Note

EXACT NECESSARY CONDITIONS FOR OSCILLATORY BEHAVIOUR IN A CLASS OF CLOSED ISOTHERMAL REACTION SYSTEMS

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Abstract

In this note we present analytically proved necessary conditions for the occurrence of oscillatory behaviour in an important class of closed isothermal reaction systems. The classical Lotka scheme with the uncatalyzed reaction path included and the full Autocatalator scheme are chosen as representative examples.

In this note we present a possible solution to an analytically unsolved problem in the investigations of the Leeds group [1–4] on the closed and isothermal variant of the Autocatalator model. For the sake of generality, we shall consider the reaction system

$$\mathrm{P} \to \mathrm{X} \qquad r = k_0 p, \tag{1a}$$

$$a\mathrm{X} + b\mathrm{Y} \to c\mathrm{Y} \qquad r = f(x)y^n, \quad c > b, \quad n \geq 1, \tag{1b}$$

$$a\mathrm{X} \to (c-b)\mathrm{Y} \qquad r = g(x), \tag{1c}$$

$$\mathrm{Y} \to \mathrm{Q} \qquad r = k_2 y, \tag{1d}$$

where n is an integer; the functions f and g describing the various reaction rates are continuously differentiable for $x \geq 0$ and satisfy the following (natural) requirements: (a) $f(0) = 0$ and $g(0) = 0$; (b) $f'(x) > 0$ and $g'(x) \geq 0$ if $x > 0$. These conditions imply the validity of the formulas $f(x) > 0$ and $g(x) \geq 0$ if $x > 0$. Since g can vanish, the case when reaction (1c) is missing is also included. When the reaction vessel is closed to matter transport and the temperature is constant, the concentration changes of the key species in the general scheme (1a)–(1d) are described by the differential equations

$$x'(t) = k_0 p_0 \mathrm{e}^{-k_0 t} - af(x(t))y^n(t) - ag(x(t)), \tag{2a}$$

$$y'(t) = (c-b)f(x(t))y^n(t) + (c-b)g(x(t)) - k_2 y(t), \tag{2b}$$

the right-hand sides of which are defined for $t \geq 0$, $x(t) \geq 0$ and $y(t) \geq 0$. A reaction scheme given by eqs. (1) is said to be oscillatory in a closed and isothermal system if its differential equations have a solution with many extrema for appropriate values of the parameters. For example, the sets

$$\{a = b = 1;\; c = 2;\; n = 1;\; f(x) = k_1 x;\; g(x) = k_3 x\} \tag{3}$$

and

$$\{a = 1;\; b = 2;\; c = 3;\; n = 2;\; f(x) = k_1 x;\; g(x) = k_3 x\} \tag{4}$$

define two models with the above property, the classical Lotka model [5] with the uncatalyzed step included and the full Autocatalator model [1–4], respectively. On the basis of the earlier considerations and numerical calculations concerning the Autocatalator [1–4], it is clear that the oscillatory behaviour of the schemes in eqs. (1) crucially depends on the value of the k_0/k_2 ratio measuring the "distance" from the open state of the given reaction system. However, exact bounds for the k_0/k_2 values necessary for oscillatory behaviour have not yet been established in any special case of eqs. (1) and (2). Because of the central importance of the Autocatalator-like models, we believe that the following theorem makes a contribution to the theory of oscillations occurring in closed isothermal reaction systems.

THEOREM

Let $(x, y):[0, \beta) \to \mathbb{R}^2$ $(0 < \beta \leq +\infty)$ be a solution of eqs. (2a) and (2b), with $x(t) > 0$, $y(t) > 0$ for $t > 0$.

(a) If x has more than one local extremum, then

$$k_0/k_2 < n \tag{5a}$$

is valid.

(b) If y has more than two extrema, then

$$k_0/k_2 < 1 \tag{5b}$$

must be satisfied.

Equations (5a) and (5b) are necessary conditions for the occurrence of trains of oscillatory excursions in x and y. When they are satisfied with the sign $\ll$, we can say that the depletion of the reactants is slow and the system is in a "quasi-open" state.

In the proof of the theorem, we shall employ the following lemma inspired by ref. [6]:

LEMMA

Let $\upsilon:[0, \beta) \to \mathbb{R}$ and $\phi:[0, \beta) \to \mathbb{R}$ be differentiable and continuous functions, respectively. If the number of zeros of υ in $(0, \beta)$ is Z, the function w defined by

$$w(t) = \upsilon'(t) + \phi(t)\upsilon(t) \tag{6}$$

has at least $Z-1$ zeros there.

The proof is a straightforward generalization of that given in ref. [6].

Having this lemma, we can prove our theorem in an easy way. If we assume that x attains more than one local extremum, then x' has more than one zero in $(0, \beta)$. A brief calculation yields the formula

$$\begin{aligned} x''(t)+[a f'(x(t))y^n(t)+ag'(x(t))+k_0]x'(t) &= -a(k_0-nk_2)f(x(t))y^n(t) \\ -a(c-b)nf^2(x(t))y^{2n-1}(t) &-a(c-b)nf(x(t))g(x(t))y^{n-1}(t)-ak_0g(x(t)), \end{aligned} \tag{7}$$

the left-hand side of which vanishes for at least one value of t according to the lemma. If eq. (5a) were not valid, we would obtain a contradiction since the right-hand side of eq. (7) would be negative for $t > 0$. Thus, the statement concerning x has been proved.

In order to prove the statement concerning y, we start with the formula

$$\begin{aligned} &y''(t)+[k_2-(c-b)nf(x(t))y^{n-1}(t)+af'(x(t))y^n(t)+ag'(x(t))]y'(t) \\ &\quad =[f'(x(t))y^n(t)+g'(x(t))]\upsilon(t), \end{aligned} \tag{8}$$

where

$$\upsilon(t) = (c-b)x'(t)+ay'(t). \tag{9}$$

If y has more than two local extrema, y' has more than two zeros in $(0, \beta)$ and the lemma shows that the left-hand side of eq. (8) vanishes for at least two values of t. Since the multiplier of $\upsilon(t)$ on the right-hand side is positive for $t > 0$, υ must also have at least two zeros. By virtue of the lemma, the left-hand side of the equation

$$\upsilon'(t)+k_2\upsilon(t) = (c-b)[k_0p_0(k_2-k_0)\exp(-k_0t)-ak_2f(x)y^n-ak_2g(x)] \tag{10}$$

must have at least one zero. If eq. (5b) were not valid, the right-hand side would be negative for $t > 0$, and this would be a contradiction. Thus, the theorem has been completely proved.

The accuracy of eqs. (5) was briefly investigated using the full Autocatalator as a reference system. In the case of species X, the numerical solution of the corresponding differential equations showed that the bound given by eq. (5a) for $n = 2$ could be lowered by less than 2.5%. In the case of species Y, the same method yielded that the bound given by eq. (5b) could be lowered by less than 70%. Taking into account the simplicity and generality of our approach, these results are satisfactory.

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