React. Kinet. Catal. Lett., Vol. 9, No. 4, 377–381 (1978)

WHAT IS ESSENTIAL TO EXOTIC KINETIC BEHAVIOR?

J. Tóth

Computing Group, Semmelweis University Medical School, H-1089 Budapest, Kulich Gy. tér 5

Received April 27, 1978
Accepted July 24, 1978

If the complex vectors of a chemical mechanism are independent, the deficiency of the mechanism is zero. Some nonlinear systems without autocatalysis, autoinhibition and cooperativity are shown to have this property and, therefore, to have a unique equilibrium point that is globally asymptotically stable if weak reversibility is fulfilled.

Если комплексные векторы химического механизма являются независимыми, то дефицитность механизма равна нулю. Было показано, что некоторые нелинейные системы без автокатализа, автоингибирования и кооперативности обладают этим свойством, поэтому они имеют уникальную точку равновесия, которая является глобально асимптотически стабильной, если выполняется условие слабой обратимости.

INTRODUCTION AND MAIN RESULT

The aim of the present paper is to bring into connection the modern theory of formal reaction kinetics and some old vague beliefs. Our method is to give a sufficient condition for $\delta = 0$, a fact implying – together with weak reversibility – the existence, uniqueness and global asymptotic stability of the equilibrium point, therefore excluding periodicity and multistationarity.

We use mainly the notions and notations introduced by Feinberg, Horn and Jackson /1/.

Let the chemical components of the mechanism be $A(1), \ldots, A(M)$, the complexes

$$C(n) = \sum_{m=1}^{M} y^m(n) A(m) \qquad (n = 1, 2, \ldots, N) \tag{1}$$

Therefore, the complex vectors of stoichiometric coefficients are

$$y(n) = [y^1(n), \ldots, y^M(n)]^T \qquad (n = 1, 2, \ldots, N) \tag{2}$$

The elementary reactions of the mechanism are

$$C(i) \longrightarrow C(j) \qquad (i \neq j,\ i, j = 1, 2, \ldots, N) \tag{3}$$

Let L be the number of the connected subgraphs of the directed graph obtained from the complexes as vertices and reactions as edges, i. e. L is the number of the (coarse) linkage classes. The reaction is weakly reversible, if the transitive closure or the relation determined by the above defined directed graph (the FHJ graph) is a symmetric relation. Let s be the dimension of the stoichiometric space S, where

$$S := \mathrm{span}\ \{y(j)-y(i); \qquad C(i) \longrightarrow C(j)\} \tag{4}$$

The deficiency δ of the mechanism is

$$\delta := N-L-s \tag{5}$$

THEOREM 1. The deficiency of a chemical mechanism with independent complex vectors – except possibly the zero vector corresponding to the empty complex – is zero.

Proof. At first, let us suppose that $L = 1$. Then s equals to the number of the edges of the spanning tree of the FHJ graph, i. e. $s = N-1$. Therefore $\delta = 0$.

In the general case let the number of complexes contained in the l-th linkage class ($l = 1, 2, \ldots, L$) be N_l, then the stoichiometric subspace S is the direct sum of subspaces $S_1, \ldots, S_L$, where the numbering may be chosen so that $\dim S_l = N_l - 1$. Therefore, $N = \sum_{l=1}^{L} N_l$, $s = \sum_{l=1}^{L} \dim S_l$, thus $\delta = 0$.

COROLLARIES

Immediate application of the zero deficiency theorem (see e.g. Ref. /1/) proves corollary 1.

COROLLARY 1. In a chemical mechanism with independent complex vectors – except possibly the zero vector –

(i) for arbitrary (not necessarily mass action) kinetics, there can exist an equilibrium concentration with positive coordinates only if the mechanism is weakly reversible;

(ii) if the mechanism is weakly reversible, then for mass action kinetics with any choice of positive reaction rate constants, there exists in each reaction simplex $c_0 + S$ a unique positive equilibrium concentration c^* every equilibrium concentration with positive coordinates is asymptotically stable relative to the reaction simplex in which it resides, and the kinetic equation $\dot{c} - f \cdot c$ cannot give rise to nontrivial sustained periodic solutions with positive coordinates.

A special case where the sufficient condition of the theorem is fulfilled will be obtained if all of the components occur in exactly one complex. In this case none of the components occurs as reactant and product in the same reaction:

$$\sum_{m=1}^{M} y^m(i) y^m(j) = 0 \tag{6}$$

what is equivalent to the exclusion of this special kind of autocatalysis and autoinhibition.

A further specialization provides the generalized compartment system, i.e. the system where it is also true that all of the complexes contain not more than one component. This means that only complexes of the form $y(m)\ A(m)$ $(m = 1, 2, \ldots, M)$ are allowed except perhaps the empty complex. (Compartment systems – often applied in biology – are obtained when all of the stoichiometric coefficients $y(m)$ are equal to 1 /2, 3/.

We may say that a certain kind of cooperativity is excluded in generalized compartment systems, because no (reactant) complex contains more than one kind of the different chemical components. In other words, this kind of nonlinearity excludes exotic behavior.

In the case of generalized compartment systems, exotic behavior can be excluded also for some further, not weakly reversible mechanisms using the results of Volpert /4/.

THEOREM 2. In every generalized compartment system having an acyclic FHJ graph and being endowed with arbitrary kinetics and not containing the zero complex

(i) the solution of the kinetic differential equation is bounded on $[0, +\infty]$;

(ii) the kinetic equations cannot give rise to nontrivial sustained periodic solutions with nonnegative coordinates;

(iii) there exists a unique nonnegative equilibrium concentration having at least one zero coordinate;

(iv) There exists a positive constant K such that

$$\int_0^\infty |\dot{c}_m| < K \qquad (m = 1, 2, \ldots, M) \tag{7}$$

where

$$c := (c_1, \ldots, c_M)^T,$$

and

$$|\dot{c}_m|(t) := |\dot{c}_m(t)| \quad /t \in (0, \infty);\ m=1; \ldots, M/.$$

Proof. The FHJ graph of a generalized compartment system is acyclic if and only if its Voplert graph (V graph, see below) is acyclic.

The Volpert graph of a chemical mechanism is a directed bipartite graph with multiple edges constructed as follows. Each elementary reaction and each chemical component is represented by a vertex from the two classes of vertices, respectively. The number of directed edges running from A(m) to the vertex representing the elementary reaction $C(i) \longrightarrow C(j)$ is $y^m(i)$ and the number of directed edges from the vertex representing this reaction to $A(k)$ is $y^k(j)$.

Our final - trivial - statement is theorem 3.

THEOREM 3. If the V graph of the reaction is acyclic, then eq. (6) holds.

ACKNOWLEDGEMENT

The author has greatly benefited from stimulating discussions with P. Érdi and V. Hárs. This work has been supported in part by the Scientific Research Council, Ministry of Health, Hungary (1-08-0201-03-0/FS).

REFERENCES

1. M. Feinberg: Mathamatical Aspects of Mass Action Kinetics. Chapter 1 of Chemical Reactor Theory: A Review (eds. N. Amundson and L. Lapidus). Prentice Hall, Englewood Cliffs 1977, and references therein.
2. J. A. Jacquez: Compartmental Analysis in Biology and Medicine, Elsevier Publ. Co., Amsterdam-London-New York 1972.
3. J. Tóth, P. Érdi: Models, Problems and Applications of Formal Reaction Kinetics (in Hungarian). A kémia ujabb eredményei, Vol. 41, Akadémiai Kiadó, Budapest (In press).
4. A. I. Volpert, S. I. Khudaev: Uravneniya Khimicheskoi Kinetiki, Gl. XII. "Analiz v klassakh razryvnykh funktsii i uravneniya matematicheskoi fiziki", p. 365. Nauka, Moskva 1975.