Note

An uncommon form of multistationarity in a realistic kinetic model

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The stationary behaviour of a kinetic model close to that describing the real nitric acid–hydroxylamine reaction is studied under conditions of a continuously fed stirred tank reactor (c.s.t.r.). It is shown that this system has an interesting mathematical property – three positive stationary states in an *unbounded* region of the feed concentration. Two of these states are always locally asymptotically stable to perturbation while one is always unstable.

Multistationarity, in which an open system has more than one stationary state, plays a substantial role in many areas of science [1,2a]. It is especially important in chemistry [3,4a] where its features can be studied relatively easily, but the results may help to understand even difficult biological phenomena too.

While investigating the multistationary behaviour of the nitric acid–hydroxylamine reaction [5] we noticed that under conditions of a continuously fed stirred tank reactor (c.s.t.r.) the autocatalytic reaction scheme

$$\begin{aligned} &\mathrm{X}+\mathrm{Y}\rightarrow 4\mathrm{Y}\,, \quad && r = kxy/(\beta + x)\,, \\ &\mathrm{X}+\mathrm{Y}\rightarrow \mathrm{P}\,, \quad && r = k_c xy\,, \end{aligned} \tag{1}$$

which is very close to that describing the real chemical system, yields an *unbounded* region of tristationarity in the stationary concentration vs. substrate feed concentration diagram of the system (X – substrate, Y – autocatalyst, r – reaction rate, x and y – concentrations, k, k_c, β – constants). Since the best known forms of multistationarity, such as the simple S-shaped curves, mushrooms and isolas [2b,4b] are all confined to a finite interval of the bifurcation parameter, the above property of scheme (1) is surprising, and may be of interest to those studying the mathematical aspects of nonlinear behaviour in chemical kinetics.

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The kinetic equations of the c.s.t.r. with reactions (1) can be written as

$$\dot{x} = -kxy/(\beta + x) - k_c xy + k_0(x_0 - x)\,,$$
$$\dot{y} = 3kxy/(\beta + x) - k_c xy + k_0(y_0 - y)\,, \tag{2}$$

where the new quantities, k_0, x_0 and y_0, denote the reciprocal of the mean residence time, the feed concentration of species X and that of Y, respectively. In the stationary state the time derivatives in (2) vanish, and the stationary concentrations (which will also be denoted by x and y for simplicity) can be determined from the following equations:

$$-kxy/(\beta + x) - k_c xy + k_0(x_0 - x) = 0\,, \tag{3a}$$

$$3kxy/(\beta + x) - k_c xy + k_0(y_0 - y) = 0\,. \tag{3b}$$

In the rest of the paper we shall always assume that all the parameters in (3) are positive. The interesting stationary behaviour of the system is formulated mathematically in the following theorem.

THEOREM 1

Let k, k_0, k_c, β be fixed parameters that satisfy the following relationships:

$$4\beta k_c - k_0 \geqslant 0\,, \tag{4a}$$

$$9k^2 - 6k(\beta k_c + k_0) + \beta^2 k_c^2 - 2\beta k_0 k_c + k_0^2 > 0\,, \tag{4b}$$

$$6k - k_0 - 2\beta k_c > 0\,. \tag{4c}$$

Then (A) for some $x_0^* > 0$ there exist three (x_i, y_i): $[x_0^*, \infty) \to R_+^2$ $(i = 1, 2, 3)$ continuous function pairs such that (x_i, y_i) $(i = 1, 2, 3)$ are solutions of (3) in their entire domain of definition and

$$0 < y_1(x_0) < y_2(x_0) < y_3(x_0) \quad \text{and} \quad x_1(x_0) > x_2(x_0) > x_3(x_0) > 0 \tag{5}$$

are valid; (B) $y_1(x_0) \to 0$, $y_2(x_0) \to \infty$ and $y_3(x_0) \to \infty$ as $x_0 \to \infty$; $x_2(x_0) > x_2^\infty$ and $x_3(x_0) < x_3^\infty$ for any $x_0 > x_0^*$, where

$$x_{2,3}^\infty = \frac{3k - k_0 - k_c\beta \pm [(3k - k_0 - k_c\beta)^2 - 4k_0 k_c \beta]^{1/2}}{2k_c}\,; \tag{6}$$

moreover $x_1(x_0) \to \infty$, $x_2(x_0) \to x_2^\infty$ and $x_3(x_0) \to x_3^\infty$ as $x_0 \to \infty$; $x_1 y_1$ is bounded for $x_0 > x_0^*$.

Proof

After some algebraic transformations we obtain the following equations from (3):

$$x = k_0(3x_0 + y_0 - y)/(4k_c y + 3k_0)\,, \tag{7}$$

$$Ay^3 + By^2 + Cy + D = 0\,, \tag{8}$$

where

$$\begin{aligned}
A &= k_0 k_c(4\beta k_c - k_0 + 4k)\,, \\
B &= 2k_0 k_c x_0(2\beta k_c + k_0 - 6k) \\
&\quad + k_0[\beta k_c(7k_0 - 4k_c y_0) - k_0^2 + k_0(3k + 2k_c y_0) - 4kk_c y_0]\,, \\
C &= 3k_0^2 k_c x_0^2 + k_0^2 x_0(3\beta k_c + 3k_0 - 9k - 2k_c y_0) \\
&\quad + k_0^2[\beta(3k_0 - 7k_c y_0) + 2k_0 y_0 - y_0(3k + k_c y_0)]\,, \\
D &= -\,3k_0^3 y_0 x_0 - k_0^3 y_0(3\beta + y_0)\,.
\end{aligned} \tag{9}$$

Any solution (x, y) of (3), for which $4k_c y + 3k_0 \neq 0$, satisfies the system (7)–(8), and any solution (x, y) of (7)–(8) with $\beta + x \neq 0$ is that of (3). The fact that (7) provides $x > 0$ for any $y > 0$ solution of (8) follows from the following statements: (a) if $y > 0$, $\beta + x \neq 0$ is valid for the x value defined by (7); (b) if (x, y) is a solution of (3), $y > 0$ implies $x > 0$. Statements (a) and (b) can be proved by direct calculation employing (3), (4a) and (7). Now we only need to show that (8) has three distinct positive y roots for sufficiently large values of x_0. A lengthy but not difficult calculation shows that the numerator of the discriminant $\Delta = -(27A^2D^2 - 18ABCD + 4AC^3 + 4B^3D - B^2C^2)/(108A^4)$ [6a] is a sixth-order polynomial of x_0, and it follows from (4b) that the coefficient of the most rapidly increasing term x_0^6 is positive. Thus, because of $\Delta > 0$, (8) will have [6a] three distinct real roots for sufficiently large values of x_0. On the basis of Descartes' theorem [6b] the number of negative roots of (8) is less than or equal to the number of sign changes in the series

$$-A, B, -C, D\,. \tag{10}$$

The coefficients A, B, C, D in (9) are written as polynomials of x_0. While (4a) yields $A > 0$, (4c) shows that the leading term of B is negative. Thus, there are no sign changes in series (10) if x_0 exceeds a given lower limit. Let $x_0^* > 0$ be a value such that both $\Delta > 0$ and $\mathrm{sign}(A) = \mathrm{sign}(-B) = \mathrm{sign}(C) = \mathrm{sign}(-D)$ are valid for $x_0 > x_0^*$. Since $D \neq 0$ excludes the zero roots, (8) will have three distinct positive roots for $x_0 > x_0^*$. By assigning these roots to the values of x_0 we obtain three functions which, together with those defined by (7), satisfy relationships (5) in part (A) of the theorem. The continuity of these functions follows from that of the coefficients (9) and the implicit function theorem [6d].

(B) On the basis of Rolle's theorem [6c] the roots of the quadratic obtained by the differentiation of (8) with respect to y lie between those of (8). As both of these roots tend to positive infinity as $x_0 \to \infty$, the two larger roots of (8) also do this. Introducing the variable $z = 1/y$ into (8) and employing the same separation theorem it turns out that the smallest root of (8) tends to zero as x_0 tends to positive infinity. This procedure also yields the estimate

$$x_0 y_1(x_0) < \frac{3|D|x_0}{C}\left[1+\left(1-\frac{3BD}{C^2}\right)^{1/2}\right]^{-1} \quad \text{for } x_0 > x_0^* \tag{11}$$

which, together with (7) and (9), shows that $x_1 y_1$ is bounded for $x_0 > x_0^*$. The limit $x_1(x_0) \to \infty$ as $x_0 \to \infty$ readily follows from (7). Expressing x from (3b) it can be seen that $x_2(x_0)$ and $x_3(x_0)$ tend to x_2^∞ or x_3^∞ as x_0 tends to positive infinity. Creating a cubic for x from (3) and (7), and applying Rolle's theorem [6c] it turns out that there is a function of x_0 that separates $x_2(x_0)$ and $x_3(x_0)$ and tends to $(3k - k_0 - k_c\beta)/2k_c$ as $x_0 \to \infty$. A comparison with (6) shows that $x_2(x_0)$ and $x_3(x_0)$ cannot tend to the same value as $x_0 \to \infty$. The limits and relations concerning these quantities now readily follow from the continuity and the expression

$$\frac{3kx}{\beta + x} - k_c x - k_0 = -\frac{k_0 y_0}{y} < 0\,. \tag{12}$$

Multistationarity is usually accompanied by multistability. In this case at least two stationary states are locally asymptotically stable, i.e. have domains of attraction in the phase space of the dynamical system [2a,2b,4a,4b]. The stability and topological character of a given stationary state can frequently be assessed by the investigation of the appropriately linearised version of the original differential system, which describes the fate of small deviations from the stationary state [2c,4c]. In this context stability depends on the eigenvalues of the matrix of the linearized system. In the two-dimensional case these eigenvalues can be computed from the equation $\lambda_{1,2} = [\mathrm{Tr} \pm (\mathrm{Tr}^2 - 4\Delta)^{1/2}]/2$, where $\mathrm{Tr} = a_{11} + a_{22}$, $\Delta = a_{11}a_{22} - a_{12}a_{21}$ and a_{ij} are the elements of the Jacobi matrix of the original differential system evaluated at the given stationary state. After some computation we obtain from (3) that

$$\mathrm{Tr} = -\left[\frac{k\beta y}{(\beta + x)^2} + k_c y + k_0 + \frac{k_0 y_0}{y}\right] < 0 \quad \text{and}$$
$$\Delta = k_0 y_0\left[\frac{k\beta}{(\beta + x)^2} + k_c + \frac{k_0}{y}\right] + \left(\frac{k}{\beta + x} + k_c\right)\left[\frac{3k\beta}{(\beta + x)^2} - k_c\right] xy\,. \tag{13}$$

If x_0 is sufficiently large, $\Delta > 0$ and $\mathrm{Re}(\lambda_1) < 0$, $\mathrm{Re}(\lambda_2) < 0$ are valid for (x_1, y_1) and (x_3, y_3); these are locally asymptotically stable stationary points of the type of node or focus [2c,4c]. In the case of (x_2, y_2), $\Delta < 0$ is fulfilled for large values of x_0; the eigenvalues λ_1 and λ_2 being real and of opposite sign, this stationary state will be an unstable saddle point [2c,4c]. Thus, we have proved the following theorem which summarizes our results:

THEOREM 2

Under the conditions of theorem 1 there exists an $x_0^* > 0$ quantity such that eq. (2) has three different positive stationary states for any $x_0 > x_0^*$. Two of these stationary states are always locally asymptotically stable while one is always unstable.

One parameter set that satisfies the conditions of theorem 1 is $k = 0.055$, $k_c = 12.2, k_0 = 3.2 \times 10^{-3}, \beta = y_0 = 10^{-4}$.

According to our numerical calculations, the unbounded region of multistationarity does not disappear if spontaneous formation and decay of the autocatalyst ($X \rightarrow 3Y$; $r = k_f x$ and $Y \rightarrow Q$; $r = k_d y$) are added to model (1) with sufficiently small rate constants. On the other hand, numerical investigations have shown that the stationary concentration vs. k_0 diagram of scheme (1) contains a finite interval of tristationarity.

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