

Chemical systems consisting only of elementary steps - a paradigm for nonlinear behavior

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Abstract

We present a new analytic method which allows one to interpret a mass-action kinetic reaction of arbitrary molecularity as the limit case of a sequence of bimolecular steps. Together with other technics (transformation of an arbitrary ODE into a polynomial ODE [1]; transformation of a polynomial ODE into a form which can be interpreted as a mass-action kinetic system [2]), it is thus possible to construct an at most bimolecular mass-action kinetic system with the same dynamic behavior than an arbitrary ODE. Furthermore, we demonstrate necessary improvements to the transformation given in [2].

It is also shown that an arbitrary single mass-action kinetic reaction can be understood as a sequence of two reactions with a short-living intermediate. In particular it therefore follows that an autocatalytic reaction can always be approximated by two nonautocatalytic ones without changing the dynamics of the whole system.

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1 Introduction

In the last decades chemical reaction systems has become one of the favorite physical objects to study nonlinear behavior, both, experimentally and theoretically. The famous Belousov-Shabotinsky-System [3] is without doubt the most prominent experimental research object in this field. To model its dynamic behavior, it has been proposed, e.g., the well-known ‘Oregonator’ [4]. The study of oscillating reaction systems dates back to Lotka [5] (The same system has independently been studied by Volterra in a population-kinetic context [6].). Bray [7] has at first documented experimentally observed sustained oscillating reactants. However, these early observations has been ignored more or less by the most scientists, because in their eyes sustained oscillations contradicted the fundamental second law of thermodynamics. It is much owing to the work of Prigogine and his coworkers that this contradiction has been resolved. The Brussels group showed that far from equilibrium highly ordered structures in time and space (the so-called ‘dissipative structures’) can arise in accordance with the laws of thermodynamics [8]. They also proposed the much studied ‘Brusselator’ [9].

There are several approaches to construct new chemical reaction systems with ‘interesting’ dynamic behavior, mainly multistable and oscillating ones. The work of Epstein (cf.[10]), e.g., is rather experimentally oriented. In a more theoretical approach [11], based on a definition for ‘smallness’, the “smallest chemical reaction system with Hopf bifurcation” has been proposed.

A straightforward theoretical approach is based on the idea to start with an arbitrary dynamical system and to transform it into a form, which can be interpreted as a chemical system. A chemical reaction has the general ‘reaction equation’

$$\sum_i \nu_i^+ X_i \xrightleftharpoons[k_-]{k_+} \sum_i \nu_i^- X_i \quad (\nu_i^+, \nu_i^-, k_+, k_- \geq 0, i = 1, 2, \dots). \quad (1)$$

The kinetics of such a reaction is usually assumed to be of the mass-action type, i.e., the reaction velocity is assumed to be proportional to the concentrations of the involved reactants (in consideration of their molecularity). The corresponding differential equations therefore have a polynomial form. In (1) k_+ and k_- denote the rate coefficients of the forward and backward unidirectional reaction, respectively. X_i is the i -th variable reactant (Its concentration will be denoted by the small letter x_i .) and ν_i^+ and ν_i^- its stoichiometric coefficients. The constant substances and products are assumed to be incorporated into the rate constants k_+ and k_- , respectively.

The most natural way for a transformation of arbitrary differential equations into chemical ones is of course an affine one. Thereby the number of variables remains the same and the dynamic behavior is not changed because of the linearity of the procedure. For two-dimensional systems the general affine transformation of arbitrary ODE-s into quadratic mass-action kinetic (MAK) systems has been discussed in [12]. It has successfully been demonstrated that “any normal bifurcation of a limit cycle that is possible in a plane system” can “occur in quadratic mass-action systems, too.” However, for three- and higher-dimensional systems (which are necessary for, e.g., ‘chaotic’ behavior) the according calculation has not been carried out up to now. The reason is the rapidly increasing complexity of the necessary algebraic calculations if the dimension is increased only by one.

Searching for the ‘minimal MAK-system with chaotic dynamics’ one can start with the minimal polynomial chaotic systems which has been found numerically [13]. We could affine transform some of these systems into mass-action kinetic ones, but only in such a way that the interesting, the chaotic behavior occurs in regions of the phase space corresponding to negative concentrations (In contrast to Escher [12] we restricted ourselves to the only realistic case of at most bimolecular reactions, see below.). One could try nonlinear transformations (whereby the inverse of the transformation should be bounded in the whole transformed domain to ensure the global uniqueness), but generally the necessary algebraic calculations are quite cumbersome.

It has been proposed other transformations which conserve the main features of the dynamics of the system (cf.[1, 2]). These are based on the idea to introduce further suitable variables. The dynamics of the new system than takes place on an invariant manifold in the enlarged phase space. The initial conditions have to be chosen appropriately. In [1] it has been shown that “very general nonlinear ordinary differential systems (embracing all that arise in practice)” may be brought down to quadratic polynomial systems. In [2] it has been demonstrated the possibility to transform polynomial systems into a form, which can be interpreted as a MAK-system. However, it is necessary to discuss this transformation more in detail. This is done in section 2 of this work. Another transformation of arbitrary polynomial systems into chemical ones has been given in [14]. The problem is that the dynamics may be changed by this procedure.

There is one important point which needs to be discussed in the context of transformations to chemical systems. Even if a system has been transformed into a quadratic mass-action kinetic one ([1, 2] and section 2 or [1, 14]), generally there still remain terms which cannot be interpreted by

bimolecular reactions. The term $\dot{x} = kx^2$ with $k > 0$ at least corresponds to the trimolecular reaction $A + 2 X \rightarrow 3 X$ where A is supposed to be constant. Also Escher excluded only “the occurrence of higher than bimolecular reactions *with respect to the two intermediates*” and in fact in all of his examples the reaction $A + 2 X \rightarrow 3 X$ occurs (cf.[12]). It therefore remains the question how to transform systems with such ‘hidden’ trimolecularities into real at most bimolecular ones without changing the dynamic behavior. A similiar problem has been treated in another context. The ‘Brusselator’ [9] has often been criticized because of its unrealistic trimolecular reaction $X + 2 Y \rightarrow 3 Y$, where X and Y are variable intermediates. In [15] three different bimolecular schemes has been analysed which can in a limit case be approximated by the trimolecular reaction.

In a recent work [16] we have shown in the most general way how singularly perturbed systems can also in critical cases (singular singularly perturbed systems) where the standard theory does not work be approximated by regularly perturbed ones. As an example we have demonstrated how the trimolecular autocatalator (also termed Gray-Scott-, Schnakenberg- or Higgins-Selkov-system) [17] can be obtained as the limit case of an at most bimolecular reaction system. Our method is both, more rigorously and simple compared with [15].

Using the general method of [16] in section 3.1 of this work we demonstrate how *every* trimolecular reaction can be understood as the limit case of two bimolecular reactions. In section 3.2 we show how 4-molecular reactions follow as limit case of a sequence of bimolecular steps. The general n -molecular case becomes obviously.

In the context of oscillating reaction systems it has often been discussed the role of autocatalytic reactions (e.g.[8]). Whereas in general chemical systems there is no simple definition for ‘autocatalyticity’, a MAK-reaction (1) is autocatalytic if

$$\nu_i^+ \neq 0, \nu_i^- \neq 0, \nu_i^+ \neq \nu_i^- \quad (2)$$

for at least one reactant X_i . Note that both transformations of polynomial systems into mass-action kinetic ones [2, 14] yield for all systems with nontrivial dynamics also autocatalytic reactions. However, in [18] we have proven that in contrast to former assumptions an autocatalytic reaction is not necessary for a locally unstable steady state of the considered system and have given a counterexample with a supercritical Hopf bifurcation of the steady state. In section 4 we show that an arbitrary single MAK-reaction can be understood as a sequence of two reactions with a short-living intermediate. Together with the results of [1, 2] and sections 2,3 it follows

that (nearly, cf.[1]) every dynamic behavior can be realized by mass-action systems without autocatalytic reactions in the sense of (2).

In [19], e.g., it has been claimed that “reactions in which the same substance appears both as reactant and as product”, even if they are of bimolecular type, are not *elementary* reactions. It follows from the result of section 4 that every such reaction can be decomposed into two real elementary reactions, yielding in the limit case exactly the same dynamic behavior than in the original system.

All together, the results of [1, 2] and of this work justify the statement that *mass-action kinetic systems consisting only of elementary reactions are a paradigm for nonlinear behavior*.

2 Transformation of an arbitrary ODE into a form which can be interpreted as a MAK-system

Based on “an ancient and very simple device, that of introducing appropriate collectives of variables and parameters as new variables” in [1] it has been shown that without changing the dynamics a very general ODE may be transformed into a polynomial ODE with only quadratic nonlinearities. For a demonstration of the idea we consider the simple initial value problem (IVP)

$$\dot{x} = x \exp(x) \tag{3}$$

with $x(t = 0) = x_0$. With the further variable $y = \exp(x)$ system (3) is transformed into the polynomial form

$$\begin{aligned} \dot{x} &= xy \\ \dot{y} &= xy^2 \end{aligned} \tag{4}$$

which has exactly the same dynamics than the IVP (3) for the initial values $x(t = 0) = x_0, y(t = 0) = y_0 = \exp(x_0)$. The dynamics of the two-dimensional system (4) than takes place on the one-dimensional invariant manifold $y = \exp(x)$:

$$\frac{d(y - \exp(x))}{dt} = x(y^2 - \exp(2x)),$$

so that $\frac{d(y - \exp(x))}{dt} = 0 \ \forall \ t$ if $y_0 = \exp(x_0)$. Note that the invariant manifold is not a first integral, because the latter exists independently of the initial

values (cf.[16]). With the further variable $z = xy$ the cubic polynomial system (4) is transformed into the quadratic one

$$\begin{aligned}\dot{x} &= z \\ \dot{y} &= yz \\ \dot{z} &= z(y + z),\end{aligned}\tag{5}$$

again with the property $\frac{d(z-xy)}{dt} = 0 \forall t$ if $z_0 = x_0 y_0$.

Of course, not every quadratic polynomial system can be interpreted as a mass-action kinetic one. A MAK-system is confined to the positive cone of the phase space. Consider, e.g., two variables x and y , then the term

$$\dot{x} = -y^2\tag{6}$$

violates this condition. In [2] it has been proposed a special introduction of further variables to transform arbitrary polynomial differential systems into chemical ones. With the variable $z = 1/x$ (with the fixed initial value $z_0 = 1/x_0$) (6) is transformed into the MAK-system

$$\begin{aligned}\dot{x} &= -xy^2z \\ \dot{z} &= y^2z^2.\end{aligned}\tag{7}$$

However, it is necessary to discuss the following problem more in detail. We now study the *invariance of the dynamic behavior during the transformation* (of [2]). We consider the general polynomial system

$$\begin{aligned}\dot{x} &= f(x, y) \\ \dot{y} &= g_1(x, y) + g_2(x, y)\end{aligned}\tag{8}$$

with $x \in \mathbb{R}^m, y \in \mathbb{R}^n$ where f, g_2 contain only monomials which can be interpreted as MAK-reactions and g_1 contains only ‘non-chemical’ monomials. With the further variables

$$z_i = 1/y_i\tag{9}$$

with $z_{i_0} = 1/y_{i_0}$ ($i = 1, \dots, n$) one obtains the system

$$\begin{aligned}\dot{x} &= f(x, y) \\ \dot{y}_i &= y_i z_i g_{1_i}(x, y) + g_{2_i}(x, y) \\ \dot{z}_i &= -z_i^2 (y_i z_i g_{1_i}(x, y) + g_{2_i}(x, y)),\end{aligned}\tag{10}$$

which can be interpreted as a mass-action kinetic one. It follows

$$\frac{d}{dt} \left(z_i - \frac{1}{y_i} \right) = z_i g_{1_i}(x, y) \left(\frac{1}{y_i} - y_i z_i^2 \right) + g_{2_i}(x, y) \left(\frac{1}{y_i^2} - z_i^2 \right),$$

and therefore $\frac{d(z_i - 1/y_i)}{dt} = 0 \ \forall \ t$ if $z_{i_0} = 1/y_{i_0}$. Thus the dynamics of the enlarged system (10) is confined to the invariant manifold $z_i = 1/y_i$ ($i = 1, \dots, n$).

A problem arises at the singularity at $y_i = 0$. The original continuous trajectories connecting negative and positive y_i -values in the new system (10) become discontinuous. It follows that an arbitrary dynamic behavior of system (8) containing positive *and* negative y_i -values is *never* invariant under the transformation (9). If a system with such a dynamics should be transformed into a chemical one, *at first* it is necessary to *translate* the relevant phase space points into the positive cone. *Afterwards* one should *introduce* the necessary *further variables* (9).

We illustrate the procedure at the following example. In [2] it was discussed the Lorenz system

$$\begin{aligned}\dot{x} &= \sigma(y - x) \\ \dot{y} &= rx - y - xz \\ \dot{z} &= xy - bz.\end{aligned}\tag{11}$$

After introducing the further variable $u = 1/y$ it was obtained the so-termed “chemical Lorenz”

$$\begin{aligned}\dot{x} &= \sigma(y - x) \\ \dot{y} &= rx - y - xyz u \\ \dot{z} &= xy - bz \\ \dot{u} &= u + xu^2(z - r).\end{aligned}\tag{12}$$

However, the original Lorenz attractor contains positive *and* negative x, y -values, thus system (12) does *not* show this attractor, the dynamics diverges. Because it is possible to construct a ‘confined set’ containing the Lorenz attractor [20], the interesting dynamics is confined to a finite region of the phase space. Therefore, it must be possible to find a translation in order to construct a ‘true chemical Lorenz’. Indeed, after an appropriate translation ($x + t_x \rightarrow x$, $y + t_y \rightarrow y$, $t_x > -x_{min}$, $t_y > -y_{min}$ (the index *min* denotes the minimal value of the Lorenz attractor.)) and an introduction of three further variables ($x_1 = 1/x$, $y_1 = 1/y$, $z_1 = 1/z$), from (11) one obtains the MAK-system

$$\begin{aligned}\dot{x} &= \sigma(t_x - x + y) - \sigma t_y x x_1 \\ \dot{y} &= t_y + rx + t_x z - y - (t_x r + xz) y y_1 \\ \dot{z} &= t_x t_y + xy - bz - (t_x y + t_y x) z z_1\end{aligned}\tag{13}$$

$$\begin{aligned}
\dot{x}_1 &= -x_1^2(\sigma(t_x - x + y) - \sigma t_y x x_1) \\
\dot{y}_1 &= -y_1^2(t_y + r x + t_x z - y - (t_x r + x z) y y_1) \\
\dot{z}_1 &= -z_1^2(t_x t_y + x y - b z - (t_x y + t_y x) z z_1)
\end{aligned}$$

which shows the Lorenz attractor (Fig.1).

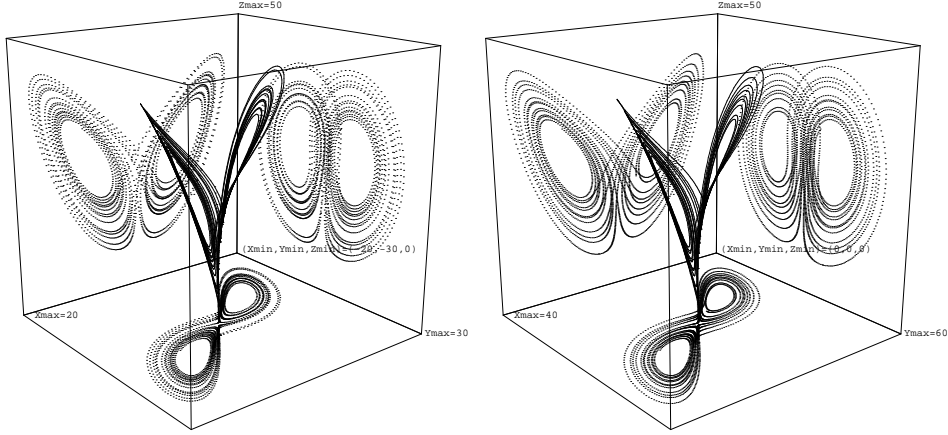


Fig.1. Attractor of (left) the original (11) and (right) the chemical (13) Lorenz system ($\sigma = 10$, $r = 28$, $b = 8/3$, $t_x = 20$, $t_y = 30$).

Thus we state the first general result: by introduction of further variables (at first in a way proposed by Kerner [1] and, if necessary after a suitable translation, secondly in the way of Kowalski [2]) it is possible to construct a MAK-system with the same dynamic behavior than an (nearly, cf.[1]) arbitrary (nonchemical) ODE.

An arbitrary MAK-system can furthermore be brought into a form containing only linear and quadratic terms (cf.[1]). Thereby one has to choose the new variables thoroughly in order to conserve the property of the system to be of the MAK-type. With the new variable $z = xy$, for instance, the MAK-term $\dot{x} = -x^2 y^2$ would be transformed into the quadratic non-MAK-term $\dot{x} = -z^2$.

However, as we have shown in the introduction, there are quadratic terms which cannot be interpreted as bimolecular reactions, but only as unrealistic trimolecular ones. A system containing, e.g., the term $\dot{x} = kx^2$ with $k > 0$

cannot be transformed into a bimolecular system with the methods discussed so far, independently of the number of further variables. Note furthermore, that the number of cubic or higher order terms is not always reduced by one if one introduces one further variable in the way of Kerner [1]. An example is the cubic nonlinearity $\dot{x} = -xy^2$. If the differential equation for y contains at least one quadratic term consisting of other variables than x and y , the whole system after the introduction of a new variable still contains at least one cubic term.

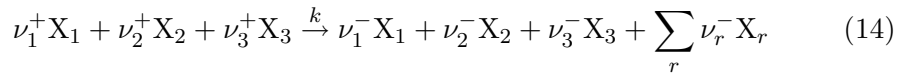
In the next section we show that *every* tri- or higher-molecular reaction can be interpreted as the limit case of a sequence of bimolecular steps. Thereby with one further variable at least one trimolecular reaction can be interpreted as limit case of bimolecular reactions, with two further variables at least one 4-molecular reaction (or two trimolecular ones) can be approximated by bimolecular ones, and so on.

3 Highmolecular reactions as limit case of bimolecular ones

3.1 Trimolecular reactions as limit case of bimolecular ones

We demonstrate the general formalism which allows one to interpret an arbitrary trimolecular reaction as the asymptotic limit case of two bimolecular reactions.

Consider as special case of (1) the general irreversible trimolecular reaction



($\sum_i \nu_i^+ = 3$, $i = 1, 2, 3$, $r = 4, 5, \dots$). The corresponding dynamic behavior of the concentrations is under the assumption of mass-action kinetics described by the equations

$$\begin{aligned} \dot{x}_1 &= (\nu_1^- - \nu_1^+) k x_1^{\nu_1^+} x_2^{\nu_2^+} x_3^{\nu_3^+} \\ \dot{x}_2 &= (\nu_2^- - \nu_2^+) k x_1^{\nu_1^+} x_2^{\nu_2^+} x_3^{\nu_3^+} \\ \dot{x}_3 &= (\nu_3^- - \nu_3^+) k x_1^{\nu_1^+} x_2^{\nu_2^+} x_3^{\nu_3^+} \\ \dot{x}_r &= \nu_r^- k x_1^{\nu_1^+} x_2^{\nu_2^+} x_3^{\nu_3^+} . \end{aligned} \quad (15)$$

Examples are the reaction



($\nu_1^+ = 2, \nu_1^- = 3, \nu_i^{+/-} = 0, i = 2, \dots$), described by

$$\dot{x} = \tilde{k}x^2 \quad (17)$$

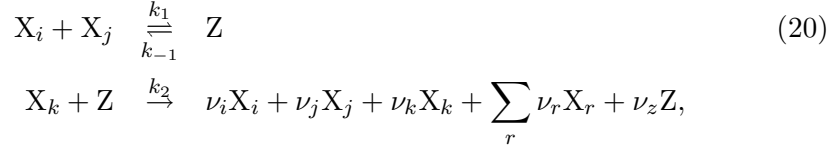
($\tilde{k} = ka$) and the ‘Brusselator’-reaction (cf.[9])



($\nu_1^+ = 1, \nu_1^- = 0, \nu_2^+ = 2, \nu_2^- = 3, \nu_i^{+/-} = 0, i = 3, \dots$), described by the equations

$$\begin{aligned} \dot{x} &= -kxy^2 \\ \dot{y} &= kxy^2. \end{aligned} \quad (19)$$

We now show that the same dynamics than (15) is obtained as limit case ($k_{-1} \rightarrow \infty$) by two bimolecular reactions:



where the further intermediate Z has been introduced. With the small parameter $\varepsilon = 1/k_{-1}$ the corresponding dynamics is described by the equations

$$\begin{aligned} \varepsilon \dot{x}_i &= z + \varepsilon(\nu_i k_2 x_k z - k_1 x_i x_j) \\ \varepsilon \dot{x}_j &= z + \varepsilon(\nu_j k_2 x_k z - k_1 x_i x_j) \\ \dot{x}_k &= (\nu_k - 1)k_2 x_k z \\ \varepsilon \dot{z} &= -z + \varepsilon((\nu_z - 1)k_2 x_k z + k_1 x_i x_j) \\ \dot{x}_r &= \nu_r k_2 x_k z. \end{aligned} \quad (21)$$

In [16] we have discussed equations of such a type in a general manner. In order to approximate these equations asymptotically it is necessary to make the transformations (without loss of generality, cf.[16])

$$(\sigma_1, \sigma_2) = (x_i + z, x_j + z), \quad (22)$$

yielding

$$\begin{aligned} \dot{\sigma}_1 &= (\nu_i + \nu_z - 1)k_2 x_k z \\ \dot{\sigma}_2 &= (\nu_j + \nu_z - 1)k_2 x_k z \\ \dot{x}_k &= (\nu_k - 1)k_2 x_k z \\ \varepsilon \dot{z} &= \varepsilon k_1 (\sigma_1 - z)(\sigma_2 - z) - z + \varepsilon(\nu_z - 1)k_2 x_k z \\ \dot{x}_r &= \nu_r k_2 x_k z. \end{aligned} \quad (23)$$

Because the adjoint system $\dot{z} = -z$ to the fast subsystem (the z -system) has the globally stable steady state $\bar{z} = 0$ one can use the Ansatz

$$z = A(\sigma_1, \sigma_2, x_k, x_r) + \varepsilon B(\sigma_1, \sigma_2, x_k, x_r) + \mathcal{O}(\varepsilon^2) \quad (24)$$

to approximate the slow manifold (cf.[16]). By inserting this into the \dot{z} -equation in (23) one obtains by comparison of the coefficients for equal power of ε the first order approximation for the fast variable z :

$$z = \frac{k_1}{k_{-1}} \sigma_1 \sigma_2. \quad (25)$$

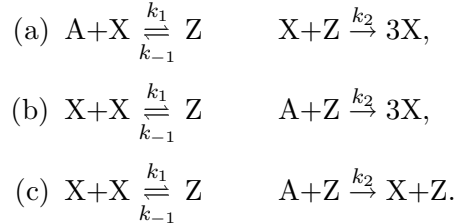
(The zeroth order approximation $z = 0$ is not sufficient for our result.) From (23) it therefore follows

$$\begin{aligned} \dot{\sigma}_1 &= (\nu_i + \nu_z - 1) \frac{k_1 k_2}{k_{-1}} x_k \sigma_1 \sigma_2 \\ \dot{\sigma}_2 &= (\nu_j + \nu_z - 1) \frac{k_1 k_2}{k_{-1}} x_k \sigma_1 \sigma_2 \\ \dot{x}_k &= (\nu_k - 1) \frac{k_1 k_2}{k_{-1}} x_k \sigma_1 \sigma_2 \\ \dot{x}_r &= \nu_r \frac{k_1 k_2}{k_{-1}} x_k \sigma_1 \sigma_2. \end{aligned} \quad (26)$$

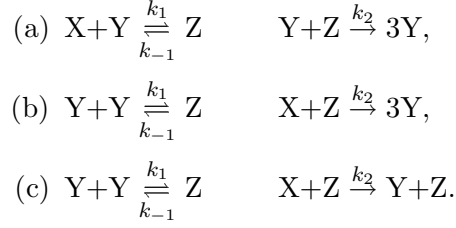
These equations resemble the equations (15) describing the trimolecular reaction (14). Indeed, for *every* concrete trimolecular reaction one can specify the reaction equations (20) in such a way, that (15) and (26) become identically.

Generally there is no unique way to specify the equations (20). Consider the examples (16,18) described by the equations (17,19). For each one there are three possibilities:

1. The reaction (16) can be approximated by

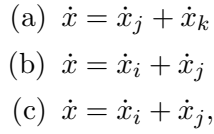


2. The reaction (18) can be approximated by

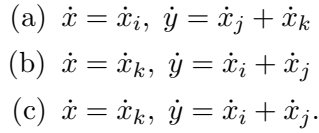


Comparison with (20) yields

1. reaction (16)

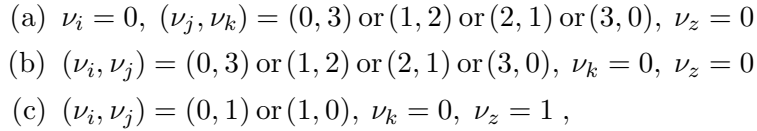


2. reaction (18)

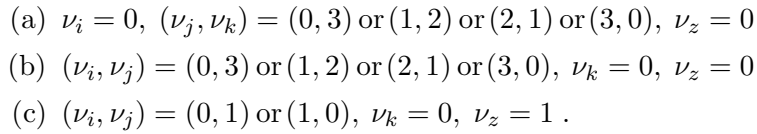


For each of these cases there are again different possibilities to adjoin to them the proper stoichiometric coefficients ν :

1. reaction (16)



2. reaction (18)



However, for both reactions (16,18) each of the possibilities (a,b,c) including their sub-cases for the adjointment of the stoichiometric coefficients yields in the limit case $k_{-1} \rightarrow \infty$, i.e. $\varepsilon \rightarrow 0$, (cf.(22,25)) from (26) the unambiguous equations

1. reaction (16)

$$\dot{x} = \frac{k_1 k_2}{k_{-1}} a x^2 \quad (27)$$

2. reaction (18)

$$\begin{aligned} \dot{x} &= -\frac{k_1 k_2}{k_{-1}} x y^2 \\ \dot{y} &= \frac{k_1 k_2}{k_{-1}} x y^2. \end{aligned} \quad (28)$$

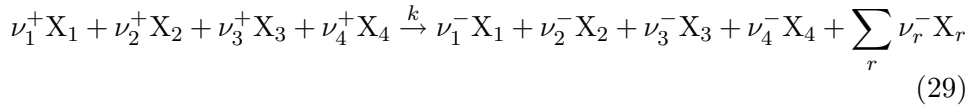
which are identically to (17,19) with $k = k_1 k_2 / k_{-1}$.

In the same way than we have demonstrated for the example reactions (16,18) it can be shown for *every* trimolecular reaction that the corresponding cubic term in the differential equation follows as limit case ($k_{-1} \rightarrow \infty$) from the two bimolecular reactions (20).

Generally for a transformation of a MAK-system containing trimolecular reactions into a MAK-system with at most bimolecular ones (which has as limit case exactly the same dynamics than the trimolecular scheme) one does not need one further intermediate for each trimolecular reaction. For several trimolecular reactions which all have two reactants in common one further intermediate is sufficient.

3.2 Highermolecular reactions as limit case of bimolecular ones

Here we show generally that the dynamics of every 4-molecular reaction can asymptotically be approximated by three bimolecular reactions. The general case of arbitrary high-molecular reactions becomes obviously. The irreversible 4-molecular reaction

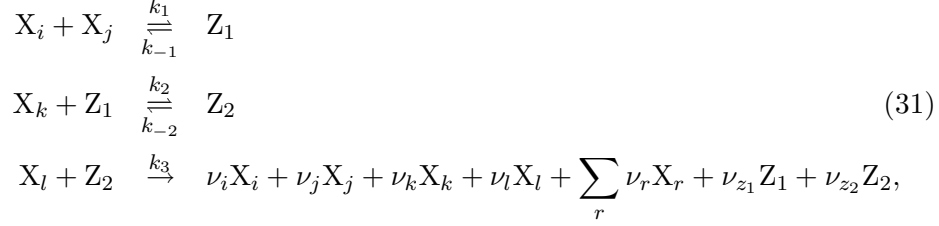


($\sum_i \nu_i^+ = 4$, $i = 1, \dots, 4$, $r = 5, 6, \dots$) is under the assumption of mass-action kinetics described by the equations

$$\begin{aligned} \dot{x}_1 &= (\nu_1^- - \nu_1^+) k x_1^{\nu_1^+} x_2^{\nu_2^+} x_3^{\nu_3^+} x_4^{\nu_4^+} \\ \dot{x}_2 &= (\nu_2^- - \nu_2^+) k x_1^{\nu_1^+} x_2^{\nu_2^+} x_3^{\nu_3^+} x_4^{\nu_4^+} \\ \dot{x}_3 &= (\nu_3^- - \nu_3^+) k x_1^{\nu_1^+} x_2^{\nu_2^+} x_3^{\nu_3^+} x_4^{\nu_4^+} \end{aligned} \quad (30)$$

$$\begin{aligned}\dot{x}_4 &= (\nu_4^- - \nu_4^+) k x_1^{\nu_1^+} x_2^{\nu_2^+} x_3^{\nu_3^+} x_4^{\nu_4^+} \\ \dot{x}_r &= \nu_r^- k x_1^{\nu_1^+} x_2^{\nu_2^+} x_3^{\nu_3^+} x_4^{\nu_4^+}.\end{aligned}$$

We show that the same dynamics is obtained as limit case $k_{-1} = \mathcal{O}(k_{-2}) \rightarrow \infty$ of the bimolecular reactions



where two further intermediates, Z_1 and Z_2 , has been introduced. With the small parameter $\varepsilon = 1/k_{-1}$ the corresponding dynamics is described by the equations

$$\begin{aligned}\varepsilon \dot{x}_i &= z_1 + \varepsilon(-k_1 x_i x_j + \nu_i k_3 x_l z_2) \\ \varepsilon \dot{x}_j &= z_1 + \varepsilon(-k_1 x_i x_j + \nu_j k_3 x_l z_2) \\ \varepsilon \dot{x}_k &= k_{-2}/k_{-1} z_2 + \varepsilon(-k_2 x_k z_1 + \nu_k k_3 x_l z_2) \\ \dot{x}_l &= (\nu_l - 1) k_3 x_l z_2 \\ \varepsilon \dot{z}_1 &= -z_1 + k_{-2}/k_{-1} z_2 + \varepsilon(k_1 x_i x_j - k_2 x_k z_1 + \nu_{z_1} k_3 x_l z_2) \\ \varepsilon \dot{z}_2 &= -k_{-2}/k_{-1} z_2 + \varepsilon(k_2 x_k z_1 + (\nu_{z_2} - 1) k_3 x_l z_2) \\ \dot{x}_r &= \nu_r k_3 x_l z_2.\end{aligned}\tag{32}$$

After the transformations

$$(\sigma_1, \sigma_2, \sigma_3) = (x_i + z_1 + z_2, x_j + z_1 + z_2, x_k + z_2)\tag{33}$$

it follows

$$\begin{aligned}\dot{\sigma}_1 &= (\nu_i + \nu_{z_1} + \nu_{z_2} - 1) k_3 x_l z_2 \\ \dot{\sigma}_2 &= (\nu_j + \nu_{z_1} + \nu_{z_2} - 1) k_3 x_l z_2 \\ \dot{\sigma}_3 &= (\nu_k + \nu_{z_2} - 1) k_3 x_l z_2 \\ \dot{x}_l &= (\nu_l - 1) k_3 x_l z_2 \\ \varepsilon \dot{z}_1 &= -z_1 + k_{-2}/k_{-1} z_2 + \varepsilon(k_1(\sigma_1 - z_1 - z_2)(\sigma_2 - z_1 - z_2) \\ &\quad - k_2(\sigma_3 - z_2)z_1 + \nu_{z_1} k_3 x_l z_2) \\ \varepsilon \dot{z}_2 &= -k_{-2}/k_{-1} z_2 + \varepsilon(k_2(\sigma_3 - z_2)z_1 + (\nu_{z_2} - 1) k_3 x_l z_2) \\ \dot{x}_r &= \nu_r k_3 x_l z_2.\end{aligned}\tag{34}$$

Because the adjoint system ($\dot{z}_1 = -z_1 + k_{-2}/k_{-1} z_2$, $\dot{z}_2 = -k_{-2}/k_{-1} z_2$) to the fast subsystem (z_1, z_2 -system) has the globally stable steady state (0,0), we can use the Ansatz

$$\begin{aligned} z_1 &= A_1(\sigma_1, \sigma_2, \sigma_3, x_l, x_r) + \varepsilon B_1(\sigma_1, \sigma_2, \sigma_3, x_l, x_r) + \mathcal{O}(\varepsilon^2) \\ z_2 &= A_2(\sigma_1, \sigma_2, \sigma_3, x_l, x_r) + \varepsilon B_2(\sigma_1, \sigma_2, \sigma_3, x_l, x_r) + \mathcal{O}(\varepsilon^2) \end{aligned} \quad (35)$$

to approximate the slow manifold (cf.[16]). Inserting this into the fast subsystem one obtains by comparison of the coefficients for equal power of ε as approximation for the fast variables

$$\begin{aligned} z_1 &= \frac{k_1}{k_{-1}} \sigma_1 \sigma_2 \\ z_2 &= \frac{k_1 k_2}{k_{-1} k_{-2}} \sigma_1 \sigma_2 \sigma_3. \end{aligned} \quad (36)$$

From (34) one therefore obtains

$$\begin{aligned} \dot{\sigma}_1 &= (\nu_i + \nu_{z_1} + \nu_{z_2} - 1) \frac{k_1 k_2 k_3}{k_{-1} k_{-2}} \sigma_1 \sigma_2 \sigma_3 x_l \\ \dot{\sigma}_2 &= (\nu_j + \nu_{z_1} + \nu_{z_2} - 1) \frac{k_1 k_2 k_3}{k_{-1} k_{-2}} \sigma_1 \sigma_2 \sigma_3 x_l \\ \dot{\sigma}_3 &= (\nu_k + \nu_{z_2} - 1) \frac{k_1 k_2 k_3}{k_{-1} k_{-2}} \sigma_1 \sigma_2 \sigma_3 x_l \\ \dot{x}_l &= (\nu_l - 1) \frac{k_1 k_2 k_3}{k_{-1} k_{-2}} \sigma_1 \sigma_2 \sigma_3 x_l \\ \dot{x}_r &= \nu_r \frac{k_1 k_2 k_3}{k_{-1} k_{-2}} \sigma_1 \sigma_2 \sigma_3 x_l. \end{aligned} \quad (37)$$

These equations, obtained from a bimolecular approximation of an arbitrary 4-molecular reaction (29), resemble the equations (30). This result is the 4-molecular equivalent to the corresponding equations (26), which were obtained from a bimolecular approximation (20) of the general trimolecular reaction (14). In the same way as for every trimolecular reaction it can for every 4-molecular reaction be shown that the equations (30) and (37) are identically. Transforming a reaction network with several 4-molecular reactions into the corresponding bimolecular form, as in the trimolecular case, generally not for every 4-molecular reaction one needs two further intermediates.

In the same manner n -molecular reactions can be obtained as limit case ($k_{-1} = \mathcal{O}(k_{-i}) \rightarrow \infty$ ($i = 2, \dots, n-2$)) of $n-1$ bimolecular reactions with $n-2$ further intermediates.

4 Interpretation of an arbitrary MAK-reaction as sequence of two reactions with a short-living intermediate

Here we show that an arbitrary MAK-reaction

$$\sum_i \nu_i^+ X_i \xrightarrow{k} \sum_i \nu_i^- X_i \quad (i = 1, 2, \dots) \quad (38)$$

(This is the irreversible case of reaction (1).) can be understood as the limit case ($k_2 \rightarrow \infty$) of two corresponding MAK-reactions with a short-living intermediate Z which have the form

$$\sum_i \nu_i^+ X_i \xrightarrow{k_1} Z \xrightarrow{k_2} \sum_i \nu_i^- X_i . \quad (39)$$

Reaction (38) is described by the differential equations

$$\dot{x}_i = (\nu_i^- - \nu_i^+) k \prod_i x_i^{\nu_i^+} . \quad (40)$$

Reaction (39) implies

$$\begin{aligned} \varepsilon \dot{x}_i &= -\varepsilon \nu_i^+ k_1 \prod_i x_i^{\nu_i^+} + \nu_i^- z \\ \varepsilon \dot{z} &= \varepsilon k_1 \prod_i x_i^{\nu_i^+} - z \end{aligned} \quad (41)$$

with the small parameter $\varepsilon = 1/k_2$. With the transformations

$$\sigma_i = x_i + \nu_i^- z \quad (42)$$

one obtains

$$\begin{aligned} \dot{\sigma}_i &= (\nu_i^- - \nu_i^+) k_1 \prod_i (\sigma_i - \nu_i^- z)^{\nu_i^+} \\ \varepsilon \dot{z} &= \varepsilon k_1 \prod_i (\sigma_i - \nu_i^- z)^{\nu_i^+} - z. \end{aligned} \quad (43)$$

Because the adjoint system $\dot{z} = -z$ has the globally stable steady state $\bar{z} = 0$ one can approximate the fast variable in zeroth order by

$$z = 0. \quad (44)$$

It therefore follows

$$\dot{\sigma}_i = (\nu_i^- - \nu_i^+)k_1 \prod_i \sigma_i^{\nu_i^+}, \quad (45)$$

which is, taking into account (42,44), exactly the equation (40).

Note that in contradiction to the approximations made in section 3, here already the zeroth order is sufficient to gain the desired result.

From this calculation it immediately follow two main results. At first, every MAK-reaction which is autocatalytic in the sense of (2) can be approximated by two reactions in the form of (39), which are not autocatalytic in that sense. Secondly, every MAK-reaction which is *not elementary*, because “the same substance appears both as reactant and as product” (cf.[19]) can be approximated by two *really elementary* reactions.

5 Discussion

Summarizing, we have shown in section 3 and 4 that it is possible to transform an arbitrary MAK-system into a form, which contains only mono- and elementary bimolecular reactions. In the limit case the long-time dynamics of this system is exactly identical with the dynamics of the original MAK-system. Together with the results of [1, 2] and section 2 this leads to the statement: for every dynamic phenomenon which can occur in an ODE one can construct an elementary bimolecular MAK-system which shows this behavior. The only restriction is that it must be possible to transform a non-polynomial system into a polynomial one, but this can be done for all cases “that arise in practice” (cf.[1]). This justifies the title of this work: elementary chemical reaction systems are a paradigm for nonlinear behavior.

For the transformation of an arbitrary ODE into an elementary MAK-system we thus have the general scheme: 1. transformation of a non-polynomial ODE into a polynomial one [1], 2. transformation of a non-MAK-polynomial system into a MAK-system ([2] *and* section 2), 3. transformation of an arbitrary MAK-system into a bimolecular one (section 3), 4. transformation of a bimolecular MAK-system into a MAK-system consisting only of elementary reactions (section 4).

Note that for the second step the results of [2] are not sufficient. For instance, non of the 19 small ‘chaotic’ polynomial systems of [13] can in the way of [2] be transformed into MAK-systems. For such a transformation a further translation is necessary. This we have discussed in detail in section 2.

Another way for step 2 has been proposed in [14]. There the confinement of the trajectories to the positive cone of the phase space is forced simply by a multiplication of the phase flow by $\text{diag}(x)$. This transformation has the advantage that the number of variables is *not* increased. However, the dynamics may be changed by this procedure and there is no way to guarantee exactly the same dynamics than in the original system, neither by fixing the initial values like in [1, 2] nor in the asymptotic limit like in sections 3 and 4. Nevertheless, the transformed system often shows similar dynamics than the original one (cf.[14]).

Alternative to make the transformation of an arbitrary MAK-system into a bimolecular one (step 3) only in the way proposed in section 3, one can at first transform the general MAK-system into a form which contains only quadratic terms (cf. [1, 2] and section 2). Afterwards one can transform these quadratic terms which cannot be interpreted as a bimolecular reaction into the bimolecular form in the way of section 3. However, using this way at first one must take care that one does not violate the MAK-property (this can be done by thoroughly choosing the new variables), secondly this way generally needs more further variables (cf. section 2).

Note that in contrast to the methods of [1, 2] for the new introduced variables in sections 3 and 4 there is no restriction of the initial values. Every initial value of the new variable yields the same long-time behavior of the system, because the steady state of the adjoint system is always globally stable. The disadvantage is that the dynamics is only in the limit case exactly the same as in the untransformed system. Therefore, the question remains what happens if the small parameter ε is highered to finite values. In most cases surely the qualitative behavior will remain unchanged but also further bifurcations can occur.

Transforming highmolecular reactions into elementary bimolecular ones we restricted ourselves to the irreversible case. Because every reversible reaction can be understood as the sum of 2 independent irreversible reactions, all statements are valid also for the reversible case.

The proposed scheme for a transformation of an arbitrary ODE into a MAK-system (including steps 3 and 4 or not) can be used to propose a suitable MAK-model if the behavior of the system which one wants to simulate resembles the behavior of a known (non-MAK) dynamical system. This model may be reduced by successively cancelling not necessary elements (reactions, variables) and/or improved by adding further elements.

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References

- [1] E. N. Kerner, Universal formats for nonlinear ordinary differential systems, J. Math. Phys. 22 (1981) 1366-1371.
- [2] K. Kowalski, Universal formats for nonlinear dynamical systems, Chem. Phys. Lett. 209 (1993) 167-170.
- [3] A. N. Zaikin and A. M. Zhabotinsky, Concentration wave propagation in two-dimensional liquid-phase self-oscillating systems, Nature 225 (1970) 535-537.
- [4] R. J. Field and R. M. Noyes, Oscillations in chemical systems. IV. Limit cycle behavior in a model of a real chemical reaction, J. Chem. Phys. 60,5 (1974) 1877-1884.
- [5] A. J. Lotka, Zur Theorie der periodischen Reaktionen, Z. Physik. Chem. 72 (1910) 508-511.
A. J. Lotka, Undamped oscillations derived from the law of mass action, J. Am. Chem. Soc. 42 (1920) 1595-1599.
- [6] V. Volterra, Fluctuations in the abundance of a species considered mathematically, Nature 118 (1926) 558-560.
- [7] W. C. Bray, A periodic chemical reaction and its mechanism, J. Am. Chem. Soc. 43 (1921) 1262.
- [8] P. Glansdorff and I. Prigogine, *Thermodynamic theory of structure, stability and fluctuations*, Wiley, 1971.
- [9] I. Prigogine and R. Lefever, Symmetry breaking instabilities in dissipative systems II, J. Chem. Phys. 48,4 (1968) 1695-1700.
- [10] I. R. Epstein, Oscillations and chaos in chemical systems, Physica D, 7 (1983) 47-56.
- [11] T. Wilhelm and R. Heinrich, Smallest chemical reaction system with Hopf bifurcation, J. Math. Chem. 17 (1995) 1-14.
T. Wilhelm and R. Heinrich, Mathematical analysis of the smallest chemical reaction system with Hopf bifurcation, J. Math. Chem. 19 (1996) 111-130.

- [12] C. Escher, Bifurcation and coexistence of several limit cycles in models of open two-variable quadratic mass-action systems, *Chem. Phys.* 63 (1981) 337-348.
- [13] J. C. Sprott, Some simple chaotic flows, *Phys.Rev.E* 50,2 (1994) R647-R650.
J. C. Sprott, Simplest dissipative chaotic flow, *Phys. Lett. A* 228 (1997) 271-274.
- [14] N. Samardzija, L. D. Greller, and E. Wasserman, Nonlinear chemical kinetic schemes derived from mechanical and electrical dynamical systems, *J. Chem. Phys.* 90,4 (1989) 2296-2304.
- [15] G. B. Cook, P. Gray, D. G. Knapp, and S. K. Scott, Bimolecular routes to cubic autocatalysis, *J. Phys. Chem.* 93 (1989) 2749-2755.
- [16] K. R. Schneider and T. Wilhelm, Model reduction by extended quasi-steady-state approximation, Preprint No.457, Weierstraß-Institut für Angewandte Analysis und Stochastik, Berlin, 1998.
- [17] K. Alhumaizi and R. Aris, *Surveying a Dynamical System: A Study of the Gray-Scott Reaction in a Two-Phase Reactor*, Longman, 1995.
- [18] T. Wilhelm and P. Hänggi, What can be stated by the Glansdorff-Prigogine criterion concerning the stability of mass-action kinetic systems, *J. Chem. Phys.* 110 (1999) xxx.
- [19] G. A. M. King, Reactions for chemical systems far from equilibrium, *J. Chem. Soc., Faraday Trans. 1*, 79 (1983) 75-80.
- [20] C. Sparrow, *The Lorenz Equations: Bifurcations, Chaos, and Strange Attractors*, Springer, 1982, *Appl. Math. Sci.* 41.