GENERATION OF MODEL REACTIONS
LEADING TO LIMIT CYCLE BEHAVIOR

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The system of differential equations by Feistel and Ebeling has been generalized. Some new formal kinetic reactions with two internal components, which may exhibit limit cycle behavior have been studied. Based upon the numerical integration of the deterministic models of these reactions the oscillatory character of the systems has been confirmed.

Была обобщена система дифференциальных уравнений Феистеля и Эбелинга. Были рассмотрены некоторые новые случаи формальной кинетики с двумя внутренними компонентами, которые представляют собой граничное циклическое поведение. На основе численного интегрирования детерминистических моделей этих реакций был подтвержден осциллирующий характер систем.

INTRODUCTION

Exotic phenomena of complex chemical systems are in the center of experimental and theoretical investigations. The most important exotic kinetic behavior is the limit cycle behavior, because it is supposed that by them one can explain oscillatory phenomena in biological systems.

Based on a literature survey, it seems to us that the small number of systems showing limit cycle behavior hinder the investigations. The authors use only two or three different models. These models certainly cannot describe all experimental data exactly. Our aim in the present paper is to give a method to construct many kinds of systems with two internal components leading to a limit cycle.

MAIN TOOLS

A general study of limit cycle behavior was made by Feistel and Ebeleing /2/. They studied the oscillatory behavior of complex chemical reactions in some cases. One of the main tools they used is the following (for details, see Ref. /6/, Section 6.5):

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Theorem 1. A system of two differential equations (henceforth system of DE) leads to limit cycle only if

$$\text{tr } A > 0$$

$$\text{tr}^2 A - 4 \det A \leqslant 0$$

where A is the coefficient matrix of the linearized form around the stationary point of the equations.

Our other tools will be the following theorems:

Theorem 2. The zero deficiency theorem /1/.

Theorem 3. The Volpert-theorem /11/.

Theorem 4. The Hanusse–Tyson–Light theorem /3, 10/.

The following system of DE for modelling a class of chemical reactors has been postulated in Ref. /2/:

$$\dot{x} = y \cdot g(x) - b(x) - x \tag{1a}$$

$$\dot{y} = 1 - y \cdot g(x) + b(x) \tag{1b}$$

This model has two advantages:

(i) it is easy to calculate the coordinates of the stationary point;

(ii) a special form of this model is the well known Brusselator model with dimensionless concentration and time.

This system is the starting point of our analysis.

RESULTS

When constructing a more complex model our aim was to save the easy computability of the coordinates of stationary point(s).

Our system of DE is:

$$\dot{x} = g(y) \cdot f(x) - b(x) + k(x) [h(y) - x \cdot c(y) - l(x)] + l(x) \tag{2a}$$

$$\dot{y} = -g(y) \cdot f(x) + b(x) - h(y) + c(y) \cdot k(x) \tag{2b}$$

In the stationary point(s) $\dot{x} = \dot{y} = 0$. From this condition we get

$$x_0 = 1 + \frac{[h(y_0) - l(x_0)] [k(x_0) - 1]}{k(x_0) \cdot c(y_0)}$$

Obviously, if we choose usual functions, the value x_0 will not be easy to handle, and changing the functions h, l, k, c we can obtain more than one stationary points.

If we want to have the simplest case of $x_0 = 1$, we can take two choices:

$$\text{(a)} \quad h(y_0) = l(x_0)$$

$$\text{(b)} \quad k(x_0) = 1$$

Having chosen either (a) or (b) we can calculate the y_0 value too, and knowing these two values, we can apply Theorem 1.

If we choose $k(x) = 0$, we obtain a system of DE fulfilling condition (a). This is the general form of two well-known systems of DE: Brusselator and Lotka–Volterra mechanism. It has been mentioned that the Lotka–Volterra model, which exhibits conservative oscillations – and does not lead to limit cycle – is a special case of system (2).

The system with $k(x) = 1$ is a more simple generalization of the system by Feistel and Ebeling.

In the case of $k(x) = x$ we can easily get more than one stationary points (in the simplest case we get two) by appropriately choosing the functions h, l, c.

Our system of DE can be applied not only for modelling chemical systems, but it may be useful in mathematics and physics as well. In chemical applications, the system of DE has to comply with the requirements of reaction kinetics.

THE MODELS

Let us see what systems we obtain if we have different functions in (2).

The new complex chemical reactions are (X and Y are the internal components; A, B, C symbolize external components in the systems):

Our systems fulfill the conditions of Theorem 1, are of positive deficiency, have a cyclic Volpert graph and are either non-conservative or their elementary reactions have a molecularity not more than three. (The numerical solution and trajectories of these DE are shown in Figs 1–6).

Our results are complementary to those by Schnakenberg /7/ as far as he treats reversible reactions only, whereas all of our models are irreversible (sometimes with reversible steps). However, all of our models contain one of the complex chemical reactions obtained from his replacing some of his elementary reactions by irreversible steps.

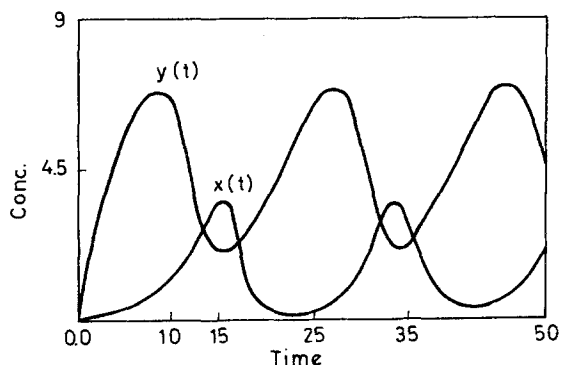|		A1	A2	A3
Models		$A \to Y$	$X \rightleftharpoons Y$	$A \rightleftharpoons X$
		$X \to B$	$X + Y \to X + A$	$B \to Y$
		$Y \to X$	$X + Y \to Y + B$	$X \rightleftharpoons Y$
		$2X \to Y + C$	$2X + Y \to 3X$	$2X + Y \rightleftharpoons 3X$
		$2X + Y \to 3X$	$2X \to Y + X$	$X + Y \rightleftharpoons 2X$
			$C + Y \to 2Y$	
Functions	$k(x)$	0	1	x
	$b(x)$	$0.1x^2$	$0.4x^2 + 0.15x$	$0.04x^3 + 0.07x^2$
	$f(x)$	$0.1x^2 + 0.05$	$0.6x^2 + 0.2x$	$0.11x^2 + 0.02x + 0.02$
	$l(x)$	$-x$	0	$0.07 - 0.1x$
	$c(y)$	0	y	0.1
	$g(y)$	y	y	y
	$h(y)$	-1	$0.3y$	-0.93
The FHJ graph of the system		$2X \quad Y \leftarrow \sigma$ $\downarrow \quad \downarrow \quad \nearrow$ $X + Y \quad X$ $2X + Y \to 3X$	$2X \to X + Y \to X$ $\searrow \quad \nearrow$ $2Y \leftarrow Y$ $2X + Y \to 3X$	σ $\downarrow \quad \searrow$ $Y \rightleftharpoons X$ $X + Y \rightleftharpoons 2X$ $2X + Y \rightleftharpoons 3X$
Stationary points	x_0	1.00	1.00	1.00
	y_0	7.33	5.50	7.60
Deficiency		2	3	2
tr **A**		0.117	1.155	0.314
tr^2 **A**-4det**A**		-0.586	-0.358	-0.501

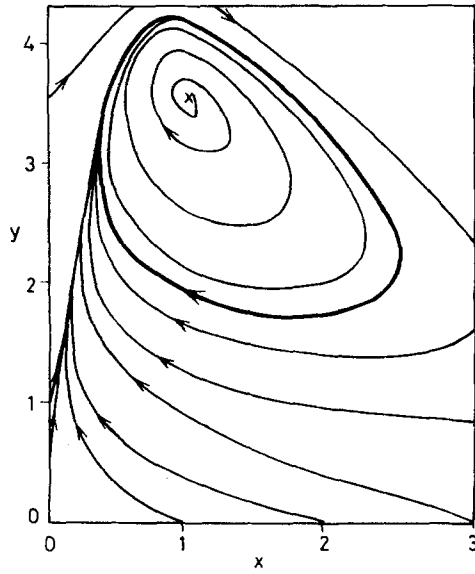Fig. 1. Concentration vs. time diagram of system (A1)

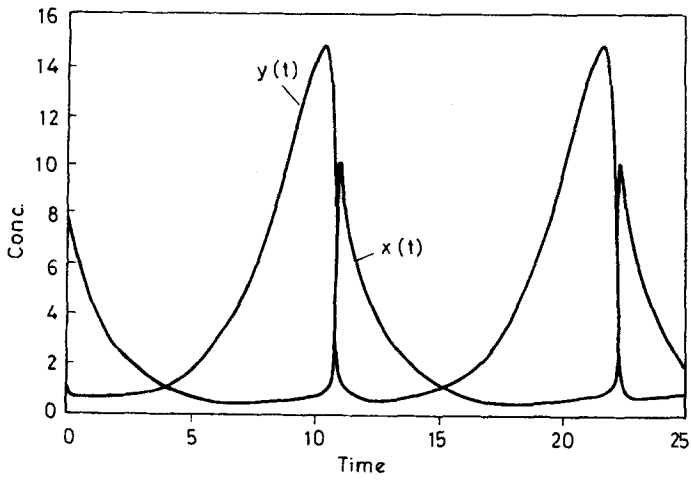Fig. 2. Trajectories of system (a1) in the neighborhood of the limit cycle

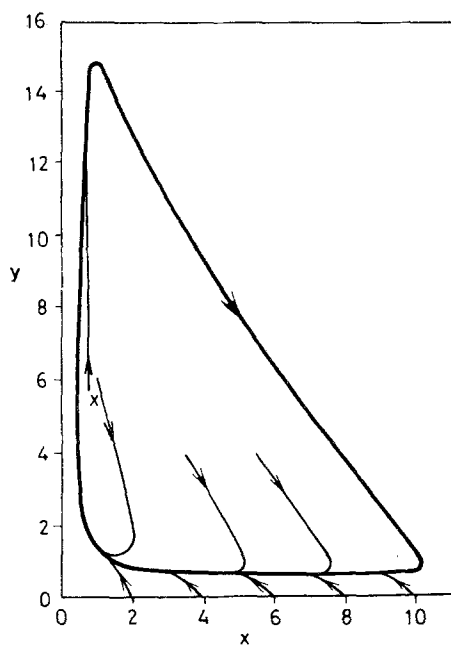Fig. 3. Concentration vs. time diagram of system (A2)

Fig. 4. Trajectories of system (A2) in the neighborhood of the limit cycle
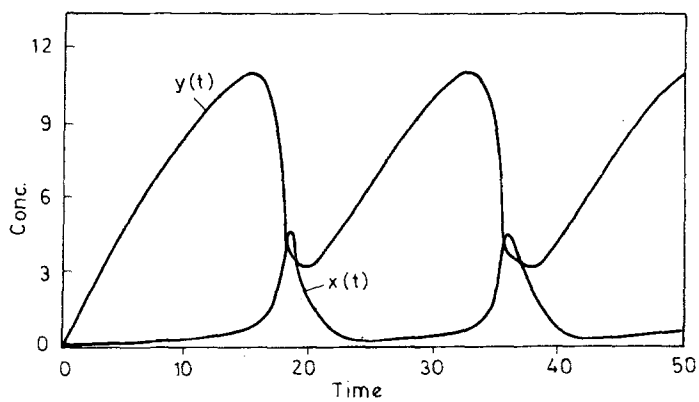

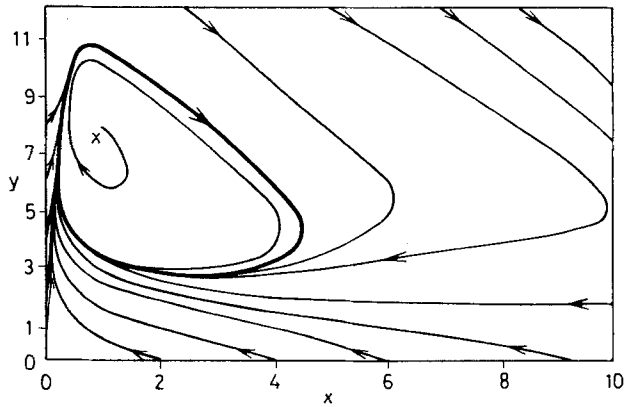Fig. 5. Concentration vs. time diagram of system (A3)

Fig. 6. Trajectories of system (A3) in the neighborhood of the limit cycle

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