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

\[ \begin{align*}
X + Y & \rightarrow 4Y, \quad r = k_{xy}/(\beta + x), \\
X + Y & \rightarrow P, \quad r = k_{cy},
\end{align*} \]

(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, \beta – 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

\[ \begin{align*}
    \dot{x} &= -k_{xy}(\beta + x) - k_{c}xy + k_{0}(x_{0} - x), \\
    \dot{y} &= 3k_{xy}(\beta + x) - k_{c}xy + k_{0}(y_{0} - y),
\end{align*} \]

(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:

\[ \begin{align*}
    -k_{xy}(\beta + x) - k_{c}xy + k_{0}(x_{0} - x) &= 0, \\
    3k_{xy}(\beta + x) - k_{c}xy + k_{0}(y_{0} - y) &= 0.
\end{align*} \]

(3a) (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 \( k, k_{0}, k_{c}, \beta \) be fixed parameters that satisfy the following relationships:

\[ \begin{align*}
    4\beta k_{c} - k_{0} &\geq 0, \\
    9k^{2} - 6k(\beta k_{c} + k_{0}) + \beta^{2}k_{c}^{2} - 2\beta k_{0}k_{c} + k_{0}^{2} &> 0, \\
    6k - k_{0} - 2\beta k_{c} &> 0.
\end{align*} \]

(4a) (4b) (4c)

Then (A) for some \( x_{0} > 0 \) there exist three \( (x_{i}, y_{i}) : [x_{0}^{i}, \infty) \rightarrow R^{2} (i = 1, 2, 3) \) continuous function pairs such that \( (x_{i}, y_{i}) (i = 1, 2, 3) \) are solutions of (3) in their entire domain of definition and

\[ \begin{align*}
    0 < y_{1}(x_{0}) < y_{2}(x_{0}) < y_{3}(x_{0}) \quad \text{and} \quad x_{1}(x_{0}) > x_{2}(x_{0}) > x_{3}(x_{0}) > 0
\end{align*} \]

(5)

are valid; (B) \( y_{1}(x_{0}) \rightarrow 0, y_{2}(x_{0}) \rightarrow \infty \) and \( y_{3}(x_{0}) \rightarrow \infty \) as \( x_{0} \rightarrow \infty \); \( x_{2}(x_{0}) > x_{2}^{\infty} \) and \( x_{3}(x_{0}) < x_{3}^{\infty} \) for any \( x_{0} > x_{0}^{*} \), where

\[ x_{2,3}^{\infty} = \frac{3k - k_{0} - k_{c}\beta \pm [(3k - k_{0} - k_{c}\beta)^{2} - 4k_{0}k_{c}\beta]^{1/2}}{2k_{c}}, \]

(6)

moreover \( x_{1}(x_{0}) \rightarrow \infty, x_{2}(x_{0}) \rightarrow x_{2}^{\infty} \) and \( x_{3}(x_{0}) \rightarrow x_{3}^{\infty} \) as \( x_{0} \rightarrow \infty \); \( x_{1}y_{1} \) is bounded for \( x_{0} > x_{0}^{*} \).

**Proof**

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

\[ x = k_{0}(3x_{0} + y_{0} - y)/(4k_{c}y + 3k_{0}) , \]

(7)