A BISTABLE KINETIC SYSTEM WITH OSCILLATIONS ON THE THERMODYNAMIC AND FLOW-THROUGH BRANCHES

Antonín TOCKSTEIN

Department of Physical Chemistry,
Institute of Chemical Technology, 532 10 Pardubice

A model of a flow-through perfectly stirred reactor comprising three consecutive competitive reactions with parallel reactions of some intermediates and exhibiting bistable behaviour and possessing regions with an oscillatory character on the thermodynamic branch is treated. The stationary concentration *vs* parameter dependence is of the fourth degree and the characteristic equation, of the fifth degree.

The situation, where the mathematical solution of the stationary concentrations in a kinetic system leads to a cubic equation possessing three real roots over a certain parameter region and where the branches corresponding to the existence of a single root (the so-called thermodynamic branch and flow-through branch) are stable, is referred to as bistability. This behaviour has been described by Schlögel[1] for a system with a single time-variable reaction component, and by Edelstein[2] and Vidal[3] for two time-variable reaction components. The degree of the characteristic equation, whose roots determine the stability of the system, is given by the number of time-variable reaction components. For one or two reaction components, the characteristic equations are of the first and second degrees, respectively, hence a simultaneous existence of real and complex roots is not feasible. If, however, the characteristic equation is of the third or a higher degree, the possibility of the simultaneous occurrence of real and complex roots exists, and this may result in oscillations over a certain region of the thermodynamic and flow-through branches. Such behaviour has been observed recently by Nagy and Treindl[4] for the reaction of permanganate with hydrogen peroxide in a stirred flow-through reactor.

Since this behaviour has not been so far treated in terms of a model kinetic system, this treatment is the objective of the present work.

THEORETICAL

For a system of kinetic equations

$$dc_i/dt = f_i(c_j, p) \quad (i = 1, ..., n \,; \quad j = 1, ..., n) \tag{1}$$

with a parameter p, the limiting (turning) points on the curve of dependence of the stationary concentration c_i^0 on the parameter p $(C^0{}_j = f(p)$ curve) are associated[5] with a zero value of det $\mathbf{G}\{\partial f_i/\partial c_j\}$ where $\mathbf{G}\{\partial f_i/\partial c_j\}$ is the Jacobi matrix in the stationary points of the system (1). Since the absolute term of the characteristic equation

$$\sum_{k=0}^{n} a_{n-k}\lambda^k = 0$$

for the eigenvalues λ of matrix $\mathbf{G}$ is equal to det $\mathbf{G}$, for a bistable system some real eigenvalues of matrix $\mathbf{G}$ change their sign in the limiting points. For the particular case of a bistable system where the $c_i^0(p)$ dependence is cubic this implies that along the entire thermodynamic branch as well as along the entire flow-through branch, as far as the limiting points, all the real eigenvalues are negative.

If the kinetic system is such that the existence of both real roots and complex conjugate roots is permitted by the characteristic equation and that in some points of the thermodynamic and flow-through branches the real part of a pair of complex roots passes zero, the requirements of Hopf's bifurcation[6] are satisfied and oscillatory behaviour appears on the given branch.

The conditions for the occurrence of two pure imaginary roots can be formulated in terms of coefficients of the characteristic equation, and they are in a way connected with the violation of some of the Hurwitz's stability conditions[7] (see Table I).

For quadratic and cubic polynomials the calculation of the conditions in the third column in Table I is straightforward. For a fourth degree polynomial, if the roots are λ_1, λ_2, $\lambda_{3,4} = \pm ib$, we have

$$a_4 = \lambda_1\lambda_2 b^2 \qquad a_3 = -(\lambda_1 + \lambda_2) b^2 \qquad\qquad (2a, b)$$

$$a_2 = \lambda_1\lambda_2 + b^2 \qquad a_1 = -(\lambda_1 + \lambda_2) \qquad\qquad (2c, d)$$

so that

$$a_3(a_1 a_2 - a_0 a_3) - a_4 a_1^2 = (\lambda_1 + \lambda_2)(\lambda_1\lambda_2)(\lambda_1 + \lambda_2) b^2 -$$
$$- (\lambda_1 + \lambda_2)^2 (\lambda_1\lambda_2) b^2 = 0. \qquad\qquad (3)$$

It is clear from Table I that in each row, the penultimate expression is always nullified with the existence of a pair of pure imaginary roots.

Zero values of the expressions in the last column in Table I are both sufficient and necessary for the existence of two pure imaginary conjugate roots. Frequently, however, it suffices to consider conditions sufficient for stability breakdown; for instance, for a cubic polynomial with a positive a_3 a sufficient condition is $a_2 = 0$, and for a fourth degree polynomial with a positive a_4, $a_3 = 0$ or $a_2 = 0$ is sufficient.

Since the partial derivatives $\partial f_i/\partial c_j$ in the stationary point are functions of the stationary concentration c^0 of the reaction component under consideration and of

TABLE I
Conditions for pure imaginary roots

Polynomial degree	Hurwitz's stability conditions	Zero real part of a pair of complex roots requires
2	$a_1 > 0$, $a_1 a_2 > 0$	$H_1 \equiv a_1 = 0$, $a_2 > 0$
3	$a_1 > 0$, $a_1 s_2 - a_3 a_0 > 0$, $a_3(a_1 a_2 - a_3 a_0) < 0$	$H_2 \equiv a_1 a_2 - a_3 a_0 = 0$
4	$a_1 > 0$, $a_1 a_2 - a_3 a_0 > 0$, $a_3(a_1 a_2 - a_3 a_0) - a_4 a_1^2 > 0$, $[a_3(a_1 a_2 - a_3 a_0) - a_4 a_1^2]\, a_4 > 0$	$H_3 \equiv a_3(a_1 a_2 - a_3 a_0) - a_4 a_1^2 = 0$
5	$a_1 > 0$, $\begin{vmatrix} a_1 & a_0 \\ a_3 & a_2 \end{vmatrix} > 0$, $\begin{vmatrix} a_1 & a_0 & 0 \\ a_3 & a_2 & a_1 \\ a_5 & a_4 & a_3 \end{vmatrix} > 0$, $\begin{vmatrix} a_1 & a_0 & 0 & 0 \\ a_3 & a_2 & a_1 & a_0 \\ a_5 & a_4 & a_3 & a_2 \\ 0 & 0 & a_5 & a_4 \end{vmatrix} > 0$, $\begin{vmatrix} a_1 & a_0 & 0 & 0 & 0 \\ a_3 & a_2 & a_1 & a_0 & 0 \\ a_5 & a_4 & a_3 & a_2 & a_1 \\ 0 & 0 & a_5 & a_4 & a_3 \\ 0 & 0 & 0 & 0 & a_5 \end{vmatrix} > 0$	$H_4 \equiv (a_3 a_4 - a_5 a_2)(a_1 a_2 - a_0 a_3) -$ $- (a_1 a_4 - a_0 a_5)^2 = 0$

the parameter p, the coefficients of the characteristic equation a_i also depend on these variables, and so the zero values of the expressions in the last column in Table I determine a certain curve of dependence of the stationary concentration on parameter p (the $c^0 = g(p)$ curve). The points of intersection of the $c^0 = f(p)$ and $c^0 = g(p)$ curves then correspond to a state where the stationary concentration c^0 and parameter p admit the existence of a pair of pure imaginary roots; in their neighbourhood the conditions of Hopf's theorem are satisfied and concentration oscillations will appear.
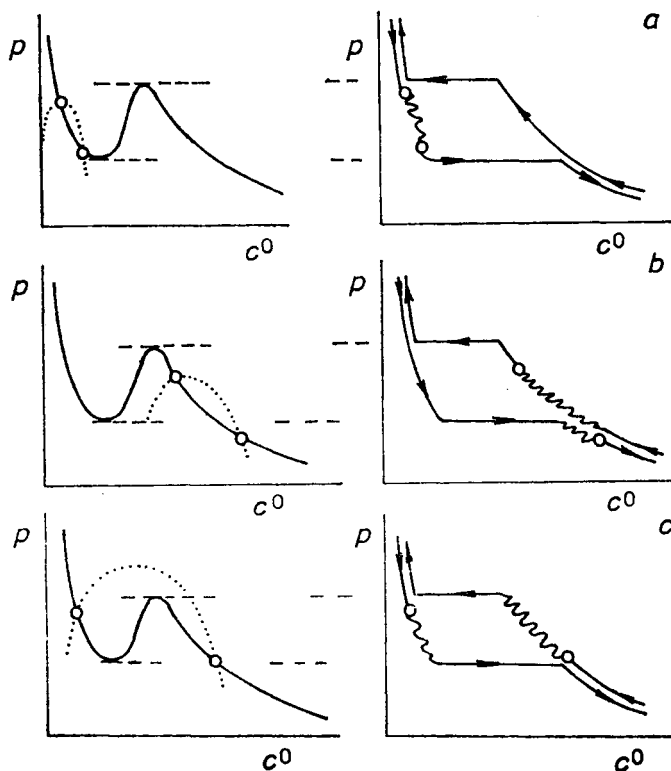

FIG. 1

Schematic illustration of the mutual position of $c^0 = f(p)$ and $c^0 = g(p)$ curves. In the left column, the two curves are shown in full and dotted lines, respectively, the points of their intersection are represented by open circles, the level of the turning points is shown by dashed line. In the right column, the resulting behaviour of the stationary concentration is given in dependence on parameter; the hysteresis and regions where oscillations exist are shown. For illustration, the branches off the hysteresis region are shown separately for the two directions although in reality hey coincide

The various alternative that can take place depend on the mutual position of the $c^0 = f(p)$ and $c^0 = g(p)$ curves as are shown in Fig. 1.

Since for a bistable system the side (thermodynamic and flow-through) branches of the $c^0 = f(p)$ curve are stable (the real parts of the eigenvalues are all negative), an even number of points of intersection of the $c^0 = f(p)$ and $c^0 = g(p)$ curves must exist: In one point the instability (oscillation) commences and in another it must terminate. Because the instable central branch of the saddle-shaped $c^0 = f(p)$ curve actually cannot be reached, the attainment of the turning point is followed by a jump from the thermodynamic branch to the flow-through branch and *vice versa*, which is associated with a hysteresis according to the direction of the change in parameter p. According to the mutual position of the $c^0 = f(p)$ and $c^0 = g(p)$ curves, oscillations can take place either on the thermodynamic branch solely or on the flow-through branch solely or on both, or else no oscillations will appear if the two curves do not intersect.

Kinetic Model

For illustrating the above thoeretical treatment, we shall consider a perfectly stirred flow-through reactor of a volume V to which a solution of substance A and reagent P are fed. The concentration of substance A is a, its flow rate is $\bar{v}$. This substance is transformed by reagent P in four steps $(1, 2, 3, 4)$ consecutively into products B, C, D, E, F by a series of consecutive reactions. Reagent P is assumed to be present in such an excess that its concentration can be regarded as pseudoconstant. The substances are removed from the reactor all at a flow rate $\bar{w}$. Furthermore, the reactants are assumed to mutually react by second order reactions as follows:

$$D + F = 2E \quad (\text{step } 5) \tag{A}$$

$$A + D = B + C \quad (\text{step } 6) \tag{B}$$

$$B + D = 2C \quad (\text{step } 7). \tag{C}$$
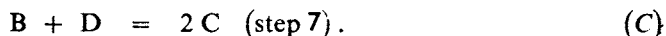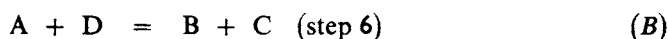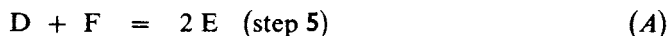
The entire process can be expressed schematically (Scheme 1)
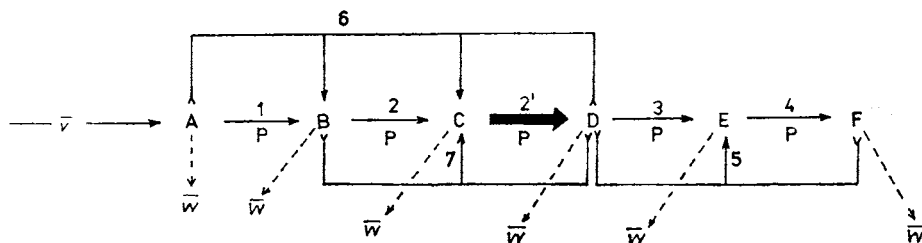
SCHEME 1

and described by kinetic equations (where $v = \bar{v}a/V$, $w = \bar{w}/V$, and the symbols $A - F$, P denote the respective concentrations) as follows:

$$dA/dt = v - k_1PA - k_6AD - wA \tag{4a}$$

$$dB/dt = k_1PA + k_6AD - k_7BD - k_2PB - wB \tag{4b}$$

$$dC/dt = k_2PB + 2k_7BD - k_2'PC + k_6AD \tag{4c}$$

$$dD/dt = -k_7BD - k_6AD + k_2'PC - k_3PD - k_5DF - wD \tag{4d}$$

$$dE/dt = 2k_5DF + k_3PD - k_4PE - wE \tag{4e}$$

$$dF/dt = -k_5DF + k_4PE - wF . \tag{4f}$$

Moreover, step 2′ is assumed to be so fast that the concentration of substance C is in a steady state and negligibly low, so that the term wC approaches zero.

Considering this steady state and introducing the relative concentrations $\alpha = A/\bar{a}$, $\vartheta = D/\bar{a}$, $\varepsilon = E/\bar{a}$, $\varphi = F/\bar{a}$, $\beta = B/\bar{a}$, where $\bar{a} = a\bar{v}/\bar{w}$, and dimensionless quantities $tu = \tau$, $w/u = f$, $k_1P/u = r$, $k_2P/u = h$, $k_3P/u = m$, $k_4P/u = n$, $k_5/k = \xi$, $k_6/k = \Delta$, $k_7/k = \gamma$ (where $u = kv/w$ and $k = 1 \, \mathrm{dm^3 \, mol^{-1} \, s^{-1}}$) we obtain five differential equations for relative concentrations of reactants A, B, D, E, F:

$$d\alpha/d\tau = f - r\alpha - \Delta\alpha\vartheta - f\alpha \tag{5a}$$

$$d\beta/d\tau = r\alpha + \Delta\alpha\vartheta - \gamma\beta\vartheta - h\beta - f\beta \tag{5b}$$

$$d\vartheta/d\tau = h\beta + \gamma\beta\vartheta - m\vartheta - \xi\vartheta\varphi - f\vartheta \tag{5c}$$

$$d\varepsilon/d\tau = 2\xi\vartheta\varphi + m\vartheta - n\varepsilon - f\varepsilon \tag{5d}$$

$$d\varphi/d\tau = -\xi\vartheta\varphi + n\varepsilon - f\varphi . \tag{5e}$$

For concentrations in the stationary state we have

$$\alpha^0 = f/(r + f + \Delta\vartheta^0) \tag{6a}$$

$$\beta^0 = \alpha^0(r + \Delta\vartheta^0)/(h + f + \gamma\vartheta^0) \tag{6b}$$

$$\varepsilon^0 = \varphi^0(\xi\vartheta^0 + f)/n \tag{6c}$$

$$\varphi^0 = nm\vartheta^0/[f(n + f) + \xi\vartheta^0(f - n)] \tag{6d}$$

and the balance condition

$$\alpha^0 + \beta^0 + \vartheta^0 + \varepsilon^0 + \varphi^0 = 1 \tag{7}$$

In the following treatment, we shall keep the stationary concentration ϑ^0 as the only variable; substituting α^0, β^0, ε^0, φ^0 from Eqs (6a,b,c,d) in Eq. (7) an equation of

fourth degree is obtained for the relative stationary concentration of the product D in the form

$$(\vartheta^0)^4 \, b_0 + (\vartheta^0)^3 \, b_1 + (\vartheta^0)^2 \, b_2 + \vartheta^0 b_3 + b_4 = 0 \tag{8}$$

$$b_0 = \xi(f - n + m) \tag{9a}$$

$$b_1 = (f + m)(f + n) + \left[(h + f)/\gamma + (r + f)/\varDelta - 1\right] \xi(f - n + m) + m\xi \tag{9b}$$

$$b_2 = \left[(h + f)/\gamma + (r + f)/\varDelta - 1\right](f + n)(f + m) + m(f + n) +$$
$$+ \xi(f - n + m)\left[(r + f)(h + f)/(\gamma\varDelta) - r/\varDelta - h/\gamma\right] + m\xi(r/\varDelta + h/\gamma) \tag{9c}$$

$$b_3 = \left[(r + f)(h + f)/(\gamma\varDelta) - h/\gamma - r/\varDelta\right](f + n)(f + m) -$$
$$- \xi(f - n) \, rh/(\gamma\varDelta) + m(n + f)(r/\varDelta + h/\gamma) \tag{9d}$$

$$b_4 = -f(f + n) \, rh/(\gamma\varDelta) \tag{9e}$$

Eq. (8) represents the dependence of the relative stationary concentration of component D on the variable parametr f which is determined by the outflow rate w (Fig. 2). The ϑ^0–f dependence decomposes into two curves from which only one has a physical meaning. The second curve represents physically inadmissible roots

FIG. 2
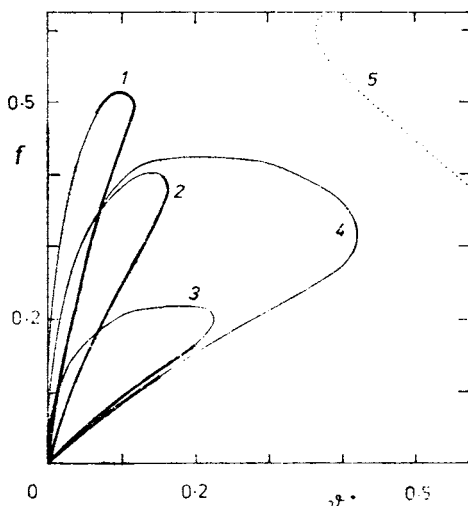
Dependence of parametr f on the relative stationary concentration of component D. Parameters $h = r = 0.001$, $n = \varDelta = 1$, $m = 0.01$, parameters γ and ξ are as follows: *1* 10, 10; *2* 4, 4; *3* 1, 1; *4* 4, 1; *5* inadmissible roots for curve *1*

(for example $\vartheta^0 \to 1$ for $f \to 0$). For suitably chosen r, h, m, n, ξ, γ, Δ the f–ϑ^0 curve displays a region where three positive roots ϑ^0 exist for a chosen f.

The stability of the stationary points on the saddle shaped f–ϑ^0 curve will be considered based on the characteristic equation. For the kinetic system under study the partial derivatives of the reaction rates are

$$\partial\dot\alpha/\partial\alpha = -r - \Delta\vartheta^0 - f = -f/\alpha^0 \tag{10a}$$

$$\partial\dot\alpha/\partial\beta = 0 \tag{10b}$$

$$\partial\dot\alpha/\partial\vartheta = -\Delta\alpha^0 \tag{10c}$$

$$\partial\dot\alpha/\partial\varepsilon = 0 \tag{10d}$$

$$\partial\dot\alpha/\partial\varphi = 0 \tag{10e}$$

$$\partial\dot\beta/\partial\alpha = r + \Delta\vartheta^0 \tag{11a}$$

$$\partial\dot\beta/\partial\beta = -h - f - \gamma\vartheta^0 = -(r + \Delta\vartheta^0)\,\alpha^0/\beta^0 \tag{11b}$$

$$\partial\dot\beta/\partial\vartheta = \Delta\alpha^0 - \gamma\beta^0 \tag{11c}$$

$$\partial\dot\beta/\partial\varepsilon = 0 \tag{11d}$$

$$\partial\dot\beta/\partial\varphi = 0 \tag{11e}$$

$$\partial\dot\vartheta/\partial\alpha = 0 \tag{12a}$$

$$\partial\dot\vartheta/\partial\beta = h + \gamma\vartheta^0 \tag{12b}$$

$$\partial\dot\vartheta/\partial\vartheta = \gamma\beta^0 - m - f - \xi\varphi^0 = -h\beta^0/\vartheta^0 \tag{12c}$$

$$\partial\dot\vartheta/\partial\varepsilon = 0 \tag{12d}$$

$$\partial\dot\vartheta/\partial\varphi = -\xi\vartheta^0 \tag{12e}$$

$$\partial\dot\varepsilon/\partial\alpha = 0 \tag{13a}$$

$$\partial\dot\varepsilon/\partial\beta = 0 \tag{13b}$$

$$\partial\dot\varepsilon/\partial\vartheta = 2\xi\varphi^0 + m = \varepsilon^0(n + f)/\vartheta^0 \tag{13c}$$

$$\partial\dot\varepsilon/\partial\varepsilon = -n - f \tag{13d}$$

$$\partial\dot\varepsilon/\partial\varphi = 2\xi\vartheta^0 \tag{13e}$$

$$\partial\dot\varphi/\partial\alpha = 0 \tag{14a}$$

$$\partial\dot\varphi/\partial\beta = 0 \tag{14b}$$

$$\partial\dot\varphi/\partial\vartheta = -\xi\varphi^0 \tag{14c}$$

$$\partial\dot\varphi/\partial\varepsilon = n \tag{14d}$$

$$\partial\dot\varphi/\partial\varphi = -f - \xi\vartheta^0 = -n\varepsilon^0/\varphi^0 \tag{14e}$$

so that the characteristic equation is

$$
\begin{vmatrix}
-(f/\alpha^0 + \lambda) & 0 & -\Delta\alpha^0 & 0 & 0 \\
r + \Delta\vartheta^0 & [(r + \Delta\vartheta^0)\,\alpha^0/\beta^0 + \lambda] & \Delta\alpha^0 - \gamma\beta^0 & 0 & 0 \\
0 & h + \gamma\vartheta^0 & -(h\beta^0/\vartheta^0 + \lambda) & 0 & -\xi\vartheta^0 \\
0 & 0 & 2\xi\varphi^0 + m & -(n + f + \lambda) & 2\xi\vartheta^0 \\
0 & 0 & -\xi\varphi^0 & n & -(n\varepsilon^0/\varphi^0 + \lambda)
\end{vmatrix} = 0 \quad (15)
$$

which gives an equation of the fifth degree in λ:

$$
\lambda^5 + a_1\lambda^4 + a_2\lambda^3 + a_3\lambda^2 + a_4\lambda + a_5 = 0 . \tag{16}
$$

The side branches of the ϑ^0-f curve *i.e.* for $f \to \infty$, $\vartheta^0 \to 0$, $\alpha^0 \to 1$ or for $f \to 0$, $\vartheta^0 \to 0$, $\varphi^0 \to 0$, are stable. In the former case this follows from the fact that under these conditions, where $\varphi \approx 0$, $\beta^0 \approx 0$, $h\beta^0/\vartheta^0 \approx n + f$, $n\varepsilon^0/\varphi^0 \approx f$, $(r + \Delta\vartheta^0)\,\alpha^0/\beta^0 \approx h + f$, Eq. (15) can be simplified to

$$
(f + \lambda)(n + f + \lambda)\{(f + \lambda)\,[(f + h + \lambda)(n + f + \lambda) - h] - rh\} = 0 \quad (17)
$$

so that for $f \gg n$, $f \gg h$ all roots are negative: $\lambda_{1,2} = -f$, $\lambda_{3,4} = \pm\sqrt{h} - f$, $\lambda_5 = r - f$.

In the latter case, the stability follows from the form of the determinant (15), where for $f \to 0$ all the elements above the diagonal are zeroes, so that the determinant can be written as the product

$$
(f + \lambda)^2 \cdot (h + f) \cdot (n + f)^2 = 0 \tag{18}
$$

whose roots are all negative.

Inasmuch as the real roots can only change their sign in the limiting turning points of the f-ϑ^0 curve and lead to instability of the central branch of the saddle-shaped curve, the question remains to be answered as to whether no instability can take place off this centrale part of the saddle due to the occurrence of complex conjugate roots with a positive real part, hence by nullification of the expression $H_4 \equiv \equiv (a_3a_4 - a_5a_2)(a_1a_2 - a_0a_3) - (a_1a_4 - a_0a_5)^2$.

We have numerically calculated the term H_4 for individual points on the f-ϑ^0 curves and those regions whose points give $H_4 < 0$ are presented as heavy lines

in Fig. 2. Those regions which are outside of saddle fulfill the conditions of the undamped oscillations. By numerical integration of Eqs $(5a-f)$ these oscillations have been verified. For example the parameters $r = 0.02$, $h = m = 0.002$, $n = \Delta = 0.7$, $\gamma = \xi = 10$, $f = 0.3$ give amplitude of $\vartheta^0 = 0.43$ in distances of 44 units of τ.

REFERENCES

1. Schlögel F.: Z. Phys. *248*, 446 (1971).
2. Edelstein B. B.: J. Theor. Biol. *29*, 57 (1970).
3. Vidal Ch.: C. R. Acad. Sci., C *275*, 523 (1972).
4. Nagy A., Treindl L.: Lett. Nature *320*, 344 (1986).
5. Kubíček M.: *Numerické algoritmy řešení chemicko-inženýrských úloh*. Published by SNTL — Nakladatelství technické literatury, Prague 1983.
6. Holodniok M., Klíč A., Kubíček M., Marek M.: *Metody analýzy nelineárních dynamických modelů*. Academia, Prague 1986.
7. Schwarz Š.: *Základy nauky o riešení rovníc*. Published by Vydavateľstvo Slovenskej akadémie vied, Bratislava 1967.

Translated by P. Adámek.