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Roger H. Hering
Missouri University of Science and Technology

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OSCILLATIONS IN LOTKA–VOLTERRA SYSTEMS OF CHEMICAL REACTIONS

Roger H. HERING
Department of Mathematics and Statistics, University of Missouri-Rolla, Rolla, Missouri 65401, USA

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Abstract

For a chemical reaction system modeled by $\dot{x} = k_1Ax - k_2x^2 - k_3xy + k_4y^2$, $\dot{y} = k_3xy - k_4y^2 - k_5y + k_6B$, it is shown that for each positive choice of parameters k_i, A, B there exists a unique stationary state which is globally asymptotically stable in the positive quadrant. A criterion for the non-existence of periodic solutions is given for the generalized Lotka–Volterra system: $\dot{x} = f(x)h(x, y)$, $\dot{y} = g(y)k(x, y)$.

Oscillations in chemical systems have been regarded as important to the understanding of highly organized structures, such as biological organisms [10]. Even simple chemical systems can exhibit sustained oscillations and self-organization. For example, such behavior is observed in the Belousov–Zhabotinskii reaction, which may be described as follows: an initially homogeneous medium with a color indicator to display the concentrations of components begins to change color periodically and eventually organizes spatially into alternating red and blue bands which are constant in color [10].

Historically, one approach to understanding such phenomena has consisted of using the law of mass action to characterize the chemical system by differential equations and examine these for multiple stationary states or sustained oscillations, such as limit cycles.

The model

$$\begin{aligned} A + X &\underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2X, \\ X + Y &\underset{k_4}{\overset{k_3}{\rightleftharpoons}} 2Y, \\ Y &\underset{k_6}{\overset{k_5}{\rightleftharpoons}} B, \end{aligned} \tag{1}$$

has been extensively studied in this connection [11,12]. It incorporates factors thought to be necessary for a chemical system to exhibit such behavior: it is an open, autocatalytic system with nonlinear rate dependences, which can be removed arbitrarily far from thermodynamic equilibrium by varying the parameters (ref. [11], p. 120). It warranted early attention, since bimolecular mechanisms are common. Moreover, for $k_2 = k_4 = k_6 = 0$, model (1) reduces to a Lotka–Volterra model in which any initial conditions lead to sustained oscillations [9].

Previous results for (1) show that a stationary state for positive X and Y is either a saddle point, center or stable node or focus, and that for some values of parameters, oscillatory decay to the stationary state can occur. In particular, a limit cycle cannot surround an unstable node or focus [6,7,12].

It is shown here that for each positive choice of parameters, there is a unique stationary state in the positive quadrant which is globally asymptotically stable there. The system can have no multiple stationary states or sustained oscillations, but damped oscillations may occur for some values of parameters.

Therefore, more general models must be considered to account for systems with sustained oscillations. In theorem (8), a criterion for the non-existence of periodic solutions is developed for generalized Lotka–Volterra (LV) models of the form

$$\dot{x} = f(x)h(x, y), \qquad \dot{y} = g(y)k(x, y).$$

In (1), the components A and B have constant concentrations, while those of X and Y can vary in time. Applying the law of mass action to (1) yields:

$$\dot{x} = k_1 A x - k_2 x^2 - k_3 xy + k_4 y^2 \overset{\text{def}}{=} P(x,y),$$

$$\dot{y} = k_3 xy - k_4 y^2 - k_5 y + k_6 B \overset{\text{def}}{=} Q(x,y). \tag{2}$$

Attention is restricted to I, the quadrant where X and Y have non-negative concentrations. The positive parameters k_i, A, B are fixed but arbitrary.

Let (x_0, y_0) be a singular point of (2) in I,

$$P(x_0, y_0) = 0, \quad Q(x_0, y_0) = 0, \quad x_0 \geq 0, \quad y_0 \geq 0. \tag{3}$$

The eigenvalues of the linear part of (2) at (x_0, y_0) are given by:

$$\lambda = \frac{T \pm \sqrt{T^2 - 4J}}{2}, \tag{4}$$

where

$$T = \left(\frac{\partial P}{\partial x}\right)_0 + \left(\frac{\partial Q}{\partial y}\right)_0,$$

$$J = \left(\frac{\partial P}{\partial x}\right)_0 \left(\frac{\partial Q}{\partial y}\right)_0 - \left(\frac{\partial Q}{\partial x}\right)_0 \left(\frac{\partial P}{\partial y}\right)_0.$$

THEOREM (5)

The stationary state solution $x = x_0$, $y = y_0$ is asymptotically stable. A solution's approach to it may be monotone or oscillatory, depending on parameters.

Proof

Inspection of (2) shows $(x_0, y_0) \in I^0$. From the expressions

$$T = -\left[\frac{k_4 y_0^2}{x_0} + k_2 x_0 + \frac{k_6 B}{y_0} + k_4 y_0\right] < 0$$

and

$$J = \frac{y_0^2\left[k_4 y_0 - k_3 x_0\right]^2 + k_4 k_6 B y_0^2 + k_2 k_6 B x_0^2 + k_2 k_4 x_0^2 y_0^2}{x_0 y_0} > 0,$$

it follows that all eigenvalues have negative real parts and $x = x_0$, $y = y_0$ is asymptotically stable. (x_0, y_0) is a spiral point or a node, depending on the sign of $T^2 - 4J$. Numerical examples show that both cases are possible for appropriate values of the parameters. Phase portraits are found in ref. [2], p. 389, and show that the approach is monotone for nodes and oscillatory for spiral points. □

Consider the parabola $R(x, y) = P(x, y) + Q(x, y) = k_1 Ax - k_2 x^2 - k_5 y + k_6 B = 0$. Since $(0, 0) \notin R(x, y) = 0$, we may construct the curve C = LMNO, as shown in fig. 1,

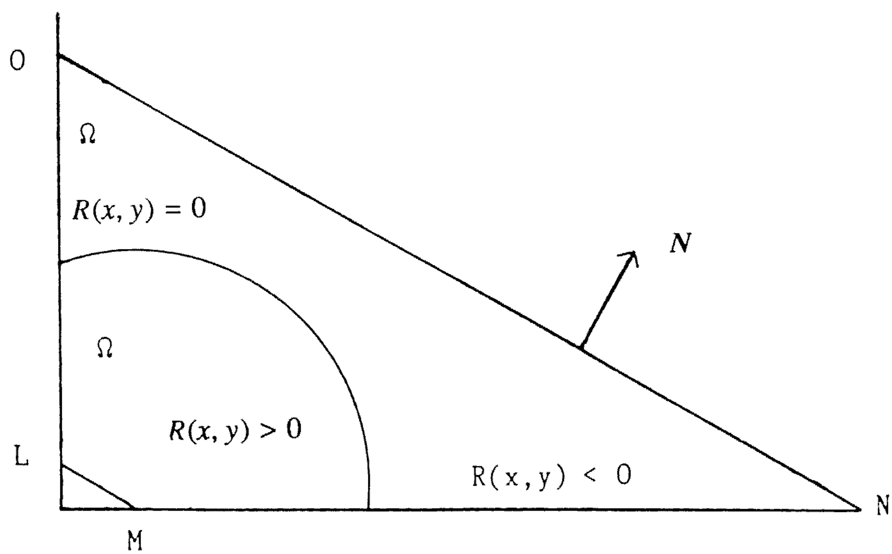

Fig. 1. Illustration of curve C = LMNO and the region Ω.

where LM and NO are lines of slope −1. Ω denotes the region consisting of C and its interior. $N = (\frac{1}{2}\sqrt{2}, \frac{1}{2}\sqrt{2})$ is a vector perpendicular to lines of slope −1.

THEOREM (6)

For each positive choice of parameters k_i, A, B, there is a unique stationary state solution in closed quadrant I and it is globally asymptotically stable there.

Proof

The direction field along ∂I shows that all solutions in I move into I^0 and thus eventually enter some region of the form Ω in fig. 1. The component of the direction field along N is given by $F(x,y)\cdot N = \frac{1}{2}\sqrt{2}(P(x,y) + Q(x,y)) = \frac{1}{2}\sqrt{2}\,R(x,y)$. Then solutions along LM move parallel to N since $R(x,y) > 0$ there, and solutions along NO move antiparallel to N. Then solutions everywhere along C move into Ω^0 and the index of C is +1 [1]. There are finitely many, say n, singular points of (2) in I and these lie along $R(x,y) = 0$ in I^0. Since each has index +1 by asymptotic stability, the index of C which encloses them all is n [1]. Thus, $n = 1$ and there exists a unique singular point of (2) in I. In Ω, we have with $B(x,y) = 1/xy$ that

$$\frac{\partial}{\partial x}(BP) + \frac{\partial}{\partial y}(BQ) = -\frac{1}{xy}\left[k_2 x + \frac{k_4 y^2}{x} + k_4 y + \frac{k_6 B}{y}\right] < 0. \qquad (7)$$

Then by the Bendixson–Dulac Theorem (ref. [3], p. 213), there exist no periodic solutions in Ω. Summarizing, we have that any solution in I enters some compact invariant region Ω containing no periodic solutions and exactly one asymptotically stable singular point. Thus, by the Poincaré–Bendixson Theorem [3], all solutions in I approach the unique stationary state solution $x = x_0$, $y = y_0$. Since k_i, A, B were arbitrary throughout, this result holds for any positive choice of parameters. □

We therefore conclude that the only evolution possible for this model is asymptotic decay to the unique stationary state. Fluctuations from the stationary state cannot approach some new stationary state or give rise to sustained oscillations, although in the appropriate range of parameters, the concentrations of components will undergo damped oscillations.

Although this quadratic system can have no periodic solutions, higher-order models involving, for instance, cubic autocatalysis, have been shown to have limit cycle solutions [12]. In particular, cubic autocatalysis has been proposed to account for the iodate–arsenous acid reaction [8] which, experimentally, exhibits oscillatory behavior [5]. Therefore, constructing generalized LV models admitting sustained oscillations is currently of great interest in characterizing experimentally observed oscillatory reaction systems.

To help identify and exclude generalized LV systems which can have no periodic solutions in the positive region, we apply the Bendixson–Dulac criterion.

THEOREM (8)

$$\dot{x} = f(x)h(x,y) = P(x,y), \quad f,g \in C^1(\Re^+);$$

$$\dot{y} = g(y)k(x,y) = Q(x,y), \quad h,k \in C^1(\Re^+ \times \Re^+). \tag{9}$$

If

$$L(x,y) = \frac{h_x(x,y)}{g(y)} + \frac{k_y(x,y)}{h(x)}$$

exists and is definite in I^0, then (9) has no periodic solution there.

Proof

For $B(x,y) = 1/(f(x)g(y))$, $(BP)_x + (BQ)_y = L(x,y)$ is definite in I^0. □

Consider the generalized LV system in ref. [4]:

$$\dot{x} = f(x)\left[\frac{f^*(x)}{f(x)} - g(y)\right], \tag{10a}$$

f^*, f, g positive and C^1 in $\Re^+$,

$$\dot{y} = g(y)[\beta f(x) - b], \tag{10b}$$

$\beta, b \in \Re^+$ and f^*/f strictly monotone in $\Re^+$. Here,

$$L(x,y) = \frac{1}{g(y)}\left[\frac{f^*(x)}{f(x)}\right]_x$$

is definite in I^0 and thus (10) has no periodic solutions in I^0.

A special case of (10), analyzed in ref. [4], is

$$A + m^*X \xrightarrow{k_1} (m^*+1)X, \quad mX + nY \xrightarrow{k_2} (n+1)Y, \quad nY \xrightarrow{k_3} B, \tag{11}$$

with kinetic equations $\dot{x} = k_1Ax^{m^*} - mk_2x^my^n$, $\dot{y} = k_2x^my^n - k_3y^n$. Then, $f^*/f = x^{m^*-m}$ and (11) can undergo no sustained oscillations when $m^* \neq m$.

The case $m^* = 2$, $m = 1$, $n = 1$ gives:

$$A + 2X \xrightarrow{k_1} 3X, \quad X + Y \xrightarrow{k_2} 2Y, \quad Y \xrightarrow{k_3} B. \tag{12}$$

Then (12), although it is an LV system with cubic autocatalysis, cannot serve as a model for oscillatory reactions.

The conclusions here for (10)–(12) agree with the results in ref. [4], and illustrate that (8) has useful application for analyzing generalized LV schemes proposed as models for oscillatory chemical reaction systems.

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