Contributions to the Theory of Mass Action Kinetics

II. Representation of Closed and Open Kinetics

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By introducing the notion of μ-molar mass action kinetics it will be shown that μ-molar mass action kinetics describe completely the qualitative dynamical behaviour of all mass action kinetics. Since there are much fewer μ-molar mass action kinetics than general mixed molar ones, this notion reduces the complexity of investigating mass action kinetics.

1. Introduction

In chemical kinetics the rate law is often modeled according to the law of mass action. In [1] Horn and Jackson formulated a theory of general mass action kinetics which allows to discuss closed and open mass action kinetics (MAK) within a common mathematical framework.

Subsequent publications by Horn [2–4], Feinberg [5], and Feinberg and Horn [6] showed the power of this formulation of MAK in proving and applying the so-called "zero deficiency theorem". This theorem connects in a very simple way the algebraic structure of a MAK with its dynamical behavior. It is a useful and readily applicable criterion for deciding whether a given MAK will show regular behavior (i.e. decay to a single equilibrium point) or may exhibit more interesting dynamical behavior (e.g. multistability, oscillations). For a recent review and new results see [7].

Although the formulation of MAK as derived by Horn and Jackson [1] seems to be satisfactory throughout, a minor technical disadvantage arises persistently when dealing with open MAK: Under certain conditions, systems of differential equations of open MAK may exhibit unbounded solutions, as can be seen in the reaction $A + B \rightarrow 2A$, where the concentration of B is assumed to be constant ($a \rightarrow \infty$ for $t \rightarrow \infty$). Thus, in a general investigation of MAK it is necessary to distinguish between MAK with bounded and those with unbounded solutions. This distinction sometimes imposes severe restrictions on the kinetics to be considered. Therefore it seems to be desirable to overcome these (as will be demonstrated) solely technical difficulties which only restrain the further development of the theory of general mass action kinetics.

The aim of this paper is to avoid this disadvantage by rigorously applying the concept of μ-molarity formerly used by Horn [3] in another context. It will be shown that every MAK can be transformed into a μ-molar one which has the property that the solutions of the according system of differential equations are bounded. It is, however, not only the boundedness of the solutions that can be demonstrated by using the notion of μ-molarity. When comparing a MAK which is not μ-molar with its associated μ-molar MAK, it can be shown that their solution curves are, loosely speaking, identical. Thus, when discussing the dynamical behavior of MAK it is sufficient to consider μ-molar MAK whose amount is much smaller than the total amount of all MAK (see [8] for the case $\mu = 2$).

2. Mathematical Description of Mass Action Kinetics [1, 3, 6, 7]

Consider a spatially homogeneous chemical reaction system at constant temperature and which has time invariant volume consisting of m different chemical species $X_1, X_2, \ldots, X_m$ and a finite set of elementary reactions. An *elementary reaction* of such a system takes the form

$$\sum_{l=1}^{m} y_l^i X_l \rightarrow \sum_{l=1}^{m} y_l^j X_l , \qquad (1)$$

where the stoichiometric coefficients y_l^i, y_l^j are non-negative real numbers. The entities appearing on either side of the reaction arrow will be called *complexes*, which are completely determined by the m-tuple of its stoichiometric coefficients. The number of different complexes is finite, too, because the set of elementary reactions is finite.

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Assigning to each species X_i the i-th canonical basis vector $\boldsymbol{e}_i = (0, \ldots, 0, 1, 0, \ldots, 0)^T$ with the i-th component equal to one and all the other components equal to zero, a vector space $V = \mathbb{R}^m$ is defined, called *species space*. In a similar way another vector space $W = \mathbb{R}^n$, called *complex space*, is defined by assigning to each complex a basis vector $\boldsymbol{f}_i \in W$. These two vector spaces are connected by a linear map $Y\colon W \to V$, which assigns to each $\boldsymbol{f}_i \in W$ a unique vector in V by $Y \boldsymbol{f}_i = \boldsymbol{y}^i$. It can be seen that Y, written as a matrix, is given by $Y = (\boldsymbol{y}^1 \boldsymbol{y}^2 \ldots \boldsymbol{y}^n)$ where the n complexes $\boldsymbol{y}^1, \boldsymbol{y}^2, \ldots, \boldsymbol{y}^n$ form the columns of Y.

The set $\{\boldsymbol{y}^1, \boldsymbol{y}^2, \ldots, \boldsymbol{y}^n\}$ is called *complex set* and denoted by C.

To each elementary reaction, i.e. to each element of $C \times C$ or to each ordered pair $(\boldsymbol{y}^i, \boldsymbol{y}^j)$, there is assigned a non-negative number k_{ji} called rate constant. If there are species γ_i, $i = 1, 2, \ldots, \alpha$, called external species, whose concentrations are assumed to be given and fixed, their respective concentrations will be assumed to be part of the rate constant, i.e.

$$k_{ji} = \varkappa_{ji} \prod_{i=1}^{\alpha} \gamma_i . \tag{2}$$

It is assumed that

$$\begin{aligned} k_{ji} &> 0 \quad \text{if} \quad \boldsymbol{y}^i \to \boldsymbol{y}^j , \\ k_{ji} &= 0 \quad \begin{cases} \text{if} & \boldsymbol{y}^i \not\to \boldsymbol{y}^j , \\ \text{if} & \boldsymbol{y}^i = \boldsymbol{y}^j . \end{cases} \end{aligned} \tag{3}$$

The main interest will be focused on the initial value problem

$$\dot{\boldsymbol{x}}(t) = \boldsymbol{f}(\boldsymbol{x}(t)) , \quad \boldsymbol{x}(0) = \boldsymbol{x}^0 \in \mathbb{R}_+^m , \tag{4}$$

where $\boldsymbol{x}(t) = (x_1(t), x_2(t), \ldots, x_m(t))^T$ is the vector of the concentrations of the species X_i at time t. By defining

$$\boldsymbol{x}^{\mathbf{Y}} = \prod_{i=1}^{m} x_i^{y_i}, \quad \boldsymbol{x} \in V, \quad \boldsymbol{y} \in V \tag{5}$$

and, if $\mathbf{Y}$ is an $n \times m$-matrix,

$$\boldsymbol{x}^{\mathbf{Y}} = (\boldsymbol{x}^{\boldsymbol{y}^1}, \boldsymbol{x}^{\boldsymbol{y}^2}, \ldots, \boldsymbol{x}^{\boldsymbol{y}^n})^T \tag{6}$$

the *species formation function* $\boldsymbol{f}(\boldsymbol{x})$ is given by

$$\boldsymbol{f}(\boldsymbol{x}) = \sum_{i=1}^{n} \sum_{j=1}^{n} r_{ij}(\boldsymbol{x}) \{\boldsymbol{y}^i - \boldsymbol{y}^j\} . \tag{7}$$

Here the $r_{ij}(\boldsymbol{x})$ are the elements of the rate matrix $\mathbf{R}(\boldsymbol{x})$ given by

$$\mathbf{R}(\boldsymbol{x}) = \mathbf{K} \, \mathrm{dg}(\boldsymbol{x}^{\mathbf{Y}}) , \tag{8}$$

where $\mathbf{K}$ is the matrix of rate constants and $\mathrm{dg}(\boldsymbol{x}^{\mathbf{Y}})$ is a diagonal matrix whose elements are the components of $\boldsymbol{x}^{\mathbf{Y}}$. Inserting (8) into (7) and defining a matrix $\mathbf{A}$ by

$$\mathbf{A} = \mathbf{K} - \mathrm{dg}(\mathbf{K}^T \boldsymbol{e}_{\mathrm{W}}) , \quad \boldsymbol{e}_{\mathrm{W}} = (1, 1, \ldots, 1)^T \in W ,$$

the species formation function is given by

$$\boldsymbol{f}(\boldsymbol{x}) = \mathbf{Y} (\mathbf{R}(\boldsymbol{x}) - \mathbf{R}^T(\boldsymbol{x})) \, \boldsymbol{e}_{\mathrm{W}} = \mathbf{Y} \mathbf{A} \, \boldsymbol{x}^{\mathbf{Y}} . \tag{9}$$

It can be seen from (9) that a mass action kinetics is completely determined if $\mathbf{Y}$ and $\mathbf{A}$ are given. $\mathbf{Y}$, then, describes the molecular make up of the complexes, and the positive elements of $\mathbf{A}$ define the elementary reactions taking place. Thus, Eq. (9) defines in a unique way the reaction mechanism of a MAK.

To model open MAK with species formed by a constant rate of infusion from the outside (i.e. $\to X_i$) or removed from the system (i.e. $X_i \to$), a zero complex is introduced on the left or right hand side of the reaction arrow. The corresponding complex vector is given by the zero vector $\mathbf{0} \in V$.

With respect to a given MAK, the stoichiometric subspace S and the reaction simplex $\hat{S}$ are defined as follows. The subspace $S \subset V$ defined by

$$S = \mathrm{span}\, \{\boldsymbol{y}^i - \boldsymbol{y}^j \,|\, \boldsymbol{y}^j \to \boldsymbol{y}^i\} \tag{10}$$

is called *stoichiometric subspace* S. It follows from this definition and Eq. (7) that

$$\boldsymbol{f}(\boldsymbol{x}) \in S \quad \text{for all } \boldsymbol{x} \in \bar{V}^+ , \tag{11}$$

where $\bar{V}^+$ denotes the non-negative orthant of V. This implies that any solution of Eq. (4) is completely contained in a translate $\boldsymbol{x}(0) + S$ of S. The intersection of this translate with $\bar{V}^+$

$$\hat{S} = \bar{V}^+ \cap (\boldsymbol{x}(0) + S) \tag{12}$$

is called *reaction simplex* $\hat{S}$.

A MAK will be called *conservative* if there exists a vector in the orthogonal complement $S^\perp$ of S which lies in the positive orthant V^+. A consequence of the conservativity of a MAK is that its reaction simplex $\hat{S}$ is bounded if and only if it is conservative (for a proof see [1], p. 113). Thus, as the solutions of (4) are confined to $\hat{S}$, the solutions of conservative MAK are always bounded. A MAK which is not conservative will be called non-conservative.

Besides the conservativity, another property of MAK, called μ-molarity, is now of great importance. It is defined as follows.

The *molarity* μ_i of a complex $\boldsymbol{y}^i \in C$ is given by the sum of the components of $\boldsymbol{y}^i$:

$$\mu_i = \sum_{j=1}^{m} y_j{}^i . \tag{13}$$

A complex set C will be called μ-molar if all of its complexes are of the same molarity. A μ-molar complex set will be denoted by C_μ. The stoichiometric subspace and the reaction simplex derived from a μ-molar complex set C_μ will be denoted by S_μ and $\hat{S}_\mu$, respectively. A MAK which is not μ-molar will be called mixed molar MAK.

In defining the species set of MAK it was assumed that none of the X_i, $i = 1, 2, \ldots, m$ is an external species. For technical reasons it will be convenient to enlarge the species set by an external species X_0, if the complex set of the MAK under consideration is mixed molar. Thus, for MAK which are mixed molar the species space will be $V = \mathbb{R}^{m+1}$. As X_0 does not participate in any elementary reaction, the first component of all complex vectors is equal to zero. The first line of the rate equation of this enlarged MAK then reads

$$\dot{x}_0 = 0; \quad x_0(0) := 1 , \tag{14}$$

thus fixing the concentration of X_0.

3. μ-Molarity

The notion of μ-molarity for MAK allows to avoid the disadvantage of unbounded solutions which may occur in the theoretical treatment of open MAK. This is due to the following lemma.

Lemma: Every μ-molar MAK is conservative.

Proof: Obviously, $\boldsymbol{e}_V = (1, 1, \ldots, 1)^T \in V^+$ lies in the orthogonal complement $S^\perp$ of the stoichiometric subspace.

This lemma guarantees the boundedness of solutions of every μ-molar MAK no matter whether it is a closed system or not. It should be noted, however, that conservativity does not imply μ-molarity, as can be seen from the MAX $X_1 \rightleftharpoons 2X_2$.

As non-conservative MAK which model open systems are never μ-molar, a μ-molar complex set C_μ will be associated with a non-conservative complex set C. This can be done by an affine transformation Φ which is defined by (see [3])

$$\Phi(\boldsymbol{y}^i) = \varphi\, \boldsymbol{y}^i + \underline{\boldsymbol{\mu}} := \tilde{\boldsymbol{y}}^i , \tag{15}$$

where $\boldsymbol{y}^i \in C$, $\underline{\boldsymbol{\mu}} = (\mu, 0, 0, \ldots, 0)^T \in V = \mathbb{R}^{m+1}$ and φ is a linear transformation φ: $V \to V$ defined by the matrix

$$\varphi = \begin{pmatrix} 1 & -1 & -1\ldots\ldots & & -1 \\ 0 & 1 & 0\ldots & & 0 \\ . & 0 & . & & 0 \\ . & & .\,. & & . \\ . & & .\;\;. & & . \\ . & & . & .\;1 & 0 \\ 0 & & 0\ldots & 0 & 1 \end{pmatrix} .$$

Thus, C_μ is the image of C under this affine transformation, $\Phi(C) = C_\mu$. (It is obvious that $\tilde{\boldsymbol{y}}^i$ is μ-molar.) The molarity of the associated complex set C_μ is defined to be the maximum of the molarities μ_i of the $\boldsymbol{y}^i \in C$, i.e.

$$\mu := \max\{\mu_i\} . \tag{16}$$

Note that the application of Φ is not restricted to non-conservative MAK, but is valid for all mixed molar MAK.

As the stoichiometric subspace S of a MAK is spanned by differences of the complex vectors $\boldsymbol{y}^i$, the stoichiometric subspaces S_μ associated with S is given by

$$\Phi(S) = \varphi(S) = S_\mu . \tag{17}$$

This can be seen as follows: Let $\varDelta = \{\boldsymbol{\Delta}_1, \ldots, \boldsymbol{\Delta}_s\}$ be a linear independent set of difference vectors forming a basis of S where $\boldsymbol{\Delta}_i \in \{\boldsymbol{y}^i - \boldsymbol{y}^j \mid k_{ij} > 0\}$ for a fixed $\boldsymbol{y}^j \neq \boldsymbol{y}^i$. Then the effect of Φ on the basis vectors of S is

$$\begin{aligned} \Phi(\boldsymbol{\Delta}_i) &= \Phi(\boldsymbol{y}^i - \boldsymbol{y}^j) \\ &= \Phi(\boldsymbol{y}^i) - \Phi(\boldsymbol{y}^j) \\ &= \varphi\, \boldsymbol{y}^i + \underline{\boldsymbol{\mu}} - \varphi\, \boldsymbol{y}^j - \underline{\boldsymbol{\mu}} \\ &= \varphi(\boldsymbol{y}^i - \boldsymbol{y}^j) = \tilde{\boldsymbol{y}}^i - \tilde{\boldsymbol{y}}^j = \tilde{\boldsymbol{\Delta}}_i , \end{aligned} \tag{18}$$

which shows that S_μ is the image of S under the linear transformation φ.

Thus we have

Proposition 1: Every mixed molar MAK can be transformed by Φ into a μ-molar associate.

4. Dynamical Equivalence of Non-Conservative MAK and Their μ-Molar Associates

Until now, only the formal construction of μ-molar associates of mixed molar MAK was considered. The problem to be considered now is the relation between the dynamic behavior of the original MAK and their μ-molar associates.

The dynamical equations of every MAK are derived from the complex matrix $\mathbf{Y}$ and the kinetic matrix $\boldsymbol{A}$ (see Equation (9)). The transformation Φ, however, affects only the complex matrix $\mathbf{Y}$ whose columns are given by the complex vectors $\boldsymbol{y}^i$. Transforming the $\boldsymbol{y}^i \in C$ to $\tilde{\boldsymbol{y}}^i \in C_\mu$ thus changes the columns of $\mathbf{Y}$ and yields a transformed complex matrix $\tilde{\mathbf{Y}}$. Inserting $\tilde{\mathbf{Y}}$ into Eq. (9) then gives

$$\dot{\tilde{\boldsymbol{x}}} = \boldsymbol{f}^\mu(\tilde{\boldsymbol{x}}) = \tilde{\mathbf{Y}} \mathbf{A}\, \tilde{\boldsymbol{x}}^{\tilde{\mathbf{Y}}} . \tag{19}$$

As can be readily verified by the definition of $\tilde{\mathbf{Y}}$ and $\tilde{\mathbf{A}}$,

$$\sum_{i=0}^{m} \dot{\tilde{x}}_i = 0 , \tag{20}$$

which implies

$$\sum_{i=0}^{m} \tilde{x}_i = \text{const.} \tag{21}$$

Without loss of generality it will be assumed that the constant in Eq. (21) is equal to unity. Thus, the transformed initial value problem is given by

$$\dot{\tilde{\boldsymbol{x}}} = \boldsymbol{f}^\mu(\tilde{\boldsymbol{x}}) , \quad \tilde{\boldsymbol{x}}^0 \in \hat{S}_\mu , \tag{22}$$

where according to Eqs. (12) and (21)

$$\hat{S}_\mu = \left\{ \tilde{\boldsymbol{x}} \in \mathbb{R}_+^{m+1} \,\middle|\, \sum_{i=0}^{m} \tilde{x}_i = 1 \right\} . \tag{23}$$

The superscript μ in Eq. (22) indicates that

$$\boldsymbol{f}^\mu(c\, \tilde{\boldsymbol{x}}) = c^\mu \boldsymbol{f}^\mu(\tilde{\boldsymbol{x}}) \tag{24}$$

for a constant positive number $c \in \mathbb{R}_+$, i.e. the $\boldsymbol{f}_i{}^\mu(\tilde{\boldsymbol{x}})$ are homogeneous polynomials in the $\tilde{x}_i$, $i = 0, 1, \ldots, m$.

Formal integration of Eq. (7) shows that the solution curves are confined to the reaction simplex $\hat{S}$ (or $\hat{S}_\mu$), i.e.

$$\boldsymbol{x}(t) = \boldsymbol{x}^0 + \sum_{i=1}^{n} \sum_{j=1}^{n} \left[\int_0^t r_{ij}(\boldsymbol{x}(\tau))\, \mathrm{d}\tau \, \{\boldsymbol{y}^i - \boldsymbol{y}^j\} \right] . \tag{25}$$

As $S_\mu = \varphi(S)$, the reaction simplices of a mixed molar MAK and its μ-molar associates are given by

$$\hat{S} = V^+ \cap (\boldsymbol{x}^0 + S) \quad \text{and}$$
$$\hat{S}_\mu = V^+ \cap (\tilde{\boldsymbol{x}}^0 + S_\mu) .$$

These simplices are connected by a map

$$\boldsymbol{\rho}\colon \hat{S} \to \hat{S}_\mu$$

defined by

$$\boldsymbol{\rho}(\boldsymbol{x}) = \frac{1}{\sum_{i=0}^{m} x_i} \boldsymbol{x} = \tilde{\boldsymbol{x}}, \quad \boldsymbol{x} \in \hat{S}, \quad \tilde{\boldsymbol{x}} \in \hat{S}_\mu \tag{26}$$

and

$$\boldsymbol{\rho}^{-1}(\tilde{x}) = (1/\tilde{x}_0)\, \tilde{\boldsymbol{x}} = \boldsymbol{x} , \quad \tilde{x}_0 \neq 0 , \tag{27}$$

which implies $\sum_{i=0}^{m} x_i = \tilde{x}_0{}^{-1}$. Thus, if $\tilde{x}_0(t) \to 0$ for $t \to \infty$, $x_i(t) \to \infty$ for at least one i, $i = 1, 2, \ldots, m$. (Recall that $x_0 = 1$ by definition.) Thus if $\boldsymbol{x}(t)$ is a solution curve of the mixed molar MAK considered as a uniquely determined sequence of points in $\hat{S}$, $\tilde{\boldsymbol{x}}(t) = \boldsymbol{\rho}(\boldsymbol{x}(t))$ is the solution curve in $\hat{S}_\mu$ of its μ-molar associate.

From the definition of $\boldsymbol{\rho}$ it can be seen that no properties of the solution curves are changed. Thus the number and stability of critical points, stability properties of limit cycles and other dynamical properties are not affected by the transformation $\boldsymbol{\rho}$ which can be interpreted as a central projection of $\hat{S}$ into $\hat{S}_\mu$. The boundary face $F^0 = \{\tilde{\boldsymbol{x}} \in \hat{S}_\mu \mid \tilde{x}_0 = 0\}$ corresponds from a geometric point of view to the hyperplane at infinity of $\hat{S}$.

Thus we have shown

Proposition 2: Every mixed molar MAK is dynamically equivalent to its μ-molar associate.

Yet, as Φ is bijective, the converse statement is also true, viz., from each μ-molar complex set C_μ a mixed molar complex set C can be derived by

$$\Phi^{-1}(\tilde{\boldsymbol{x}}^i) = \varphi^{-1}(\tilde{\boldsymbol{y}}^i - \underline{\boldsymbol{\mu}}) = \boldsymbol{y}^i , \tag{28}$$
$$\tilde{\boldsymbol{y}}^i \in C_\mu , \quad \boldsymbol{y}^i \in C ,$$

where φ^{-1} is given by

$$\varphi^{-1} = \begin{pmatrix} 1 & 1 & \cdots & 1 \\ 0 & 1 & & \\ & & 0 & \\ 0 & & & 1 \end{pmatrix} . \tag{29}$$

If $\Phi_r{}^{-1}$ is defined to be

$$\Phi_r{}^{-1}(\tilde{\boldsymbol{y}}^i) = \Phi_r{}^{-1}(\tilde{\boldsymbol{y}} - \underline{\boldsymbol{\mu}}_r) , \tag{30}$$

where $\underline{\boldsymbol{\mu}}_r = (0, 0, \ldots, \mu, 0, \ldots, 0)^T \in V$ with μ as r-th component and

$$\varphi_r{}^{-1} = \begin{pmatrix} 1 & & & & \\ 0 & \cdot & & \bigcirc & \\ 1 & \ldots & 1 & \ldots & 1 \\ & & & & 0 \\ & \bigcirc & & \cdot & 1 \end{pmatrix} \tag{31}$$

with $(1\ 1 \ldots 1)$ as r-th row, a new mixed molar MAK is generated. In this case X_r is considered to be the external species.

Thus we have

Proposition 3: From every μ-molar MAK at least one mixed molar MAK can be derived by $\varphi_r{}^{-1}$. It is dynamically equivalent to the original μ-molar MAK.

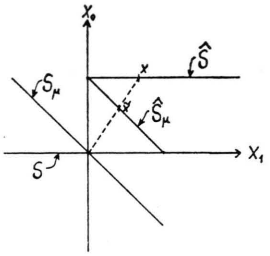

Fig. 1. Connection between S, $\hat{S}$ and S_μ, $\hat{S}_\mu$.

5. Kinetic and Geometric Interpretation of K

Now it seems to be useful to interpret the result of the transformation φ both in terms of chemical kinetics and with respect to the geometry of the reaction simplices $\hat{S}$ and $\hat{S}_\mu$. To do this the following non-conservative MAK will be considered

$$\begin{aligned} X_1 &\to 0 && \triangleq y^1 \to y^2 \\ X_1 + X_2 &\rightleftharpoons 2X_2 && \triangleq y^3 \rightleftharpoons y^4 , \end{aligned} \tag{32}$$

where 0 denotes the zero complex. The rate constants are assumed to be equal to unity.

The complex set C is

$$C = \{y^1, y^2, y^3, y^4\}$$

with

$$y^1 = (0, 1, 0)^T, \quad y^2 = (0, 0, 0)^T,$$
$$y^3 = (0, 1, 1)^T, \quad y^4 = (0, 0, 2)^T.$$

Note that for mixed molar MAK the existence of an external species X_0 with $x_0(t) = 1$ was assumed. The stoichiometric subspace S is given by

$$S = \text{span}\{(0, +1, 0)^T, (0, 1, -1)^T\}.$$

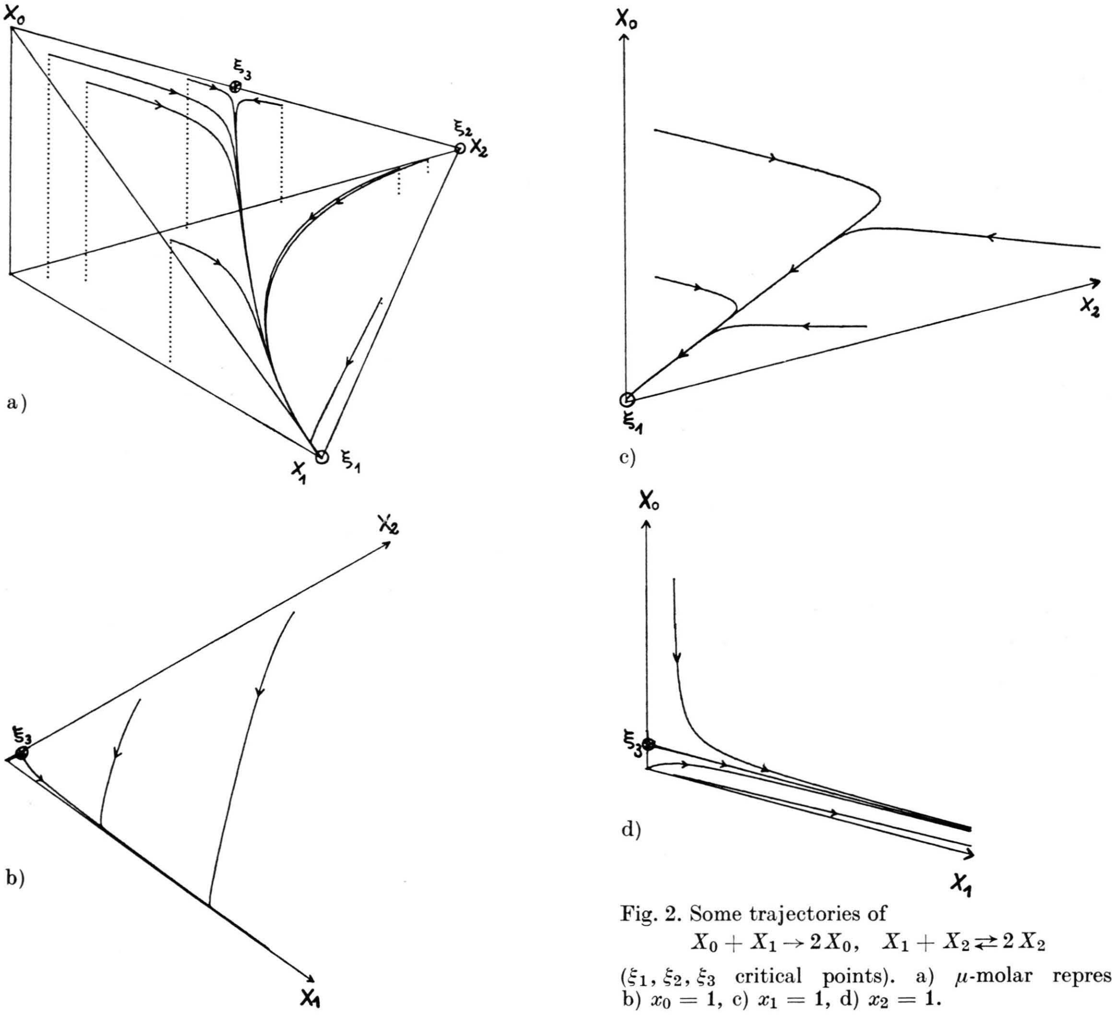

Fig. 2. Some trajectories of

$$X_0 + X_1 \to 2X_0, \quad X_1 + X_2 \rightleftharpoons 2X_2$$

(ξ_1, ξ_2, ξ_3 critical points). a) μ-molar representation, b) $x_0 = 1$, c) $x_1 = 1$, d) $x_2 = 1$.

The molarity of the associated C_μ is $\mu = 2$. Applying μ to C the associated complex set C_2 is

$$C_2 = \{\tilde{\boldsymbol{y}}^1 = (1,1,0)^T, \tilde{\boldsymbol{y}}^2 = (2,0,0)^T, \tilde{\boldsymbol{y}}^3 = (0,1,1)^T, \tilde{\boldsymbol{y}}^4 = (0,0,2)^T\}$$

and the stoichiometric subspace S_2 is given by

$$S_2 = \operatorname{span}\{(-1,1,0)^T, (0,1,-1)^T\}\,.$$

Inserting the $\tilde{\boldsymbol{y}}^i$ into the reaction scheme the μ-molar MAK reads

$$X_0 + X_1 \rightarrow 2X_0\,, \quad X_1 + X_2 \rightleftharpoons 2X_2\,. \qquad (32\text{a})$$

Comparing this with the original MAK it can be seen that the complexes were, loosely speaking, filled up with the external species X_0 such that the molarity is equal to two. Considering the associated MAK, the external species X_0 now acts as an internal species.

The above given interpretation of the geometric properties of MAK becomes obvious when considering the MAK $X_i \rightleftharpoons 0$ whose associated conservative MAK ($\mu = 1$) is $X_1 \rightleftharpoons X_0$ (rate constants equal unity). The stoichiometric subspaces are

$$S = \operatorname{span}\{(0,1)^T\} \quad \text{and} \quad S_1 = \{(-1,1)^T\}.$$

The reaction simplices are then given by

$$\hat{S} = V^+ \cap ((1, x_1{}^0)^T + S) \quad \text{and}$$
$$\hat{S}_1 = V^+ \cap ((x_0{}^0, x_1{}^0)^T + S_1)\,.$$

They are depicted in Figure 1.

In Fig. 2 some of the trajectories of MAK (32a) and their mixed molar associates are depicted.

It can be seen that φ causes a rotation of S to yield S_μ and $\boldsymbol{\rho}$ acts as a central projection which connects points of $\hat{S}$ with $\hat{S}_\mu$.

6. Discussion

The notion of μ-molarity leads to a representation of MAK which avoids the disadvantage of the occurrence of unbounded solutions. It ensures that the curves of all solutions are confined to a bounded subspace of the species spaces, the reaction simplex. Besides this advantage it could be demonstrated that μ-molar MAK represent all MAK. Therefore μ-molar MAK can be regarded as the general case of MAK: it suffices to investigate this class to get a complete insight into the qualitative dynamical behavior of all MAK.

As will be schown in a forthcoming publication, a great class of μ-molar MAK can be further reduced to bimolar ones. That makes it possible to analyze MAK in an even more convenient way than it is possible for general μ-molar MAK.

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