Mass action law conjugate representation for general chemical mechanisms

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Abstract

Power-law rates constitute a common approximation to the general analysis of the stability properties of complex reaction networks. We point out in this paper that this form for the rates does not need to be assumed as an approximation for general rate-laws. On the contrary, any functional form for a rate law can be represented exactly in terms of power-laws. Moreover, we can uniquely associate to any set of kinetic equations an equivalent ‘conjugate’ representation in terms of the well-known generalized Lotka-Volterra equations, standing for what we call per capita rates, which amounts to a great simplification in terms of the structural form of the mathematical representation of a reaction network.

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I. Introduction

Mass action law chemical kinetics, and its corresponding mathematical modelling, has for long been considered as a prototype in nonlinear science.\textsuperscript{1} We can all recall how such archetypical schemes, as the Brusselator, Oregonator, Schlögl model (to cite a few) which have constituted the vanguard in the pioneering years. The simplicity of the stoichiometric rules and that of the algebraic structure of the corresponding evolution equations has made chemical kinetics a traditional point of reference in modeling within such fields as population biology,\textsuperscript{2} quantitative sociology,\textsuperscript{3} prebiotic evolution\textsuperscript{4} and other biomathematic problems,\textsuperscript{5} where a system is viewed as a collection of ‘species’ interacting as molecules do. Moreover, as emphasised by Érdi and Tóth,\textsuperscript{1} even the algebraic structure of the evolution equations from many other fields can be converted into ‘chemical language’, where a formal ‘analog’ in terms of a chemical reaction network is defined.

The interest of this common mathematical framework provided by chemical kinetics is not only aesthetic. It has sparked the quest of theorems which connect the structure of the chemical reaction network with the qualitative features of the solutions to the corresponding differential equations.\textsuperscript{6} In fact, we are talking about the search of theorems which would permit the knowledge of behaviors open to the system from an identification of certain patterns in the network, and that of the associated algebraic structure of the differential equations. And conversely, mathematical propositions which should eventually point at which of the properties of a chemical reaction network are to be selected for the obtaining of a given behavior. The ultimate goal being that of a classification of networks, or at least of certain of their characteristics. The accomplishment of this purpose would certainly yield a tool of great practical importance in modeling. The zero deficiency theorem\textsuperscript{7,8} and Vol’pert’s theorem\textsuperscript{9} are examples of results associating graph properties of the reaction network with the existence of equilibrium points.

In the context of classification of networks, a significant step forward has been done by Clarke\textsuperscript{10} with the stoichiometric network analysis, with the help of which he addresses the issue of connecting the topology of a given chemical network with: 1) The network stability problem (necessary and sufficient conditions for ensuring stability of steady states); 2) The stability diagram problem (calculation of the bifurcation set of an unstable network). Ross and collaborators\textsuperscript{11}
have made extensive use of this tool for the categorization and obtainment of model mechanisms from experimental data in chemical oscillators.

As emphasized by Clarke, the key role in the stoichiometric network analysis is played by the effective power function for species \( i \) in reaction \( j \), defined at steady state \( \mathbf{X}_0 \) as:

\[
\kappa_{ij}(k) = \left[ \frac{\partial \log v_j(\mathbf{X}, k)}{\partial \log X_i} \right]_{\mathbf{X} = \mathbf{X}_0},
\]

where \( v_j(\mathbf{X}, k) \) is the reaction rate, dependent upon a concentration vector \( \mathbf{X} \), and a set of reaction constants, \( k \). Then, the stability of the steady state, in a network involving \( n \) species and \( r \) reactions, is given by the solutions of:

\[
\frac{d}{dt} \delta X_i = \sum_{m=1}^{n} \left( \sum_{j=1}^{r} \nu_{ij} \kappa_{mj} \left[ \frac{v_j}{X_m} \right]_{\mathbf{X} = \mathbf{X}_0} \delta X_m \right)
\]

where \( \nu_{ij} \) are the elements of the net stoichiometric matrix.

In principle, the rate laws \( v_j(\mathbf{X}, k) \) can have any form, but in (1) and (2) we effectively assume that in practice rate laws can be approximated locally, around the steady state, by the traditional power-law,

\[
v_j(\mathbf{X}, k) = k_j \prod_{i=1}^{n} X_i^{\kappa_{ij}},
\]

in which the reaction orders \( \kappa_{ij} \) are not restricted to the integer values given by the law of mass action. These non integer values have already been found in situations where the mean-field approximation does not hold,\(^\text{12}\) as it happens in diffusion-limited kinetics, either in disordered media with fractal structures, or on regular lattices of dimensionality smaller than the critical value, \( d = 2 \).\(^\text{13}\) Here, the single elementary reaction

\[2A \rightarrow \text{products}\]

displays a non-integer order of reaction, which may be even greater than 3 when occurring on fractal ‘dust’,\(^\text{14}\) with spectral dimension \( 0 \leq d_s \leq 1 \). Also, an extensive use of the power-law approximation has been made by Savageau and collaborators. Starting with the observation that enzyme-kinetic rates are well represented by linear relations in logarithmic space,\(^\text{15}\) they have generalized this structural pattern to the analysis of many natural systems, encapsulating their
modeling in a systematic use of a version of the power-law formalism called S-system approach.\textsuperscript{16} Finally, we can mention the different solutions suggested to solve the ‘inversion problem’: the embedding of general differential equations into a unified formalism in terms of stoichiometric networks with power-law kinetics; or, more specifically, mass-action kinetics.\textsuperscript{17} In this context, contributions from Samardzija \textit{et al.},\textsuperscript{18} Poland\textsuperscript{19} and Kowalsky\textsuperscript{20} have tried different routes for producing stoichiometric network counterparts of well known prototypical models, as Lorenz and Rössler systems, or the Van der Pol oscillator.

The assumption of power-law rates is at the heart of most treatments trying to establish a unifying mathematical framework around the concept of a stoichiometric network. This systematic approach opens, as Ross and collaborators have shown,\textsuperscript{11} new horizons to the chemical dynamicists, inasmuch as the structural analogies which might be discovered will be of help in configuring an association between the structure of a chemical mechanism and the expected behavior.

We intend in the present article to stress how general functional forms for the rate laws may be exactly encapsulated into a power-law formalism without resorting to a local approximation, as in (3). We will then rewrite the resulting kinetic equations into power-law rates equations, and that will permit to show that the evolution equations for the \textit{per capita} rates, defined as

\[
\frac{\nu_j(X, k)}{X_i},
\]

are always in the form of generalized Lotka-Volterra equations, no matter what is the particular form of the original rate equations. An equivalent ‘conjugate’ network may be associated to this generalized Lotka-Volterra representation, which involves unimolecular, bimolecular and pseudounimolecular steps. We shall discuss the properties of this transformation and show that it leads to a unique generalized Lotka-Volterra representation for a given reaction network.

\section*{II. Exact equivalence to power-law rates systems}

Within the power-law formalism, the kinetic equations for a given species involved in a mechanism with \( r \) reactions are:

\[
\dot{X}_i = \sum_{j=1}^r k_j \nu_{ij} \prod_{k=1}^n X_{k}^{x_{kj}},
\]

(4)
to which we shall refer, from now on, as power-law rates systems.

The question now is to demonstrate that general functional relations for the rate laws are amenable to an equivalent power-law form without resorting to approximations. The procedure to do so is well known\textsuperscript{21,22} and can be illustrated with a simple example. Assume the following mechanism of pseudoreactions

\[
\begin{align*}
A & \overset{k_1}{\rightarrow} Y \quad (5.a) \\
B & \overset{k_2}{\rightarrow} X \quad (5.b) \\
X & \overset{k_2'}{\rightarrow} B \quad (5.c) \\
X + Y & \overset{k_3}{\rightarrow} \text{products} \quad (5.d)
\end{align*}
\]

which constitute an early model by Degn and Harrison\textsuperscript{23,24} to account for the oscillations in the peroxidase-oxidase reaction:

\[
2 \text{NADH} + \text{O}_2 + 2\text{H}^+ \rightarrow 2 \text{NAD}^+ + 2\text{H}_2\text{O}
\]

Reaction (5.d) is the peroxidase enzyme catalyzed oxidation of the NADH ($Y$) by dilute oxygen ($X$), which was assumed in the model to be inhibited at high concentrations of the latter. According to Degn and Harrison the corresponding rate law was taken to follow a Michaelis-Menten form, suggesting for model (5), when species $A$ and $B$ are held constant, the following equations in dimensionless-form:

\[
\begin{align*}
\dot{X} &= B - X - \frac{XY}{1 + qX^2} \quad (6.a) \\
\dot{Y} &= A - \frac{XY}{1 + qX^2} \quad (6.b)
\end{align*}
\]

We now introduce the auxiliary variable $Z = (1 + qX^2)^{-1}$, which converts the r.h.s. of (6) into polynomial form, but which calls for a supplementary equation for that same auxiliary variable. It will be

\[
\dot{Z} = \frac{\partial Z}{\partial X} \dot{X},
\]

which again is polynomial provided $\partial Z/\partial X$ is already in such form. This can be proved to be the case for smooth functions, though we shall not discuss the demonstration here (interested readers are referred to Kerner\textsuperscript{21} and Hernández-Bermejo and Fairén\textsuperscript{22}). After elementary algebra, we find for (6)

\[
\dot{X} = B - X - X Y Z \quad (7.a)
\]
\[
\dot{Y} = A - XYZ \quad (7.b)
\]
\[
\dot{Z} = -2qBXZ^2 + 2qX^2Z^2 + 2qX^2YZ^3 \quad , \quad (7.c)
\]

which is written in terms of power-law rates. In going from (5) to (7) the dimensionality of the kinetic equations has been increased. The equivalence between these two sets of equations will be ensured if the initial condition for variable \(Z\) is taken to be \(Z(0) = (1 + qX(0)^2)^{-1}\) (we again refer to Kerner\(^{21}\) for further details). According to (7) the step in (5.d) is substituted by the ‘kinetically equivalent’ set of pseudoreactions

\[
X + Y + Z \rightarrow Z + \text{products} \quad (8.a)
\]
\[
Q + B + X + 2Z \rightarrow X + \text{products} \quad (8.b)
\]
\[
Q + 2X + 2Z \rightarrow 2X + 4Z \quad (8.c)
\]
\[
Q + 2X + Y + 3Z \rightarrow 2X + Y + 5Z \quad (8.d)
\]

The high molecularity of the pseudoreactions (8) might eventually be reduced if additional ‘auxiliary variables’ were introduced in (7), i.e.: \(XZ = W\); with a corresponding increase in the number of items in the kinetically equivalent set of pseudoreactions.

The previous procedure can be systematically carried out\(^{22}\) for any rate-law represented by a smooth function. It amounts to a reduction in the degree of nonlinearity to power-laws by the labelling under ‘auxiliary variables’ of functional expressions of the original independent variables. The initial conditions for these new variables are then automatically prescribed by the same functional expressions from which they are defined. Once the procedure is complete, the new variables are understood to represent the concentrations of some ‘virtual’ species, reacting in accordance to some appropriate mechanism, as in (8).

Up to this point, and before proceeding any further, a comment is needed on the procedure leading from (5) to (8). The previous method should be viewed as a ‘protocol’ for rewriting a system of ordinary nonlinear differential equations into a pattern formally identifiable as one describing the evolution of a collection of ‘objects’ interacting according to the rules of the law of mass action. We then do refer to ‘pseudospecies’, rather than to chemical species, because no actual chemical process has been found to obey such schemes (network). This is simply due to the fact that the combinations and scenarios open to objects behaving
under the simple rules of the law of mass action clearly outnumber the actually known chemical processes, including those which are seriously considered chemically plausible but have not been actually observed.

III. Conjugate representation in terms of generalized Lotka-Volterra equations

We can now return to (4) and write it in a slightly different way:

\[
\dot{X}_i = X_i \sum_{j=1}^{r} k_{ij} \nu_{ij} \prod_{k=1}^{n} X_k^{\kappa_{jk}} - \delta_{ik} = X_i \sum_{j=1}^{m} A_{ij} \prod_{k=1}^{n} X_k^{B_{jk}}
\]  

(9)

where \( i = 1, \ldots, n \) and \( \delta_{ik} \) is the Kronecker delta symbol.

The kinetic equations are now written in terms of the per capita rates

\[
Y_j = \prod_{k=1}^{n} X_k^{B_{jk}}, \quad j = 1, \ldots, m
\]  

(10)

In (9) we implicitly assume that there are actually \( m \) distinguishable per capita rates in a network with \( r \) reactions: \( m \) is not necessarily equal to \( r \), for different reactions might possess the same per capita rates, and conversely, a single reaction will generate a specific per capita rate for each of the relevant species involved.

We shall henceforth assign, in (9) and (10), the label \( j = 1 \) to the constant per capita rate (that with \( B_{1k} = 0, \ k = 1, \ldots, n \)). It will then be understood that \( Y_2, \ldots, Y_m \) will have at least one non-null \( B_{jk} \) entry. Then, \( B \) will be an \( m \times n \) matrix with a null first row, and \( A \) an \( n \times m \) matrix with its first column filled in with the coefficients of \( Y_1 \) (which will correspond to the linear rates in the network).

Let us now take time derivatives of both sides of (10). For \( Y_1 \) we have

\[
\dot{Y}_1 = 0
\]  

(11)

to which we can assign, without loss of generality, the solution

\[
Y_1 = 1
\]  

(12)

On the other hand, for \( Y_2, \ldots, Y_m \), we have

\[
\dot{Y}_j = \sum_{s=1}^{n} \frac{dY_j}{dX_s} \dot{X}_s = \sum_{s=1}^{n} B_{js} \prod_{k=1}^{n} X_k^{B_{jk}} - \delta_{ks} =
\]
Then, the resulting equations of motion for the per capita rates are in the form of generalized Lotka-Volterra equations. They might themselves, in turn, be assigned to the time evolution of a set of pseudospecies in a ‘chemical network’ comprising, at most, bimolecular steps in the relevant pseudospecies. This result is universal and applicable to any set of kinetic equations with power-law rates, and by extension, as demonstrated before, it is also valid for general functional relations for the rates.

The generalized Lotka-Volterra equations (13) constitute a conjugate representation of the original kinetic equations (4) for a given chemical network. They provide a much stronger unifying structure than that associated to (4); a structure for which there exist several tools for studying the features of the solutions, and which are straightforwardly translatable into a graph theory setting. This is not the place to discourse upon the issues related to the generalized Lotka-Volterra equations, because most of the general results of interest to the chemical dynamicist (related to stability of steady states) are highly mathematical and fall outside the scope of this paper. We shall nevertheless touch upon some aspects of interest later on, after giving an example of the procedure of obtainment of (13).

**Example:** Let us take (7). According to the notation in (9) we can write for matrices A and B:

\[
A = \begin{pmatrix}
-1 & B & -1 & 0 & 0 & 0 \\
0 & 0 & 0 & A & -1 & 0 \\
0 & 0 & 0 & 0 & -2qB & 2q \\
-2q & 2q & 2q & 2q & 2q & 2q
\end{pmatrix},
\]

\[
B = \begin{pmatrix}
0 & 0 & 0 \\
-1 & 0 & 0 \\
0 & 1 & 1 \\
0 & -1 & 0 \\
1 & 0 & 1 \\
2 & 0 & 1 \\
2 & 1 & 2
\end{pmatrix},
\]

from which we can easily calculate matrix \( L = B \cdot A \), in (13). B is simply the order matrix for the per capita rates involved in (7), and can be systematically
written down once we display (7) in the following form:

\[
\frac{d}{dt} \ln(X) = \frac{\dot{X}}{X} = -1 + BX^{-1} - YZ \tag{16.a}
\]

\[
\frac{d}{dt} \ln(Y) = \frac{\dot{Y}}{Y} = AY^{-1} - XZ \tag{16.b}
\]

\[
\frac{d}{dt} \ln(Z) = \frac{\dot{Z}}{Z} = -2qBXZ + 2qX^2Z + 2qX^2YZ^2 \tag{16.c}
\]

whilst matrix A is obtained from the corresponding coefficients. As indicated before, the first row in (15) has zero entries. Correspondingly, the generalized Lotka-Volterra matrix \( L = B \cdot A \) will also have a zero first row, which is understandably assignable to (11).

A mechanism (or network) may be associated to the generalized Lotka-Volterra equations in terms of unimolecular, pseudounimolecular and bimolecular steps which follow the law of mass-action. This mechanism is a sort of ‘conjugate’ reactional scheme to the original network, and might be as well be used as a complementary (or alternative) representation in investigations directed towards the classification of complex reaction networks.\(^{10}\) The structural simplicity of the generalized Lotka-Volterra equations (which are characterized by a single algebraic object: matrix \( L \), the properties of which are strongly related to certain important features of the solutions), as well as their ubiquity in many scientific disciplines,\(^{26}\) makes this approach particularly attractive.

Upon examination of matrix \( L \) obtained from, say, (14) and (15), we infer that its last three rows will be linear combinations of the three immediately preceding ones. By construction, this fact is generalizable to any matrix \( L \) \((m - n - 1 \text{ rows will be linearly dependent on } n \text{ rows})\). This pattern determines the establishment of an associated modular mass-action law reaction network. A pseudoreaction template is ascribed to each entry of the independent rows in matrix \( L \). Those pseudoreactions templates constitute the modules, or building blocks, which the whole reaction network is made of.

In connection to the example of the peroxidase-oxidase model (7), these constitutive units are, in view of (14) and (15), given by

\[
\pm Y_j \left( -1 - BY_2 + Y_3 \right) \tag{17.a}
\]

\[
\pm Y_j \left( AY_4 - \left( 1 + 2qB \right) Y_5 + 2qY_6 + 2qY_7 \right) \tag{17.b}
\]
\[ \pm Y_j (-AY_4 + Y_5) \quad (17.c) \]

for any \( j \geq 2 \).

Expression (17.a) might, for example, schematically represent any of the following pseudoreaction templates

with (+) sign
\[
\begin{align*}
Y_j & \rightarrow Y_j \\
Y_j + B + Y_2 & \rightarrow B + Y_2 \\
Y_j + Y_3 & \rightarrow 2Y_j + Y_3
\end{align*}
\]

with (–) sign
\[
\begin{align*}
Y_j & \rightarrow 2Y_j \\
Y_j + B + Y_2 & \rightarrow 2Y_j + B + Y_2 \\
Y_j + Y_3 & \rightarrow Y_3
\end{align*}
\]

IV. Properties of the transformation to the conjugate representation

In order to demonstrate some important results regarding the validity and scope of the previous manipulations, we will consider in this section the most usual case in which \( m > n \), that is, the number of per capita rates is greater than that of variables. For example, in the peroxidase equations (16) we have \( m = 7 \) and \( n = 3 \). We will also assume that the rank of matrix \( B \) is maximum: \( \text{rank}(B) = n \).

A necessary condition for ensuring the equivalence between system (9) and the generalized Lotka-Volterra equations (13) is that the transformation relating them preserves the topological characteristics of the solutions. We shall prove that this is indeed the case here. A sufficient condition for demonstrating this statement is the existence of a continuous, differentiable and invertible application connecting the initial and final phase spaces. Since the dimension of the generalized Lotka-Volterra system is greater than that of (9), such an application should connect the phase space of (9) and the \( n \)-dimensional subset of \( \mathbb{R}^m \) into which it is mapped.

We can write the transformation (10) relating the power-law rates system variables to the per capita rates as:

\[ Y_j = \prod_{k=1}^{m} X_k^{B_{jk}}, \quad j = 1, \ldots, m, \quad (18) \]
where \( X_{n+1} = \ldots = X_m = 1 \) and \( \tilde{B} \) is an \( m \times m \) matrix, defined as:

\[
\tilde{B} = \begin{pmatrix}
B_{1, n+1} & \ldots & B_{1, m} \\
\vdots & \ddots & \vdots \\
B_{m, n+1} & \ldots & B_{m, m}
\end{pmatrix} \equiv (B | B')
\] (19)

Here \( B \) is the already known \( m \times n \) matrix of exponents of the per capita rates, and \( B' \) is a \( m \times (m - n) \) matrix of arbitrary entries. These entries can always be selected in such a way that \( \tilde{B} \) is invertible. Equation (18) is obviously differentiable. Thus, we only need to prove that it is one to one and invertible.

If we take logarithms in both sides of (18):

\[
\begin{pmatrix}
\ln(Y_1) \\
\vdots \\
\ln(Y_m)
\end{pmatrix} = \tilde{B}
\begin{pmatrix}
\ln(X_1) \\
\vdots \\
\ln(X_n) \\
0
\end{pmatrix}
\] (20)

Since \( \text{rank}(\tilde{B}) = m \), for any two vectors \( X \) and \( X' \) we have \( \tilde{B} \ln(X) \neq \tilde{B} \ln(X') \), unless \( X = X' \). Thus the map (18) is one to one and invertible (\( \tilde{B} \) invertible) and the topology is preserved by the transformation.

The original variables of the power-law rates system (9) can be retrieved from those of the generalized Lotka-Volterra system by means of two different procedures. The first one is obtained by writing system (9) in the separable form:

\[
\frac{\dot{X}_i}{X_i} = \sum_{j=1}^{m} A_{ij} Y_j(t) , \quad i = 1, \ldots, n
\] (21)

Then the \( X_i \) result from the formal integrations:

\[
X_i(t) = X_i(0) \exp \left\{ \sum_{j=1}^{m} A_{ij} \int_0^t Y_j(t') dt' \right\}
\] (22)

The second approach is purely algebraic and does not require any integration. Since \( B \) is an \( m \times n \) matrix, with \( m > n \), and \( \text{rank}(B) \) is maximum, then there exists an \( n \times n \) invertible submatrix \( B_n \) of \( B \). Let

\[
B_n = \begin{pmatrix}
B_{i_1,1} & \ldots & B_{i_1,n} \\
\vdots & \ddots & \vdots \\
B_{i_n,1} & \ldots & B_{i_n,n}
\end{pmatrix}, \quad \{i_1, \ldots, i_n\} \subset \{2, \ldots, m\}
\] (23)
This implies that:

\[
\begin{pmatrix}
\ln(Y_{i_1}) \\
\vdots \\
\ln(Y_{i_n})
\end{pmatrix} = B_n
\begin{pmatrix}
\ln(X_1) \\
\vdots \\
\ln(X_n)
\end{pmatrix}
\] (24)

Since \(B_n\) is invertible, this finally leads to:

\[
X_k(t) = \prod_{p=1}^{n} \left[ Y_{p}(t) \right]^{(B_n^{-1})_{kp}}, \quad k = 1, \ldots, n
\] (25)

The time evolution or stability properties of a given reaction network might be analyzed in anyone of these two alternative descriptions (\(X\) or \(Y\)), for they are completely equivalent. However, as far as structural properties are concerned, the generalized Lotka-Volterra form (in terms of \(Y\)) seems preferable for it is mathematically characterized by a single algebraic object: matrix \(L\).

As we have seen, to every power-law rates system (9) a single generalized Lotka-Volterra conjugate system can be associated. The question now is to what extent this is also valid for general rate-laws:

\[
\dot{X} = F(X)
\] (26)

The way for finding the conjugate representation consists, as we saw in Sections II and III in the peroxidase-oxidase example, in the introduction of auxiliary variables for functional rate-laws in the right hand side of (26) not complying to the power-law rates system format. This always leads to a power-law rates system from which the obtainment of the generalized Lotka-Volterra system is straightforward. We shall see that, to a great extent, the generalized Lotka-Volterra representative is unique for every system of the form (26), and is independent of the specific choice of auxiliary variables. Instead of a formal approach, we shall consider in more detail the peroxidase example. However, the results that we shall display can be proved rigorously.\(^{22,28}\)

Let us generalize the procedure of Section II by introducing an auxiliary variable of the form:

\[
Z = X^{\alpha}Y^{\beta}(1 + qX^2)^{\gamma}
\] (27)

where \(\alpha, \beta\) and \(\gamma\) are real parameters and \(\gamma \neq 0\). After some algebra, the introduction of this general variable leads to a family of \((\alpha, \beta, \gamma)\)-dependent
power-law rates systems with matrices:

\[
A(\alpha, \beta, \gamma) = \begin{pmatrix}
-1 & B & -1 & 0 & 0 & 0 \\
0 & 0 & 0 & A & -1 & 0 \\
-\alpha & B\alpha & -\alpha & A\beta & 2qB\gamma & -2q\gamma \\
\end{pmatrix}
\] (28)

\[
B(\alpha, \beta, \gamma) = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 & 0 & 0 \\
\end{pmatrix}
\] (29)

However, the product \( L = B(\alpha, \beta, \gamma) \cdot A(\alpha, \beta, \gamma) \) is independent of \( \alpha \), \( \beta \), and \( \gamma \). Since \( L \) is the matrix associated to the conjugate generalized Lotka-Volterra system, this means that such representation is unique, independently of the choice of the auxiliary variables. Of course, this matrix \( L \) coincides with the one obtained from the product of (15) and (14), which are particular cases of (29) and (28), respectively, with \( \alpha = 0, \beta = 0, \gamma = -1 \). This is consistent with the fact that the variables of the generalized Lotka-Volterra representative are independent of \( (\alpha, \beta, \gamma) \). From matrix (29), they are:

\[
1; \quad X^{-1}; \quad X^{\alpha/\gamma}Y^{1+\beta/\gamma}Z^{-1/\gamma} = \frac{X}{1 + qX^2};
\]

\[
Y^{-1}; \quad X^{1+\alpha/\gamma}Y^{\beta/\gamma}Z^{-1/\gamma} = \frac{X}{1 + qX^2}; \quad X^{2+\alpha/\gamma}Y^{\beta/\gamma}Z^{-1/\gamma} = \frac{X^2}{1 + qX^2};
\]

\[
X^{2+2\alpha/\gamma}Y^{1+2\beta/\gamma}Z^{-2/\gamma} = \frac{X^2Y}{(1 + qX^2)^2} \] (30)

This implies that the initial conditions of the conjugate generalized Lotka-Volterra system will also be unique. In other words: To every general system of the form (26) a single generalized Lotka-Volterra system can be associated by means of this procedure. Although the process leads to an infinite family of intermediate power-law rates systems, all of them possess the same generalized Lotka-Volterra representative, irrespective of the parameters \( \alpha \), \( \beta \), and \( \gamma \), and are thus all equivalent. This property supports our assertions in favor of the generalized Lotka-Volterra as a unifying format.
V. Conclusions

We have stressed how the power-law formalism can be a referential format for general functional forms for chemical rate-laws. On encapsulating a chemical mechanism (or network) under a power-law formalism, there is no need to resort, as we have shown, to any kind of local approximation in terms of that same power-law formalism, even if it seems justified experimentally. Instead, simple manipulations of elementary calculus convert non polynomial kinetic equations into power-law differential equations, completely equivalent to the original ones when appropriate initial conditions are assumed.

For power-law rates an interesting universal relationship has been obtained. When these rate laws are considered as *per capita* rates (or, equivalently, in terms of logarithmic derivatives) they obey a set of generalized Lotka-Volterra equations. The specific matrix characterizing this generalized Lotka-Volterra system is independent of the particular embedding procedure when transforming general rate laws into a power-law formalism. Also, to each particular power-law rates system corresponds a unique and mathematically equivalent generalized Lotka-Volterra system. The latter may then be considered a conjugate representation of any chemical network.

Much attention has been devoted in the literature to the generalized Lotka-Volterra equations, a fact which is not independent of their structural simplicity and their ubiquity in many scientific disciplines, ranging from population biology to laser physics. This is particularly attractive in the context of classification of chemical networks.

A *conjugate chemical network*, with at most bimolecular steps in the essential species, may be associated to the generalized Lotka-Volterra equations. The network is purely conceptual and should not be thought of as the *canonical* reactional scheme of any chemical process. It should be regarded as an abstract equivalent representation of a model system in the familiar language of mass-action kinetics. Its immediate interest in the modeling of actual chemical systems may be presently a subject of debate, for many critics argue that the field of chemical network dynamics has not yet produced any result of chemical importance. This point of view should be seriously reconsidered in the light of recent work by Ross and collaborators.
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