Contributions to the Theory of Mass Action Kinetics

III. Some Dynamic Properties of Second Order Mass Action Kinetics

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Second order mass action kinetics provide the simplest models of nonlinear reaction systems. Some of their dynamic properties, viz., location, number, and stability pattern of their critical points, will be analyzed. The occurrence of periodic and chaotic solutions of these systems is discussed.

1. Introduction

Mass action kinetics whose elementary reactions are of at most second order provide the simplest models of nonlinear chemical systems. Despite their simplicity, however, only few investigations deal with second order mass action kinetics in a systematic and general setting. In [1] Aris showed the connection between these kinetics and certain non-associative algebras. Jenks [2, 3] studied general multidimensional homogeneous differential equations which also describe mass action kinetics. In [4] Horn developed a graph theoretical method for second order kinetics which allows to determine the stability properties of a kinetics by inspecting a graph. In [5] it could be demonstrated that open and closed mass action kinetics can be considered within a common mathematical framework facilitating the investigation of the dynamic behavior of nonlinear kinetic systems.

The convenience of this mathematical setting will become clear in the following discussion of some qualitative dynamic properties of mass action kinetics. The aim of this note is to investigate the dynamic properties of mass action kinetics, viz. location, number, and stability pattern of their critical points.

First, conditions for the occurrence of boundary critical points and their stability properties will be discussed. Then it will be demonstrated that a wide class of mass action kinetics, namely weakly reversible ones (defined below), exhibit only unstable boundary critical points. These mass action kinetics will be analyzed further by using well-known algebro-geometrical and topological theorems (Bézout theorem, Poincaré-Hopf theorem). The result is a coarse classification of the qualitative dynamic behavior of second order mass action kinetics.

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2. Location and Stability of Critical Points

The dynamic behavior of open and closed second order mass action kinetics is completely described by the system of n autonomous differential equations on the reaction simplex $\hat{S}$

$$\dot{\boldsymbol{x}} = \boldsymbol{f}(\boldsymbol{x}), \quad \boldsymbol{x}(0) \in \hat{S}, \tag{1}$$

where the components f_i of the vector function f are homogeneous quadratic polynomials [5].

These f_i are defined by

$$f_i(\boldsymbol{x}) = \boldsymbol{x}^T \mathbf{Q}^i \boldsymbol{x}, \quad i \in \langle 1, n \rangle = \{1, 2, \ldots, n\} \tag{2}$$

where the $\mathbf{Q}^i$'s are n $n \times n$ matrices whose real constants q^i_{jk} satisfy

$$q^i_{jk} = q^i_{kj} \quad \text{for all } i, j, k \in \langle 1, n \rangle, \tag{3a}$$

$$q^i_{jk} \geqq 0 \quad \text{for all } j \neq i,\ k \neq i \in \langle 1, n \rangle, \tag{3b}$$

$$\sum_{i=1}^{n} q^i_{jk} = 0 \quad \text{for all } j, k \in \langle 1, n \rangle, \tag{3c}$$

$$q^i_{ii} \leqq 0 \quad \text{for all } i \in \langle 1, n \rangle. \tag{3d}$$

Here the x_i represent the reduced concentration of the reacting species X_i which satisfy the conservation condition

$$\sum_{i=1}^{n} x_i = 1. \tag{4}$$

It was shown [5] that every mass action kinetics with elementary reactions up to second order may be represented by the above given system of differential equations.

The same type of differential equations (without condition (3d)) was studied by Jenks [2, 3]. He showed [3] that the trajectories of (1) are confined to the reaction simplex

$$\hat{S} = \{\boldsymbol{x} \in R^n \mid \sum_{i=1}^{n} x_i = 1,\ x_i \geqq 0 \ \text{for all } i \in \langle 1, n \rangle\} \qquad (5)$$

if the initial values $\boldsymbol{x}(0)$ of (1) lie in $\hat{S}$.

The systems (1) may be classified according to the location of their critical points on the boundary $\partial\hat{S}$ of $\hat{S}$ (notion according to [2]).

A point $\boldsymbol{\xi} \in \hat{S}$ will be called *critical point* of (1) if $\boldsymbol{f}(\boldsymbol{\xi}) = \boldsymbol{0}$. It will be called *boundary critical point* if $\boldsymbol{\xi} \in \partial\hat{S} = \{\boldsymbol{x} \in \hat{S} \mid x_i = 0 \text{ for at least one } i \in \langle 1, n \rangle\}$, and i-th *vertex point* $\boldsymbol{\xi} = \boldsymbol{v}^i$ if $v_j{}^i = 0$, $j \neq i$, and $v_i{}^i = 1$.

System (1) will be called *nondegenerate* if there exists no subset $U \subset \langle 1, n \rangle$ such that $\sum_{i \in U} Q^i \geqq 0$ ($Q^i \geqq 0$ iff $q^i_{jk} \geqq 0$ for all $j, k \in \langle 1, n \rangle$).

System (1) will be called *completely positive* if for each $i \in \langle 1, n \rangle$

$$q^i_{il(i)} < 0 \qquad \text{for some } l(i), \quad \text{and}$$

$$q^i_{j(i)k(i)} > 0 \qquad \text{for some } j(i) \neq i,\ k(i) \neq i\,.$$

System (1) will be called *irreducible* if for each $\boldsymbol{x} \in \partial\hat{S}$, $x_i = 0$ implies the existence of a first non-vanishing derivative $\mathrm{d}^m/\mathrm{d}t^m f_i(\boldsymbol{x})$ which is positive and $0 \leqq m = m(\boldsymbol{x}, i) < 2^{n-2}$.

These three classes of systems relate to the location of critical points:

A nondegenerate system may have critical points anywhere on $\partial\hat{S}$.

A completely positive system may have boundary critical points only at the vertices of $\hat{S}$.

An irreducible system has only internal critical points.

Note that a chemical system has at least one critical point [1, 2, 6].

Here only completely positive systems, of which irreducible systems are a special case, will be considered. The reason for this restriction is that the class of completely positive systems contains the so-called weakly reversible mass action kinetics.

Weak reversibility is defined as follows [4]: Let $X = \{X_1, X_2, \ldots, X_n\}$ be the set of species and $C \subseteqq X \times X$ the set of complexes. A complex $\boldsymbol{y}^i \in C$ is the entity appearing on either side of the reaction arrow. The reaction arrow "$\rightarrow$" (reacts to) is defined by

$$\boldsymbol{y}^i \rightarrow \boldsymbol{y}^j \quad \text{if} \quad \boldsymbol{y}^i = \boldsymbol{y}^j \quad \text{or}$$
$$\text{if} \quad \boldsymbol{y}^i \text{ reacts to } \boldsymbol{y}^j\,.$$

The relation "$\Rightarrow$" is defined in C as the smallest transitive extension of "$\rightarrow$", i.e.

$\boldsymbol{y}^i \Rightarrow \boldsymbol{y}^j$ if there is a sequence $\boldsymbol{y}^{i_1}, \boldsymbol{y}^{i_2}, \ldots, \boldsymbol{y}^{i_\alpha}$ of complexes such that

$$\boldsymbol{y}^i = \boldsymbol{y}^{i_1} \rightarrow \boldsymbol{y}^{i_2} \rightarrow \cdots \rightarrow \boldsymbol{y}^{i_\alpha} = \boldsymbol{y}^j\,.$$

A mass action kinetics will be called weakly reversible if the relation "$\Rightarrow$" is symmetric, i.e. if $\boldsymbol{y}^i \Rightarrow \boldsymbol{y}^j$ implies $\boldsymbol{y}^j \Rightarrow \boldsymbol{y}^i$.

Weak reversibility thus preserves the properties of an equivalence relation, as is the case for reversible reactions, but extends the notion of reversibility by allowing the occurrence of irreversible elementary reactions. An immediate consequence of weak reversibility is:

$$\text{if} \quad q^i_{ik} > 0 \quad \text{for} \quad k \in \langle 1, n \rangle, \quad \text{then} \quad q^i_{ii} < 0\,.$$

This may be interpreted as a direct or indirect autocatalysis. Note that by definition of complete positivity a species X_i can never react only in an autocatalytic reaction $2X_i \rightleftarrows X_i + X_j$. This is an important restriction on weakly reversible mass action kinetics due to complete positivity.

Another reason for choosing the class of completely positive (weakly reversible) systems lies in the stability properties of their boundary critical points, which are equivalent to the vertices of $\hat{S}$. It can be shown [2, Corollary 3] that a vertex can never be a stable critical point for a completely positive system. This fact will be used in the following section.

The *stability of a critical point* $\boldsymbol{\xi}$ of (1) is defined to be the stability of the linearized system in a neighborhood of $\boldsymbol{\xi}$. Thus, a critical point $\boldsymbol{\xi}$ of (1) will be called asymptotically stable if the eigenvalues λ_i of the Jacobian J at $\boldsymbol{\xi}$

$$\mathrm{J}_{\boldsymbol{\xi}} = (\partial f_i / \partial x_j)_{\boldsymbol{\xi}}$$

have negative real parts. The critical point $\boldsymbol{\xi}$ will be called unstable if there is at least one eigenvalue λ_j whose real part is positive.

Because of the conservation condition which follows from (3c), there is always one eigenvalue, say λ_n, with $\lambda_n = 0$. As Jenks showed [2, Theorem 8], however, $\lambda_n = 0$ does not affect the definition of stability.

A special property of the systems under consideration is that an unstable critical point always has at least one eigenvalue, say λ_1, with negative real part. This follows immediately from the nonpositivity of the trace of the Jacobian at $\boldsymbol{\xi}$ [2, Theorem 10(iii)]. Thus, unstable critical points as unstable foci or unstable nodes cannot occur for second order mass action kinetics.

The type of unstable critical points which may occur will be called *generalized saddles*, in analogy to the saddle point occurring in two dimensional systems. (In two dimensions a saddle point is characterized by a positive and a negative real eigenvalue. The generalization to higher dimensional systems thus neglects the imaginary parts of the eigenvalues.)

A critical point will be called *hyperbolic* if the real parts Re λ_i of the eigenvalues are not equal to zero.

It will be assumed in the sequel that the critical points of (1) are isolated and hyperbolic.

3. Number and Stability Pattern of Critical Points

The restriction to weakly reversible second order mass action kinetics now enables us to give a complete description of the number and stability pattern of their critical points by using well-known theorems of algebraic geometry and topology.

The *maximum number of critical points m* which may occur in second order mass action kinetics is given by

$$m = 2^{n-1}\,, \tag{6}$$

where n is the number of species. This number m is easily calculated by using the famous Bézout theorem [7, 8, 9], according to which the number of common zeroes (counting their multiplicity) of n independent homogeneous polynomials in $(n+1)$ variables with coefficients in an algebraically closed field is equal to the product of the degrees of these polynomials.

As the field of real numbers is not algebraically closed, the theorem gives only the maximum possible number of critical points. Since

$$f_1(\boldsymbol{x}), f_2(\boldsymbol{x}), \ldots, f_{n-1}(\boldsymbol{x})$$

are homogeneous of degree two ($f_n(\boldsymbol{x})$ is a linear combination of $f_1(\boldsymbol{x}), \ldots, f_{n-1}(\boldsymbol{x})$), and the conservation condition (4) after homogenization

$$0 = x_1 + x_2 + \cdots + x_n - x_0$$

is linear, the stated result (6) is obvious.

Having determined the maximum number of critical points m, one may derive their *stability pattern* by applying the Poincaré-Hopf theorem (see [10, 11]). The importance of this theorem for nonlinear kinetics was recently stated by Glass [12, 13, 14].

Assume that the boundary of the reaction simplex $\partial\hat{S}$ is unstable, i.e., all trajectories starting on $\partial\hat{S}$ enter the interior $\hat{S}^0$ of $\hat{S}$. If v^i is a critical point of (1), assume that all perturbations (except for a set of measure zero) do not return to $\partial\hat{S}$. These assumptions hold true for weakly reversible mass action kinetics. Denote by π_i the number of positive real parts of the eigenvalues of the Jacobian at the i-th internal critical point $\boldsymbol{\xi}^i \in \hat{S}^0$ and assume that the number of internal critical points k is finite. Then the application of the Poincaré-Hopf theorem gives [12]

$$\sum_{i=1}^{k} (-1)^{\pi_i} = 1\,. \tag{7}$$

This equation places restrictions on the number of internal critical points and on their stability patterns.

It follows immediately that there is always an odd number k of internal critical points which is given by

$$k \leqq 2^{n-1} - 1$$

according to Equation (6).

For $n = 2$, 3, and 4 species the stability pattern of the critical points is depicted in Table 1. Arrows indicate where Hopf bifurcations may occur.

It can be seen immediately that limit cycles cannot be found for systems with two and three species, these being identical to open systems with one and two species (see [1]). For four species systems (i.e. open systems with three species), in addition to limit cycles, a richer dynamics than was as yet found may appear. Especially the stability pattern of three, five, and seven generalized saddles looks promising for new dynamic behavior. Examples of mass action kinetics with these patterns are unknown until now.

This stability pattern suggests the application of a theorem by Cronin [15] which says that a system without any asymptotically stable critical points will exhibit a nontrivial periodic solution if there exists a bounded asymptotically stable solution for this system. Weakly reversible mass action kinetics with the stability patterns described above satisfy the sufficiency condition for the existence of a bounded asymptotically stable solution. It seems reasonable to assume that physically significant

Table 1. Stability pattern of critical points for second order mass action kinetics. n = number of species, m = maximum number of critical points, k = number of internal critical points, π_i = number of positive real parts of the eigenvalues at the i-th critical point. Arrows indicate the possible occurrence of Hopfbifurcations.

$n = 2$, $m = 2$

k	π_1	type of critical point
1	0	stable

$n = 3$, $m = 4$

k	π_1	π_2	π_3	types of critical points
1	0			stable
3	0	0	1	2 stable, 1 saddle

$n = 4$, $m = 8$

k	π_1	π_2	π_3	π_4	π_5	π_6	π_7	types of critical points
1	0 ↑							stable
1	2 ↓							saddle
3	0	0 ↑	1					2 stable, 1 saddle
3	0 ↑	2 ↓	1					1 stable, 2 saddle
3	2 ↓	2	1					3 saddle
5	0	0	0 ↑	1	1			3 stable, 2 saddle
5	0	0 ↑	2 ↓	1	1			2 stable, 3 saddle
5	0 ↑	2 ↓	2	1	1			1 stable, 4 saddle
5	2 ↓	2	2	1	1			5 saddle
7	0	0	0	0 ↑	1	1	1	4 stable 3 saddle
7	0	0	0 ↑	2 ↓	1	1	1	3 stable, 4 saddle
7	0	0 ↑	2 ↓	2	1	1	1	2 stable, 5 saddle
7	0 ↑	2 ↓	2	2	1	1	1	1 stable, 6 saddle
7	2 ↓	2	2	2	1	1	1	7 saddle

solutions of mass action systems must be stable or asymptotically stable. Nevertheless it will be a tedious task to verify this assumption for a given kinetics.

Besides periodic solutions for these systems, chaotic solutions may appear. The occurrence of chaotic solutions for open reacting systems was demonstrated by Rössler [16—20]. All the kinetics discussed in [16—20] are of Michaelis-Menten type. Recently Rössler [21] gave an example of a three component second order mass action kinetics which exhibits chaotic solutions.

The dynamic behavior which can be expected for mass action kinetics consisting of five species does not seem to differ entirely from that of four species systems. But the stability pattern alone is too weak a tool for obtaining a precise description of the phase space.

For $n = 6$ species, however, a new type of bifurcation may occur. Assume the mass action kinetics has only one internal critical point ξ. Then the number of positive real parts of the eigenvalues of the Jacobian at ξ is $\pi_1 = 0$, $\pi_1 = 2$, and $\pi_1 = 4$. The transition from $\pi_1 = 0$ to $\pi_1 = 2$ corresponds to the normal Hopf bifurcation. By a suitable change of parameters another bifurcation from $\pi_1 = 2$ to $\pi_1 = 4$ may take place. This type of dynamic behavior is still unknown in chemical kinetics. In forthcoming notes examples will be provided which exhibit the dynamic behavior corresponding to the stability patterns described above.

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