$.

$$\text{Region VII: } \tilde{\tau} = K^{-1/3} \tau = O(1), \quad \alpha_I = K^{-1/3} \tilde{\alpha} + o(K^{-1/3}),$$

$$\beta_I = K^{1/3} \tilde{\beta} + o(K^{1/3}), \quad \text{as } K \rightarrow \infty,$$

where $0 = \mu - \tilde{\alpha} \tilde{\beta}$, $0 = \tilde{\beta}^2 (\tilde{\beta} - \mu \tilde{\tau})$, and matching with the solution in region VI as $\tilde{\tau} \rightarrow \tilde{\tau}_0 + K^{-1/3} T_0 + 2/(3\mu \tilde{\tau}_0) K^{-2/3} \log K$ leads to $\tilde{\beta} \rightarrow \mu \tilde{\tau}_0$ as $\tilde{\tau} \rightarrow \tilde{\tau}_0$. The concentration $\tilde{\alpha}$ matches with higher order terms in region VI. Clearly, the appropriate solution of these equations is $\tilde{\alpha} = 1/\tilde{\tau}$, $\tilde{\beta} = \mu \tilde{\tau}$, and the solution has the asymptotic form (13b).

This completes the leading order asymptotic solution of the initial value problem (52) for $\lambda > \frac{1}{2}$ and $K \gg 1$. Although this solution develops over two more asymptotic regions than in the previous two cases, its qualitative form is very similar. Region I is again a thin initial transient region where β_I becomes of $O(K^{-1})$ and γ_I decreases to $\lambda - \frac{1}{2}$. In region II, β_I attains its minimum value, β_{\min} , when $\tau = \tau_{\min}$, where from (55a, b)

$$\tau_{\min} \sim \theta \mu^{-1/2}, \quad \beta_{\min} \sim \frac{K^{-1} \mu^{1/2} \theta}{2\lambda - 1}, \quad \text{as } K \rightarrow \infty, \quad (62a)$$

and θ is the unique positive solution of the equation,

$$e^{1/2\theta^2} - \theta \int_0^\theta e^{1/2s^2} ds = 0. \quad (62b)$$

We evaluated θ numerically as $\theta \approx 1.31$, and note that, in this case, $\tau_{\min} = O(1)$ is not the midpoint of the induction period $0 \leq \tau \leq K^{1/3} \tilde{\tau}_0$, as $K \rightarrow \infty$. The concentration α_I increases linearly and γ_I remains close to $\lambda - \frac{1}{2}$. In region III β_I is of $O(K^{-2/3})$ and continues to increase slowly, whilst α_I and γ_I behave as in region II, until $\tau \rightarrow K^{1/3} \tilde{\tau}_0$ when the form of the solution changes dramatically. Regions IV and V are thin, centred regions where β_I increases more rapidly to become of $O(K^{-1/3})$, α_I remains large of $O(K^{1/3})$ and γ_I becomes of

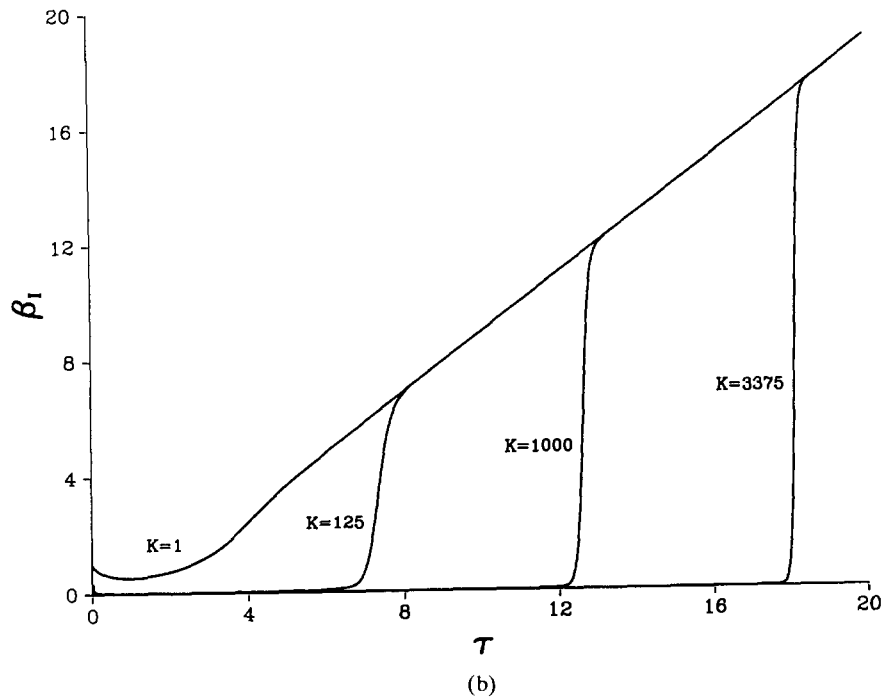
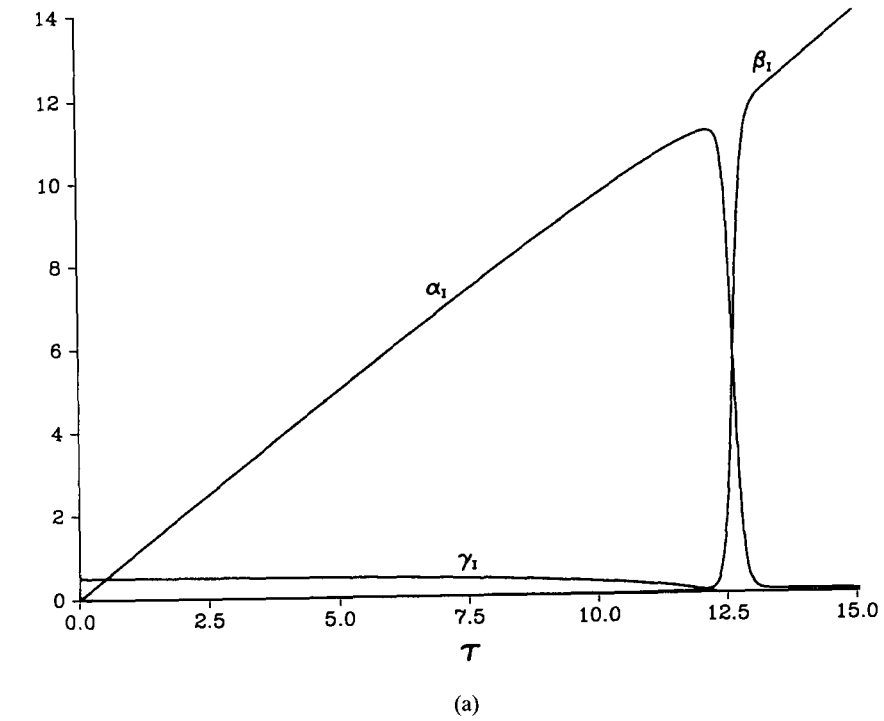


Fig. 3. The solution of the initial value problem (52) for $\lambda = 1$, $\mu = 1$ and: (a) $K = 1000$, (b) $K = 1, 125, 1000, 3375$.

$O(K^{-1/6})$. Region VI is the main transition region where α_I decreases to $K^{-1/3}\tilde{\tau}_0^{-1}$, β_I increases to $K^{1/3}\tilde{\tau}_0^{-1}$ and γ_I becomes exponentially small. Finally, the solution takes on the asymptotic form (13b) in region VII. This asymptotic solution clearly represents clock reaction behaviour. We note that in this case the rapid transition occurs when $\tau = \tau_0 \approx K^{1/3}(3(2\lambda - 1)^2/2\mu^2)^{1/3}$ whereas for $n = m = 1$ or $n = m = 2$, $\tau_0 = O(K)$ as $K \rightarrow \infty$, and hence the induction period is much shorter in this case. A numerical solution of the initial value problem (52) is illustrated in Fig. 3(a) for $K = 1000$, $\lambda = 1$, $\mu = 1$. In this case $K^{1/3}\tilde{\tau}_0 \approx 11.5$, via (57), and the numerical solution is in good agreement with the asymptotic solution described above. Figure 3(b) shows the concentration β_I for $\lambda = 1$, $\mu = 1$ and various values of K . Clock reaction behaviour now occurs for moderate values of $K^{1/3}$ (though much larger values of K) and becomes more sharply defined as K increases with $d\alpha_I/d\tau$ and $d\beta_I/d\tau$ of $O(K^{2/3})$ in the transition region. Finally, we note that we require $1 \ll K \ll \varepsilon^{-3}$ in this case for the asymptotic solution which we described above to be appropriate.

6. Cubic autocatalysis with linear inhibition, $n = 2$, $m = 1$

When $n = 2$ and $m = 1$ the reaction scheme (1) becomes, in the inner limit,



where $K = k_2/k_1 b_0$ and $\mu = k_0 p_0/k_1 b_0^3$. We require a solution of the initial value problem

$$\gamma_I = \alpha_I + \beta_I - \mu\tau + \lambda - 1, \quad (64a)$$

$$\frac{d\alpha_I}{d\tau} = \mu - \alpha_I \beta_I^2, \quad \frac{d\beta_I}{d\tau} = \alpha_I \beta_I^2 - K\beta_I(\alpha_I + \beta_I - \mu\tau + \lambda - 1), \quad (64b, c)$$

with initial conditions,

$$\alpha_I(0) = 0, \quad \beta_I(0) = 1, \quad \gamma_I(0) = \lambda. \quad (64d)$$

We can integrate equation (64c) once, making use of (64a) and the initial conditions (64d) to obtain,

$$\beta_I = \frac{\exp(-K\langle\gamma_I\rangle\tau)}{1 - \int_0^\tau \alpha_I(s) \exp(-K\langle\gamma_I\rangle s) ds}. \quad (65a)$$

For $\lambda > 1$ and $K \gg 1$ we again expect that the solution will lie close to (13a) after a short initial transient period. Under these conditions, (65a) leads to,

$$\beta_I \sim \frac{e^{-K(\lambda-1)\tau}}{1 - \mu \int_0^\tau s e^{-K(\lambda-1)s} ds}, \quad K \rightarrow \infty \text{ with } \tau = O(1). \quad (65b)$$

This suggests that the solution is asymptotic to (13a) as $\tau \rightarrow \infty$ for $\lambda > 1$ and K sufficiently large. The full asymptotic solution of the initial value problems (64) for $K \gg 1$, $\lambda > 1$, the details of which are omitted here, shows that $\alpha_I \sim \mu\tau$, $\beta_I \rightarrow 0$, $\gamma_I \sim (\lambda - 1)$ as $\tau \rightarrow \infty$. Thus, in this case, clock reaction behaviour is not possible for $K \gg 1$, $\lambda > 1$. However, numerical solutions of the initial value problem (64) for $\lambda > 1$ lead us to make the following conjecture.

C6.1: If $(\alpha_I, \beta_I, \gamma_I)$ is the solution of the initial value problem (64) with $\lambda > 1$ and $\mu > 0$, there exists a positive constant K^* such that,

$$\begin{aligned} \alpha_I &\rightarrow 0, & \beta_I &\sim \mu\tau - (\lambda - 1), & \gamma_I &\rightarrow 0, & \text{as } \tau \rightarrow \infty, & \text{for } K < K^*, \\ \alpha_I &\sim \mu\tau, & \beta_I &\rightarrow 0, & \gamma_I &\sim (\lambda - 1), & \text{as } \tau \rightarrow \infty, & \text{for } K > K^*. \end{aligned} \quad (66)$$

In addition, we find that for $0 < K^* - K \ll 1$, the solution displays clock reaction behaviour, with a rapid transition from a solution which lies close to (13a) to a solution with the asymptotic form (13b). This transition occurs in the neighbourhood of the point $\tau = \tau_0$, where $\tau_0 \rightarrow \infty$ as $K \rightarrow K^{*-}$. We note also that our numerical solutions of the initial value problem (18), (42) and (52) strongly suggest that C6.1 holds in each of these cases. The asymptotic solutions for $K \gg 1$ which we developed in the preceding sections then show that if C6.1 holds, $K^* = \infty$. The numerical solution of the initial value problem (64) with $\lambda = 2$, $\mu = 1$ and $K = 0.81$ is shown in Fig. 4(a). We note that the initial transient region, where the

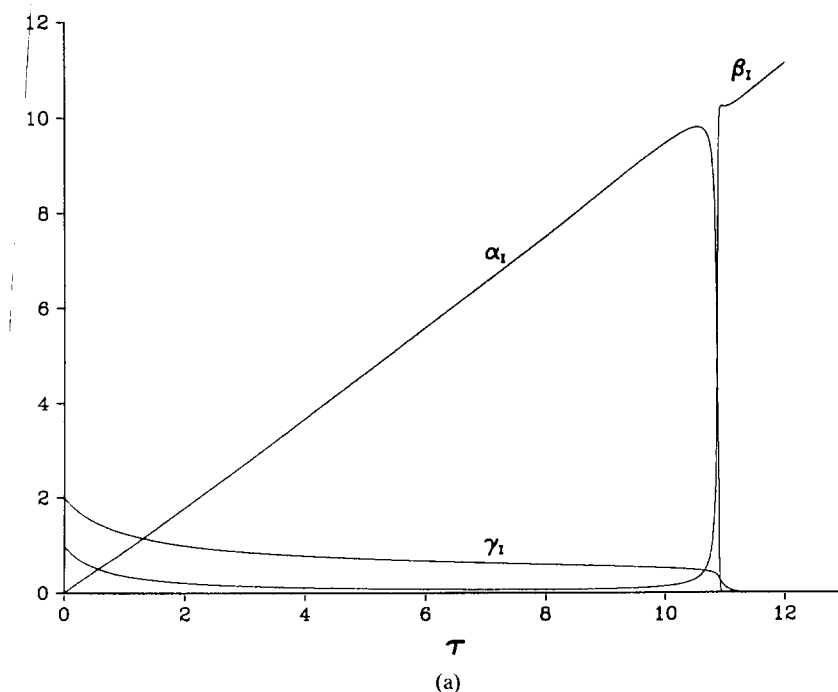
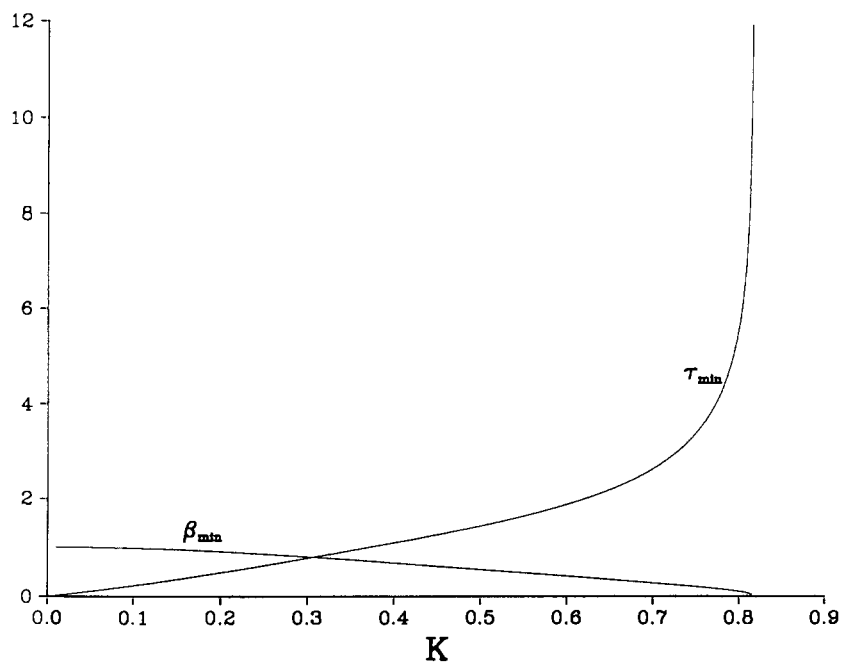
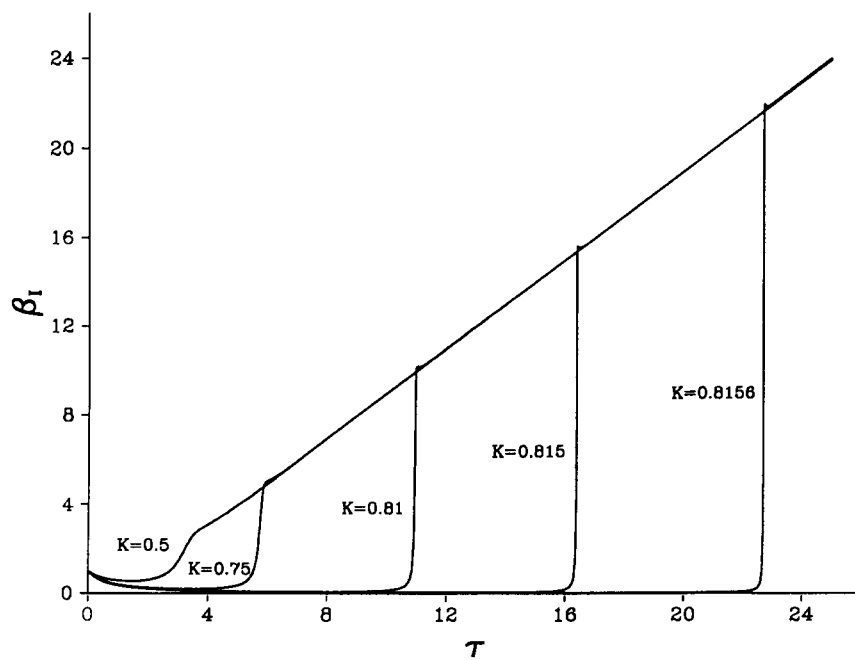


Fig. 4. (a) The solution of the initial value problem (64) for $\lambda = 2$, $\mu = 1$ and $K = 0.81$. (b) The functions $\beta_{\min}(K)$ and $\tau_{\min}(K)$ for $\lambda = 2$, $\mu = 1$. (c) The solution of the initial value problem (64) for $\lambda = 2$, $\mu = 1$ and $K = 0.5, 0.75, 0.81, 0.815, 0.8156$.



(b)



(c)

Fig. 4 (cont.).

concentration β_I becomes small, has duration of $O(1)$ in this case. The concentration β_I also has a local maximum just after the transition point at $\tau = 10.9 \dots$. This is caused by the reaction step (63c) which proceeds at an $O(1)$ rate and limits the growth of β_I until γ_I becomes small. For $\lambda = 2$ and $\mu = 1$ we find that $K^* = 0.8157 \dots$. Figure 4(b) shows graphs of the functions $\beta_{\min}(K)$ and $\tau_{\min}(K)$ for $\mu = 1, \lambda = 2$, where the minimum value of β_I is β_{\min} and $\beta_I(\tau_{\min}) = \beta_{\min}$. Clearly, $\tau_{\min} \rightarrow \infty$ and $\beta_{\min} \rightarrow 0$ as $K \rightarrow K^*$, and for $K > K^*$, β_I is monotone decreasing so that $\beta_{\min} \equiv 0$ and $\tau_{\min} \equiv \infty$. Figure 4(c) shows the behaviour of the concentration β_I for $\mu = 1, \lambda = 2$ and various values of $K < K^*$. This demonstrates that clock reaction behaviour develops and becomes more sharply defined as $K \rightarrow K^{*-}$. In order to determine $K^*(\lambda, \mu)$ for various values of $\lambda > 1$ and $\mu > 0$, we use a bisection search technique, with the search criteria, if $d\beta_I/d\tau > 0$, then $K < K^*$, and if $\beta_I < \beta_0$, then $K > K^*$, with $\beta_0 = 10^{-8}$. Graphs of $K^*(\lambda, \mu)$ for various fixed values of λ and μ are shown in Figs 5(a) and (b), respectively. These indicate that $K^* \rightarrow 0$ as $\mu \rightarrow 0$ with $K^* \rightarrow \infty$ as $\mu \rightarrow \infty$, whilst $K^* \rightarrow \infty$ as $\lambda \rightarrow 1^+$ and $K^* \rightarrow 0$ as $\lambda \rightarrow \infty$. All of this numerical evidence supports C6.1. In addition, we can investigate C6.1 analytically in the special case, $0 < \lambda - 1 \ll 1$ where our numerical results have shown that $K^* \gg 1$.

In order to develop an asymptotic solution of the initial value problem (64) when $0 < \lambda - 1 \ll 1$ and $K \gg 1$, we let $\lambda - 1 = f(K)$, where $f(K) = o(1)$ as $K \rightarrow \infty$. We now wish to examine this solution for $K/K^*(\lambda, \mu) = O(1)$ as $K \rightarrow \infty$. After a little trial and error we arrive at the substitution,

$$\lambda - 1 = f(K) = K^{-2}(k_1(\mu) \log K + k_2(\mu)) \quad (67)$$

where $k_1 \geq 0$. It will become apparent during the course of the following analysis that this is the appropriate choice for $f(K)$. Using (67) the initial value problem (64) becomes,

$$\gamma_I = \alpha_I + \beta_I - \mu\tau + k_1 K^{-2} \log K + k_2 K^{-2}, \quad (68a)$$

$$\frac{d\alpha_I}{d\tau} = \mu - \alpha_I \beta_I^2, \quad (68b)$$

$$\frac{d\beta_I}{d\tau} = \alpha_I \beta_I^2 - K\beta_I(\alpha_I + \beta_I - \mu\tau) - K^{-1} \log K k_1 \beta_I - K^{-1} k_2 \beta_I, \quad (68c)$$

subject to initial conditions,

$$\alpha_I(0) = 0, \quad \beta_I(0) = 1, \quad \gamma_I(0) = 1 + k_1 K^{-2} \log K + k_2 K^{-2}. \quad (68d)$$

We require a solution of this initial value problem for $K \gg 1$. Appropriate scaled variables for region *I* are, $\hat{\alpha} = K\alpha_I$, $\hat{\tau} = K\tau$, β_I , in terms of which equations (68b, c) and initial conditions (68d) become,

$$\frac{d\hat{\alpha}}{d\hat{\tau}} = \mu - K^{-1} \hat{\alpha} \beta_I^2, \quad (69a)$$

$$\frac{d\beta_I}{d\hat{\tau}} = -\beta_I^2 - K^{-1} \beta_I(\hat{\alpha} - \mu\hat{\tau}) - K^{-2}(\log K) k_1 \beta_I + K^{-2}(\hat{\alpha} \beta_I^2 - k_2 \beta_I), \quad (69b)$$

$$\hat{\alpha}(0) = 0, \quad \beta_I(0) = 1. \quad (69c)$$

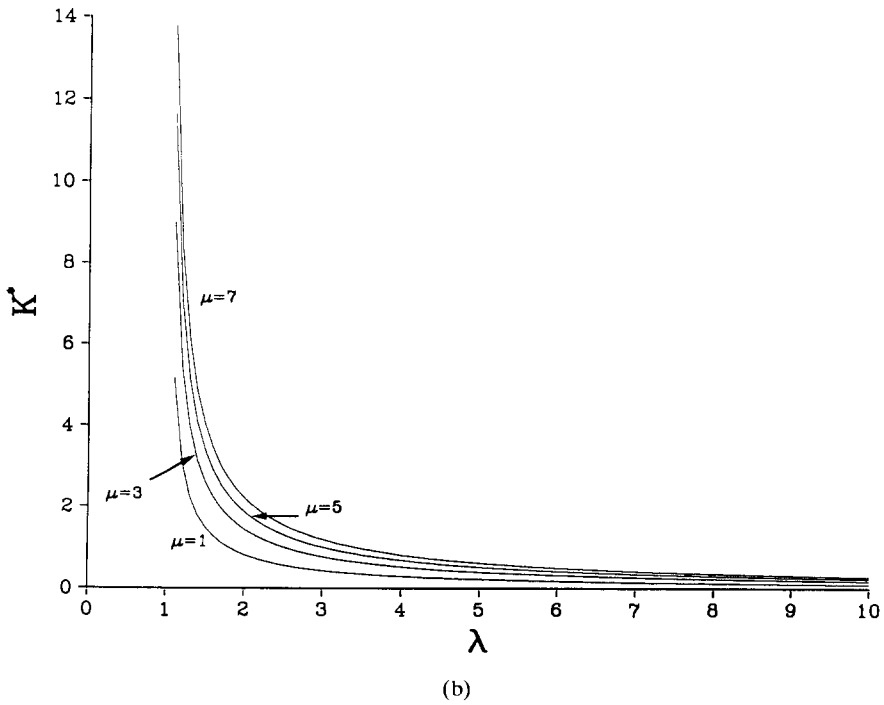
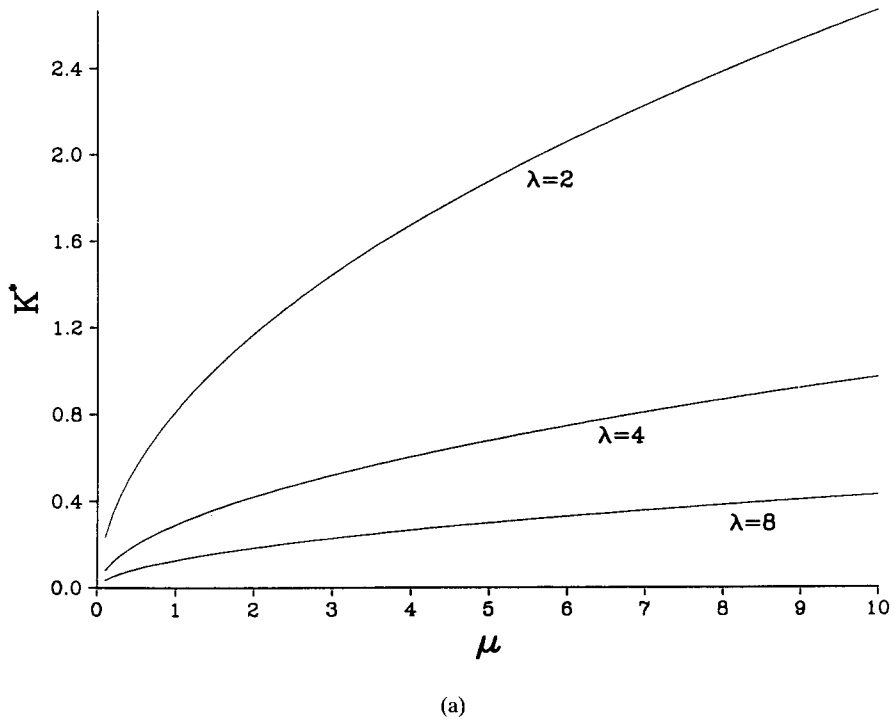


Fig. 5. The function $K^*(\lambda, \mu)$ for: (a) $\lambda = 2, 4, 8$, (b) $\mu = 1, 3, 5, 7$.

We expand $\hat{\alpha}$ and β_l as,

$$\hat{\alpha} = \hat{\alpha}_0 + K^{-1}\hat{\alpha}_1 + o(K^{-2}), \quad \beta_l = \beta_0 + K^{-1}\beta_1 + K^{-2} \log K \beta_2 + K^{-2}\beta_3 + o(K^{-2}), \quad (69d)$$

as $K \rightarrow \infty$, with $\hat{\tau} = O(1)$. After substituting these expansions into equations (69a, b) and equating coefficients we can readily solve the resulting equations for $\hat{\alpha}_0$, $\hat{\alpha}_1$, β_0 , β_1 , β_2 and β_3 to obtain,

$$\hat{\alpha} = \mu \hat{\tau} + K^{-1} \left\{ \frac{\mu \hat{\tau}}{1 + \hat{\tau}} - \mu \log(1 + \hat{\tau}) \right\} + o(K^{-1}),$$

$$\beta_l = \frac{1}{1 + \hat{\tau}} + K^{-2} \left[\frac{1}{2} \mu \log(1 + \hat{\tau}) + \left(\frac{1}{2} k_1 \log K + \frac{1}{2} k_2 + \frac{1}{4} \mu \right) \left\{ \frac{1}{(1 + \hat{\tau})^2} - 1 \right\} \right] + o(K^{-2}), \quad (70a, b)$$

as $K \rightarrow \infty$, with $\hat{\tau} = O(1)$. These expansions become non-uniform as $\hat{\tau} \rightarrow \infty$, in particular when $\hat{\tau} = O(K^2(\log K)^{-1})$, $\hat{\alpha} = O(K^2(\log K)^{-1})$ and $\beta_l = O(K^{-2} \log K)$. In order to develop uniform asymptotic expansions for α_l and β_l as $\hat{\tau} \rightarrow \infty$ we introduce region II where appropriate scaled variables are,

$$\bar{\alpha} = (K^{-1} \log K) \alpha_l, \quad \bar{\beta} = K^2 (\log K)^{-1} \beta_l, \quad \bar{\tau} = (K^{-1} \log K) \tau, \quad (71a)$$

in terms of which equations (68b, c) become,

$$\frac{d\bar{\alpha}}{d\bar{\tau}} = \mu - K^{-3} (\log K) \bar{\alpha} \bar{\beta}^2, \quad (71b)$$

$$\frac{d\bar{\beta}}{d\bar{\tau}} = -\bar{\beta}^2 - k_1 \bar{\beta} + (\log K)^{-1} (\bar{\alpha} \bar{\beta}^2 - k_2 \bar{\beta}) - K^3 (\log K)^{-2} \bar{\beta} (\bar{\alpha} - \mu \tau), \quad (71c)$$

which are to be solved subject to matching with the solution (70) in region I as $\bar{\tau} \rightarrow 0$. We expand $\bar{\alpha}$ and $\bar{\beta}$ as,

$$\bar{\alpha} = \bar{\alpha}_0 + K^{-3} (\log K)^2 \bar{\alpha}_1 + K^{-3} (\log K) \bar{\alpha}_2 + O(K^{-3}), \quad (72)$$

$$\bar{\beta} = \bar{\beta}_0 + (\log K)^{-1} \bar{\beta}_1 + O(K^{-1}), \quad \text{as } K \rightarrow \infty \text{ with } \bar{\tau} = O(1).$$

Matching with the solution (71) in region I as $\bar{\tau} \rightarrow 0$ leads to,

$$\bar{\alpha}_0 \sim \mu \bar{\tau}, \quad \bar{\alpha}_1 \sim -2\mu, \quad \bar{\alpha}_2 \sim \mu \log(\log K) + \mu - \mu \log \bar{\tau},$$

$$\bar{\beta}_0 \sim \frac{1}{\bar{\tau}} + \mu - \frac{1}{2} k_1, \quad \bar{\beta}_1 \sim -\frac{1}{2} \mu \log(\log K) - \frac{1}{2} k_2 - \frac{1}{4} \mu + \frac{1}{2} \mu \log \bar{\tau}, \quad \text{as } \bar{\tau} \rightarrow 0. \quad (73)$$

After substituting expansions (72) into equations (71b, c) and solving the resulting equations for $\bar{\alpha}_0$, $\bar{\alpha}_1$, $\bar{\alpha}_2$, $\bar{\beta}_0$ and $\bar{\beta}_1$ we obtain the solutions which satisfy the matching conditions (73) as,

$$\bar{\alpha}_0 = \mu \bar{\tau}, \quad \bar{\beta}_0 = \begin{cases} (2\mu - k_1)(1 - e^{-(2\mu - k_1)\bar{\tau}})^{-1}; & k_1 \neq 2\mu, \\ 1/\bar{\tau}; & k_1 = 2\mu, \end{cases} \quad (74a, b)$$

together with similar expressions for $\bar{\alpha}_1, \bar{\alpha}_2, \bar{\beta}_1$ which, for brevity, are not given here (but may be found in [16]). By substituting these solutions into expansions (72) and approximating for $\bar{\tau} \gg 1$, we find that,

$$\left. \begin{aligned} \bar{\alpha} &\sim \mu \bar{\tau} - 2\mu K^{-3}(\log K)^2 - \frac{1}{2}\mu(2\mu - k_1)^2 \bar{\tau}^2 K^{-3} \log K + \dots \\ \bar{\beta} &\sim (2\mu - k_1) + \frac{1}{2}\mu(2\mu - k_1)^3 \bar{\tau}^2 (\log K)^{-1} + \dots \end{aligned} \right\}; k_1 < 2\mu, \quad (75a)$$

$$\left. \begin{aligned} \bar{\alpha} &\sim \mu \bar{\tau} - 2\mu K^{-3}(\log K)^2 + \{\mu + \mu \log(\log K) - \mu \log \bar{\tau}\} K^{-3} \log K + \dots \\ \bar{\beta} &\sim \frac{1}{\bar{\tau}} - \left\{ \frac{1}{2}\mu \log(\log K) + \frac{1}{2}k_2 + \frac{1}{4}\mu - \frac{1}{2}\mu \log \bar{\tau} \right\} (\log K)^{-1} + \dots \end{aligned} \right\}; k_1 = 2\mu \quad (75b)$$

$$\left. \begin{aligned} \bar{\alpha} &\sim \mu \bar{\tau} - 2\mu K^{-3}(\log K)^2 + \bar{c} K^{-3} \log K + \dots \\ \bar{\beta} &\sim (k_1 - 2\mu) e^{(2\mu - k_1)\bar{\tau}} - (k_1 - 2\mu)(\bar{c} + k_2) \bar{\tau} e^{(2\mu - k_1)\bar{\tau}} (\log K)^{-1} + \dots \end{aligned} \right\}; k_1 > 2\mu, \quad (75c)$$

as $K \rightarrow \infty$ with $\tau \gg 1$, where

$$\begin{aligned} \bar{c} &= \mu + \mu \log(\log K) - \mu(2\mu - k_1)^2 \int_0^1 \left\{ \frac{s}{(1 - e^{-(2\mu - k_1)s})^2} - \frac{1}{(2\mu - k_1)^2 s} \right\} ds \\ &\quad - \mu(2\mu - k_1)^2 \int_1^\infty \frac{s ds}{(1 - e^{-(2\mu - k_1)s})^2}. \end{aligned} \quad (75d)$$

There are three cases to consider.

(a) $k_1 > 2\mu$

For $k_1 > 2\mu$, expression (75c) shows that $\bar{\beta} \rightarrow 0$ as $\bar{\tau} \rightarrow \infty$ and the solution is asymptotic to (13a). Although a further weak non-uniformity arises when $\bar{\tau} = O(\log K)$, β_I remains exponentially small and $\alpha_I \sim \mu \tau$ as $\tau \rightarrow \infty$. Thus, in this case, no clock reaction behaviour arises and the production of the clock chemical, B , is completely inhibited by C .

(b) $k_1 < 2\mu$

For $k_1 < 2\mu$, approximations (75a) become non-uniform as $\bar{\tau} \rightarrow \infty$, in particular when $\bar{\tau} = O((\log K)^{1/2})$, $\bar{\alpha} = O((\log K)^{1/2})$, $\bar{\beta} = O(1)$. To obtain uniform asymptotic expansions valid when $\bar{\tau} = O((\log K)^{1/2})$ we introduce region III, where appropriate scaled variables are, $\hat{A} = K^{-1}(\log K)^{1/2} \alpha_I$, $\hat{B} = K^2(\log K)^{-1} \beta_I$, $\hat{T} = K^{-1}(\log K)^{1/2} \tau$. After writing equations (68b, c) in terms of these variables, we expand \hat{A} and \hat{B} as,

$$\hat{A} = \hat{A}_0 + K^{-3}(\log K)^{3/2} \hat{A}_1 + O(K^{-3} \log K), \quad \hat{B} = \hat{B}_0 + O((\log K)^{-1/2}), \quad (76)$$

as $K \rightarrow \infty$ with $\hat{T} = O(1)$. After substituting expansions (76) into the scaled equations and solving the resulting equations for \hat{A}_0, \hat{A}_1 and \hat{B}_0 subject to the matching with (84a) as $\hat{T} \rightarrow 0$, we obtain,

$$\hat{A}_0 = \mu \hat{T}, \quad \hat{A}_1 = \frac{k_1 - 2\mu}{1 + \frac{1}{2}\mu(k_1 - 2\mu)\hat{T}^2} - k_1, \quad \hat{B}_0 = -\frac{k_1 - 2\mu}{1 + \frac{1}{2}\mu(k_1 - 2\mu)\hat{T}^2}. \quad (77a, b, c)$$

Expansions (76) become non-uniform as $\hat{T} \rightarrow \hat{T}_0 = (2/\mu(2\mu - k_1))^{1/2}$. Clearly, \hat{B} increases rapidly in the neighbourhood of the point $\hat{T} = \hat{T}_0$, which shows that the solution displays clock reaction behaviour. Further asymptotic regions are required to complete the solution for $k_1 < 2\mu$, and the details are not pursued any further in the present paper. We have shown that clock reaction behaviour occurs for $k_1 < 2\mu$ but not for $k_1 > 2\mu$ and we now consider the case $k_1 = 2\mu$.

(c) $k_1 = 2\mu$

When $k_1 = 2\mu$, expansions (75b) show that region II is entirely passive and simply transmits the asymptotic form of the solution in region I given by the matching conditions (73). However, expansion (75b) becomes non-uniform as $\bar{\tau} \rightarrow \infty$, in particular when $\bar{\tau} = O(\log K)$, $\bar{\alpha} = O(\log K)$ and $\bar{\beta} = O((\log K)^{-1})$. In order to deal with this non-uniformity we introduce region III where appropriate scaled variables are, $A = K^{-1}\alpha_I$, $B = K\beta_I$, $T = K^{-1}\tau$, in terms of which equations (68b, c) become,

$$\frac{dA}{dT} = \mu - K^{-3}AB^2, \quad (78a)$$

$$\frac{dB}{dT} = AB^2 - B^2 - k_2B - K^3B(A - \mu T + K^{-3}(\log K)2\mu), \quad (78b)$$

which are to be solved subject to matching with the expansions (75b) in region II as $T \rightarrow 0$. We expand A and B as,

$$A = A_0 + K^{-3}(\log K)A_1 + K^{-3}A_2 + o(K^{-3}), \quad B = B_0 + o(1), \quad (78c)$$

as $K \rightarrow \infty$, with $T = O(1)$, and matching with (75b) as $T \rightarrow 0$ requires,

$$A_0 \sim \mu T, \quad A_1 \sim -2\mu, \quad A_2 \sim \mu - \mu \log T, \quad B_0 \sim \frac{1}{T} + \frac{1}{2}\mu \log T - \frac{1}{2}k_2 - \frac{1}{4}\mu, \quad (78d)$$

as $T \rightarrow 0$. After substituting expansions (78c) into equations (78a, b) and solving the resulting equations for A_0 and A_1 we obtain, $A_0 = \mu T$, $A_1 = -2\mu$. The equations for A_2 and B_0 are then,

$$\frac{dA_2}{dT} = -\mu TB_0^2, \quad \frac{dB_0}{dT} = \mu TB_0^2 - B_0^2 - k_2B_0 - A_2B_0. \quad (79a, b)$$

In order to scale the parameter μ out of the problem we make the change of variable, $\tilde{T} = \mu T$, $\mu \tilde{B}_0 = B_0$, $\mu \tilde{A}_2 = A_2$, $\mu \tilde{k}_2 = k_2$, so that the system (79a, b) becomes,

$$\frac{d\tilde{A}_2}{d\tilde{T}} = -\tilde{T}\tilde{B}_0^2, \quad \frac{d\tilde{B}_0}{d\tilde{T}} = \tilde{T}\tilde{B}_0^2 - \tilde{B}_0^2 - \tilde{k}_2\tilde{B}_0 - \tilde{A}_2\tilde{B}_0, \quad (80a, b)$$

and we seek a solution subject to the matching conditions,

$$\tilde{A}_2 \sim -\log \tilde{T} + 1 - \log \mu, \quad \tilde{B}_0 \sim \frac{1}{\tilde{T}} + \frac{1}{2} \log \tilde{T} - \frac{1}{2}\tilde{k}_2 - \frac{1}{4} + \frac{1}{2} \log \mu, \quad \text{as } \tilde{T} \rightarrow 0. \quad (80c)$$

Numerical solutions of the system of equations (80a, b) subject to initial conditions (80c) show that there exists a constant \tilde{k}_2^* , such that

$$\begin{aligned} \tilde{B}_0 \rightarrow \infty, \quad \tilde{A}_2 \rightarrow -\infty, \quad \text{as } \tilde{T} \rightarrow \tilde{T}_0, \quad \text{for } \tilde{k}_2 < \tilde{k}_2^*, \\ \tilde{B}_0 \rightarrow 0, \quad \tilde{A}_2 \rightarrow \text{constant}, \quad \text{as } \tilde{T} \rightarrow \infty, \quad \text{for } \tilde{k}_2 > \tilde{k}_2^*, \end{aligned} \quad (81)$$

where \tilde{T}_0 is a positive function of \tilde{k}_2 , with $\tilde{T}_0 \rightarrow \infty$ as $\tilde{k}_2 \rightarrow \tilde{k}_2^{*-}$. However, we are unable to obtain an accurate value for \tilde{k}_2^* . We took as our initial conditions, $\tilde{A}_2 = -\log \tilde{T}_1$, $\tilde{B}_0 = 1/\tilde{T}_1 + \frac{1}{2} \log \tilde{T}_1$, with $0 < \tilde{T}_1 \ll 1$, but an initial value of \tilde{A}_2 sufficiently large to determine \tilde{k}_2^* accurately leads to such a large initial value of \tilde{B}_0 that accurate numerical integration using a simple Runge–Kutta technique is not possible. The exact value of the constant \tilde{k}_2^* remains to be determined.

We have now shown that when $k_1 = 2\mu$ and $k_2 > \tilde{k}_2^* \mu$, $\tilde{B} \rightarrow 0$ and $\tilde{A} \sim \mu \tilde{T} - 2\mu K^{-3} \log K$ as $\tilde{T} \rightarrow \infty$, and hence the solution is asymptotic to (13a). Therefore, clock reaction behaviour does not arise and the production of the clock chemical, B , is completely inhibited by C . However, when $k_1 = 2\mu$ and $k_2 < \tilde{k}_2^* \mu$, \tilde{B} and \tilde{A} become unbounded as $\tilde{T} \rightarrow \tilde{T}_0$, which shows that clock reaction behaviour arises in this case. Further asymptotic regions are required to complete the solution, the details of which are not pursued in the present paper.

Our analysis of the initial value problem (64) has shown that,

$$K^* \sim \left[\left(\frac{\mu}{\lambda - 1} \right) \left\{ \log \left(\frac{\mu}{\lambda - 1} \right) + \tilde{k}_2^* \right\} \right]^{1/2}, \quad \text{as } \lambda \rightarrow 1^+, \quad (82)$$

where K^* is defined by (66) in C6.1. Expression (82) also indicates that $K^* = O(\mu^{1/2})$ for $\mu \gg 1$ and $0 < \lambda - 1 \ll 1$, consistent with the graphs of K^* shown in Fig. 5(a). Finally, we note that we require $\tau_0 \ll \varepsilon^{-1}$ for the asymptotic solution described above to be appropriate, where

$$\tau_0 = K(\log K)^{-1/2} (2/\mu(2\mu - k_1))^{1/2}, \quad \text{for } \lambda - 1 \sim k_1 K^{-2} \log K \text{ as } K \rightarrow \infty. \quad (83)$$

Solutions of the initial value problem (64) behave very differently to solutions of (18), (42) and (52), which we examined earlier. By the same token, the reaction scheme (63) behaves very differently to the schemes (17), (41) and (51). For K sufficiently large the production of the clock chemical, B , is completely inhibited by C via the reaction step (63c), which proceeds much more rapidly than the step (63b) when β_l is small. However, for K sufficiently close to a threshold value, K^* with $K < K^*$, clock reaction behaviour arises and the concentration of B grows rapidly in the neighbourhood of the point $\tau = \tau_0$, where $\tau_0 \rightarrow \infty$ as $K \rightarrow K^{*-}$.

7. Comparison of the four reaction schemes

Firstly, we consider the cases of quadratic autocatalysis with linear inhibition and cubic autocatalysis with quadratic inhibition. These two reaction schemes lead to very similar behaviour and the main points are summarised in Table 1. We have shown that clock

Table 1. Various properties of the solution of the initial value problem (12) for $K \gg 1$

	Quadratic autocatalysis with linear inhibition, $n = m = 1$	Cubic autocatalysis with quadratic inhibition, $n = m = 2$	Quadratic autocatalysis with quadratic inhibition, $n = 1, m = 2$
K	k_2/k_1	k_2/k_1	$k_2 b_0/k_1$
τ_0	$\frac{2(\lambda-1)K}{\mu} + O(K^{-1})$	$\frac{2(2\lambda-1)K}{\mu} + O(K^{-1})$	$\left\{ \frac{3(2\lambda-1)^2}{2\mu^2} \right\}^{1/3} K^{1/3} + O(1)$
β_{\min}	$\frac{(\lambda-1)}{\lambda} \exp\left\{ -\frac{(\lambda-1)^2 K^2}{2\mu} + o(K^2) \right\}$	$\frac{2\mu K^{-2}}{(2\lambda-1)^2} + o(K^{-2})$	$\frac{\sqrt{\mu\theta}}{(2\lambda-1)} K^{-1} + o(K^{-1})$
The behaviour of β as $\tau \rightarrow 0$	$\beta \sim \frac{(\lambda-1)}{\lambda} e^{-(\lambda-1)K(\tau_0-\tau)}$	$\beta \sim \frac{K^{-1}}{(2\lambda-1)(\tau_0-\tau)}$	$\beta \sim K^{-1/2} \left\{ \frac{3}{2(\tau_0-\tau)} \right\}^{1/2}$
α_τ and β_τ in the neighbourhood of $\tau = \tau_0$	$O(K^2)$	$O(K^3)$	$O(K^{2/3})$

reaction behaviour occurs for sufficiently large values of $K = k_2/k_1$ (when $c_0 > b_0$); a condition which is independent of the initial concentration of clock chemical, B . For $K \gg 1$, β grows rapidly as $\tau \rightarrow \tau_0 = O(K)$. These similarities arise because reaction steps (1b) and (1c) proceed at a rate which is of the same order of magnitude, $O(\beta^n)$, for $\beta \ll 1$, in each case. The main difference in the behaviour of the concentration β between the two cases is that β becomes exponentially small during the induction period $0 < \tau < \tau_0$ for $n = m = 1$, but only algebraically small for $n = m = 2$. In addition, α_τ and β_τ are of $O(K^2)$ in the neighbourhood of $\tau = \tau_0$ for $n = m = 1$, but larger, of $O(K^3)$, for $n = m = 2$.

We now turn our attention to the case of quadratic autocatalysis with quadratic inhibition. The behaviour of this reaction scheme is significantly different to that of the two schemes described above, as outlined in Table 1. Clock reaction behaviour occurs for sufficiently large values of $K = k_2 b_0/k_1$, so that this type of behaviour is now possible for a sufficiently large initial concentration, b_0 , of B if the initial concentration, c_0 , of C satisfies, $c_0 > \frac{1}{2} b_0$. However, for similar values of K , the clock reaction behaviour for $n = m = 1$ or $n = m = 2$ is much more marked than for $n = 1, m = 2$, when $\tau_0 = O(K^{1/3})$, $\beta_{\min} = O(K^{-1})$ and the maximum rate of increase of β is slower of $O(K^{2/3})$ as $\tau \rightarrow \tau_0$. Finally, the case of cubic autocatalysis with linear inhibition is dramatically different to all of the other three schemes which we have studied in this section. For $K \gg 1$, or equivalently, $k_2 \gg k_1 b_0$, the production of the clock chemical, B is completely inhibited. For b_0 sufficiently small there is, therefore, no possibility of clock reaction behaviour. However, for $c_0 > b_0$ there exists a positive constant, K^* , such that the production of B is not completely inhibited for $K < K^*$, and sharply defined clock reaction behaviour is possible for $(K^* - K)$ sufficiently small and positive.

In terms of the chemical systems (1), clock reaction behaviour is less likely to be observed in the two cases where $n \neq m$ than when $n = m$. When $n = 1, m = 2$, large initial concentrations of B and C are required to produce sharp clock reaction behaviour, whilst for $n = 2, m = 1$, this type of behaviour only occurs for a very narrow range of initial concentrations of B and C . Finally, we tentatively make the following conjecture, which concerns the asymptotic behaviour of solutions of the full initial value problem (7).

C7.1: If (α, β, γ) is a solution of the full initial value problem (7), with $\lambda > 1/m$ and $\mu > 0$, there exists a positive value $K^*(\epsilon)$ such that,

$$\alpha \rightarrow 0, \quad \beta \rightarrow P_0 - (m\lambda - 1), \quad \gamma \rightarrow 0 \quad \text{as } \tau \rightarrow \infty, \text{ for } K < K^*, \quad (84a)$$

$$\alpha \rightarrow P_0 - c, \quad \beta \rightarrow 0, \quad \gamma \rightarrow \lambda + \frac{c-1}{m} \quad \text{as } \tau \rightarrow \infty, \text{ for } K > K^*, \quad (84b)$$

and

$$\begin{aligned} K^* &= O(\epsilon^{-1}), \quad \text{as } \epsilon \rightarrow 0; \quad m = n = 1 \quad \text{or} \quad m = n = 2 \\ K^* &= O(\epsilon^{-3}), \quad \text{as } \epsilon \rightarrow 0; \quad n = 1, \quad m = 2, \\ K^* &= O(1), \quad \text{as } \epsilon \rightarrow 0; \quad n = 2, \quad m = 1. \end{aligned} \quad (85)$$

Our numerical and asymptotic analysis of the initial value problem (64) strongly suggests that C7.1 holds for the case $n=2, m=1$. For the case $m=n=1$, when $K \gg \epsilon^{-1}$ the concentration of the precursor, P , is exponentially small (and hence effectively no reactant, A , is supplied to the reaction mixture) at the transition time $\tau = \tau_0 = O(K)$ as $K \rightarrow \infty$, given by our analysis of the inner problem (18). This indicates that no sudden increase in β can occur and $\beta \rightarrow 0$ as $\tau \rightarrow \infty$. We conclude that a transition between the two possible types of asymptotic behaviour (84a, b) occurs at some finite value, K^* , of K as K increases, with $K^* = O(\epsilon^{-1})$ as $\epsilon \rightarrow 0$. This conjecture can be investigated by considering the asymptotic solution of the initial value problem (7) with $n = m = 1$ and $K = O(\epsilon^{-1})$ as $\epsilon \rightarrow 0$, the details of which are not pursued in the present paper. A similar argument in each of the cases $n = m = 2$ and $n = 1, m = 2$ leads us to conjecture C7.1 which has yet to be examined. Finally, we note that our analysis indicates that the complete inhibition of the production of the clock chemical, B , for sufficiently large values of K is due to the interaction of the two reaction steps (1b) and (1c) for $n=2, m=1$, whereas, in the other three cases, it is due to the total consumption of the precursor, P , via the reaction step (1a).

8. Conclusion

In this paper we have studied the four model reaction schemes given by (1) with $n = 1, 2$ and $m = 1, 2$. We found that it is possible for the scheme to display very sharply defined clock reaction behaviour, with the concentration of the clock chemical, B , growing much more rapidly than in the slightly simpler, canonical schemes studied in [1]. These schemes are examples of induction and inhibition mechanisms, whilst scheme (1) can be referred to as an inhibited autocatalytic mechanism. The clock reaction behaviour exhibited by this inhibited autocatalysis arises because of a subtle, non-linear interaction between steps (1b) and (1c). This behaviour cannot readily be deduced simply from the nature of the reaction pathways, even though there are only three simple steps in scheme (1). Moreover, the nature of the clock reaction behaviour is dependent on n and m , the orders of the autocatalytic and inhibiting steps (1b) and (1c) respectively, in a far from obvious manner.

Inhibited autocatalysis can be added to the list of possible mechanisms postulated to explain clock reaction behaviour, presenting itself as a likely candidate when the growth of

the concentration of the clock chemical is particularly rapid compared to some typical timescale for the reaction. As an example, a recent paper by Bachmann et al. [17], describes experiments involving an autocatalytic system and gives a graph of the time dependence of the concentration of one of the important chemical species. This bears a striking resemblance to the concentration, β , in Fig. 1, and suggests that an inhibited autocatalytic mechanism may play some role in the reaction. Conversely, it should be possible to create an inhibited autocatalytic mechanism by adding a suitable inhibitor to a known autocatalytic reaction, for example the iodate-arsenous acid reaction as described in §1. A similar approach has been taken to the creation of oscillatory reactions (for example [18]).

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