Computer Algebra in Chemical Kinetics: Theory and Application

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Abstract. In this paper, we present the comprehensive approach to the polynomial elimination for Mass-Action-Law (MAL) models of chemical kinetics. We discuss the new results in the theory of the resultant of our equations (i.e. the *kinetic polynomial*). We provide the interpretation of kinetic polynomial properties in terms of A-resultants theory and discuss the symbolic algorithm of kinetic polynomial generation. We formulate the matrix method of MAL systems numeric solution. ...

1 Introduction

Differential equations of chemical kinetics in closed lumped system with chemical reactions have the form

$$d\mathbf{c}/dt = \Gamma^T \mathbf{w}, \tag{1}$$

where $\mathbf{c}$ is a vector of component concentrations, Γ is a stoichiometric matrix, and $\mathbf{w}$ is vector of rates of reaction steps. Classic kinetic problem setup assumes Mass Action Law (MAL) for elementary reactions. Each element of vector $\mathbf{w}$ is a difference of two monomials corresponding to the forward and reverse elementary reactions

$$w_i = k_i \prod_j c_j^{\alpha_{ij}} - k_{-i} \prod_j c_j^{\beta_{ij}}, \tag{2}$$

where positive integers α_{ij}, β_{ij} are stoichiometric coefficients and k_i, k_{-i} are kinetic constants. Let $\gamma_{ij} = \beta_{ij} - \alpha_{ij}$, then $\Gamma = ((\gamma_{ij}))$. Differential equations (1) often have different time scales. In this case system (1) can be represented as

$$\begin{aligned} d\mathbf{x}/dt &= \mathbf{f}(\mathbf{x}, \mathbf{y}), \\ \epsilon d\mathbf{y}/dt &= \mathbf{g}(\mathbf{x}, \mathbf{y}), \end{aligned} \tag{3}$$

where $\mathbf{x}$ and $\mathbf{y}$ are vectors of "slow" and "fast" variables and ϵ is a small parameter. The existence of different time scales could be the result of the differences in capacities between catalyst surface and gas volume or different scales of reaction rate constants. In common situations, such as heterogeneous catalysis, enzyme kinetics or chain radical reactions, time-scale split results in subdivision of reaction participants into different groups (surface intermediates and bulk reactants, radical and molecular reagents, etc.). System

$$d\mathbf{x}/dt = \mathbf{f}(\mathbf{x}, \mathbf{y}), \tag{4}$$

$$\mathbf{g}(\mathbf{x}, \mathbf{y}) = 0 \tag{5}$$

is a zero-order approximation of singularly perturbed problem (3).

This *Quasi-Steady-State-Approximation (QSSA)* technique is a common method of kinetic model generation. For general MAL model, algebraic system (5) consists of polynomial equations in $\mathbf{y}$. Generally, there are no explicit formulas for system (5) zeroes. Chemists always understood this as a major obstacle in analysis and applied approximations (most common approximation

is rate-limiting step hypothesis). Approximations result in severe limitations. It is well known at present that chemical systems with complex reactions can have multiple steady states at isothermal conditions. Approximate kinetic models cannot explain these phenomena. On the other hand, applications, such as dynamic simulation and control, require detailed kinetic models free of unnecessary simplifications.

We have to know as much as possible about the properties of our algebraic system (5). At the same time, it is necessary to have effective methods for numerical solution, allowing the reliable location of all zeroes in specified domain.

Powerful techniques of effective algebraic geometry can be applied to polynomial QSSA systems. Variable elimination reduces the system to a single polynomial equation in single variable - the system resultant. Reaction rate is a natural choice for the variable in chemical kinetics. Resultant in terms of the reaction rate (i.e. *kinetic polynomial* [1]) is a generalization of the conventional explicit reaction rate equations. It is a polynomial in terms of the reaction rate. The roots of this polynomial are values of reaction rate in the zeroes of the QSSA system.

We have developed the kinetic polynomial theory for a class of reaction mechanisms [1] and implemented it using computer algebra tools [2]. Applications include parameter estimation, model identifiability studies and asymptotic analysis [1], [3].

In recent years, the true renaissance happened in theory [4], algorithms and software implementation of polynomial elimination [5]. It became a common tool in areas such as computer graphics and robotics. There is a significant difference, however, between these areas and chemical systems. While most applications deal with systems consisting of few polynomials, we deal with multiple, structured polynomial equations. Understanding the general properties of these systems is important for constructing effective algorithms. This contribution presents the theoretical results as well as symbolic and numeric implementation of polynomial elimination for a class of mathematical models of chemical kinetics.

We provide new insight on the fundamental connection between kinetics and thermodynamics encapsulated in the structure of the kinetic model. The simple topological object, the circuit, is responsible for the correspondence between kinetics of complex reaction and chemical equilibrium of the net reaction. Applying the *"A-philosophy"* [4], we have proved that the constant term of our kinetic polynomial corresponds to the discriminant of the circuit.

We have formulated a simple and effective *matrix method* for global numeric solution of a class of MAL models via reduction to the standard matrix eigenproblem.

We have found the class of polynomial systems, the *regular systems*, that always has non-singular Macaulay matrices.

2 QSSA Problem

System (5) has the form

$$\Gamma^T \mathbf{w} = 0, \tag{6}$$

where Γ is $S \times J$ matrix, S is the number of reactions, J is the number of intermediates. Let $r = rk\Gamma$. We assume $r < S$. In this case, there exists the $S \times P$ matrix $\mathcal{N}$ such that

$$0 = \Gamma^T \mathcal{N}. \tag{7}$$

The number $P = S - r$ is the number of reaction routes. Reaction route corresponds to the column of matrix $\mathcal{N}$. These columns are linearly independent and form the *stoichiometric basis*. Elements of matrix $\mathcal{N}$ are stoichiometric numbers ν_{sp} . Stoichiometric basis is defined up to a non-singular linear transformation. We can always define stoichiometric basis in terms of integer stoichiometric numbers. We assume below that all ν_{sp} are integers. If we multiply each chemical equation of our mechanism by the corresponding stoichiometric number from some column of matrix $\mathcal{N}$ and add up the results, we obtain the chemical equation free of intermediates. This equation corresponds to the net reaction of a selected reaction route.

Vector $\mathbf{w}$ solves homogeneous linear system (6) iff it belongs to the space spanned by the columns of matrix $\mathcal{N}$. There exists such vector $\mathbf{W} = (W_1, ..., W_P)^T$ that

$$\mathbf{w} = \mathcal{N}\mathbf{W}. \tag{8}$$

Element of vector $\mathbf{W}$ is the *rate along the reaction route*. Vector $\mathbf{w}$ is composed of polynomials $w_s(\mathbf{z})$ in concentrations $\mathbf{z} = (z_1, ..., z_J)^T$ of intermediates. These concentrations satisfy $B = J - r$ linear balance equations

$$\mathbf{L}(\mathbf{z}) = 0. \tag{9}$$

System (8), (9) of $S + B$ equations in $S + B$ unknowns $\mathbf{z}, \mathbf{W}$ is equivalent to the original problem (6).

3 Kinetic Polynomial

3.1 Single-Route Mechanism: the *Base Case*

Representation (8), (9) has been applied to simplified cases (rate limiting step, vicinity of thermodynamic equilibrium). Only one case, linear mechanism, where system (8), (9) is linear, has been studied completely. Structured reaction rate equations in terms of reaction graph were obtained for enzyme and catalytic reaction mechanisms. No further progress in understanding QSSA problem seemed possible until relatively recent times - there are no explicit formulas for solution of general system (8), (9). However, MAL produces the polynomial systems (8), (9) and elimination theory can be applied. We studied the class of systems (8), (9) with $P = 1$, corresponding to the *single-route mechanism*. System has the form

$$w_s(z_1, ..., z_n) - \nu_s W = 0,\ s = 1, ..., n \tag{10}$$

$$1 - \sum_j z_j = 0,\ j = 1, ..., n, \tag{11}$$

where $w_s(z_1, ..., z_n) = b_s z^{\alpha^s} - b_{-s} z^{\beta^s}$, $z^{\alpha^s} = \prod_j {z_j}^{\alpha^{sj}}, z^{\beta^s} = \prod_j {z_j}^{\beta^{sj}}$, $\alpha^s = (\alpha_{s1}, ..., \alpha_{sn}), \beta^s = (\beta_{s1}, ..., \beta_{sn})$. As $P = 1$, we have $rk\Gamma = n - 1$, we assume also $||\alpha^s|| = \sum_j \alpha_{sj} = ||\beta^s|| = l_s$. Stoichiometric numbers ν_s in (10) are, up to scaling, the co-factors Δ_s of elements of any column of matrix Γ. We assume that $W = 0$ is not generic root of system (10), (11).

System (10), (11) has (real positive) parameters b_i, b_{-i} , the *reaction weights*. Reaction weight is a rate of corresponding elementary reaction at unit concentrations of its intermediates. Stoichiometric numbers $\nu_1, ..., \nu_s$ have the following property

$$\sum_s \nu_s(\beta^s - \alpha^s) = 0. \tag{12}$$

Let us call the system (10), (11) with assumptions listed above, the *Base Case*. This system has the resultant with respect to W [1], [2], i.e. the polynomial

$$R(W) = B_L W^L + ... + B_1 W + B_0, \tag{13}$$

vanishing iff W is the root of system (10), (11). We call (13) the kinetic polynomial. In [1], [2] the resultant was defined as

$$R(W) = \prod_j (b_1 z_{(j)}^{\alpha^1} - b_{-1} z_{(j)}^{\beta^1} - \nu_1 W), \quad \nu_1 \neq 0, \tag{14}$$

where $z_{(j)}$ are the roots of the system (at fixed W), that consists of all equations of system (10), (11) except the first one (by Lemma 14.2 [2], this system has finite number of roots). As we see below, formula (14), up to a constant multiplier, corresponds to the Poisson formula.

3.2 Regular Systems

System of algebraic equations in $\mathbf{C}^n$

$$P_i(z_1, ..., z_n) + Q_i(z_1, ..., z_n) = 0, \quad i = 1, ..., n \tag{15}$$

where P_i is homogeneous polynomial and $degP_i > degQ_i$ is *regular* if system $P_i(z_1, ..., z_n) = 0$ has only one root at point 0. By Lemma 8.1 [2], regular systems have a finite number of roots in $\mathbf{C}^n$ and they have no roots on the hyperplane at infinity.

3.3 Cayley Trick, Circuit and Equilibrium

Thermodynamic equilibrium condition requires all reactions to be at equilibrium

$$w_s(z_1, ..., z_n) = 0, \quad s = 1, ..., n \tag{16}$$

i.e. $W = 0$ at equilibrium conditions. Equilibrium constraint can be expressed as $\prod_s b_s^{\nu_s} = \prod_s b_{-s}^{\nu_s}$. It is intuitively clear that the structure of resultant (13) should reflect this condition. Let us call the binomial $s = \prod_s^n b_s^{\nu_s} - \prod_s^n b_{-s}^{\nu_s}$, the *cyclic characteristic*. Note, that we can always set the directions of elementary reactions so that all stoichiometric coefficients are non-negative. We assume below that $\nu_s > 0, \quad s = 1, ..., n$ and $GCD(\nu_1, ..., \nu_n) = 1$.

Theorem 1 *Constant term B_0 in (13) is the non-zero multiple of the cyclic characteristic.*

Proof Along with the system (10), (11), consider its projectivization. The latter, obtained by replacing each polynomial $f(z_1, ..., z_n, W)$ with the homogeneous polynomial $Z_0^l f(z_1, ..., z_n, W), \quad l = degf$, has the form

$$\begin{aligned} b_s Z^{\alpha^s} - b_{-s} Z^{\beta^s} - Z_0^{l_s} \nu_s W = 0, \ s = 1, ..., n \\ Z_0 - \sum_j Z_j = 0, \ j = 1, ..., n, \end{aligned} \tag{17}$$

Now, consider system (10), (11) as an overdetermined system of $n+1$ equations in n variables z_i . In the homogeneous setting (17) the system (10), (11) having a root is equivalent to homogeneous system (17) having the non-trivial root in $\mathbf{C}^{n+1}$. This requires the vanishing of the classic resultant $R(f_0, ..., f_n)$. The latter satisfies Poisson formula [4]

$$R(f_0, ..., f_n) = R(\tilde{f}_0, ..., \tilde{f}_n) \prod (f_0; f_1, ..., f_n), \tag{18}$$

where $R(\tilde{f}_0, ..., \tilde{f}_n)$ is the resultant of leading homogeneous parts of the original polynomials $f_1, ..., f_n$ and $\prod(f_0; f_1, ..., f_n)$ is the product of values of original polynomial f_0 at all common roots of polynomials $f_1, ..., f_n$.

By Lemma 2, system (10) has a finite number of roots at fixed W . We can set in (18) $f_0 = 1 - \sum_j z_j$ and $f_s = w_s(z_1, ..., z_n) - \nu_s W$.

It follows from Lemma 1 that

$$B_0 = R(w_1, ..., w_n), \tag{19}$$

(i.e. B_0 is the classic resultant of homogeneous polynomials w_s). By Lemma 3, the non-trivial solution of system (16) cannot have zero coordinates. Thus, we may consider the non-homogeneous setting of the problem (16)

$$w_s(x_1, ..., x_{n-1}) = 0, \quad s = 1, ..., n, \tag{20}$$

where $x_i = z_i / z_n$. Lemma 4 allows us to interpret the resultant of system (20) as the discriminant Δ_A of the polynomial f with additional variables $(y_1, ..., y_{n-1})$. By Lemma 5, Δ_A is the discriminant of the *circuit*. We can apply now the Proposition 1.8 from [4, p.274]: $\Delta_A(f)$ is a non-zero multiple of

$(\prod_{\omega \in A_+} m_\omega^{m_\omega}) \prod_{\omega \in A_-} a_\omega^{-m_\omega} - (\prod_{\omega \in A_-} m_\omega^{-m_\omega}) \prod_{\omega \in A_+} a_\omega^{m_\omega}$.

In our case, $A_+ = (\nu_1, ..., \nu_n)$ and $a_\omega = b_\omega, A_- = (-\nu_1, ..., -\nu_n)$ and $a_\omega = -b_{-\omega}$. Thus

$B_0 \sim (-1)^n \prod_s \nu_s{}^{\nu_s} (\prod_{s=1}^n b_s^{\nu_s} - \prod_{s=1}^n b_{-s}^{\nu_s})$.

Finally, integers m_ω from Proposition 1.8 [4] are normalized up to a sign by requiring that all m_ω be integers with the greatest common divisor equal to 1, i.e. $GCD(\nu_1, ..., \nu_n) = 1$.

The proof of Theorem 1 explains *why* cyclic characteristic appears in the constant term of our resultant (13). It happens due to the *circuit*.

Lemma 1 *System (16) has a unique generic zero 0 in $\mathbf{C}^n$.*

Proof Let $(z_1^*, ..., z_n^*)$ be a root. Two cases are possible: $\sum z_i^* \neq 0$ (i), and $\sum z_i^* = 0$ (ii). In case (i) we can rescale variables as $y_i = z_i^* / \sum z_i^*$ and $y_1, ..., y_n$ solves the problem (10), (11) with $W = 0$ i.e. we found a contradiction. Case (ii) contradicts Lemma 14.2 from [2].

Lemma 2 *System (10) has a finite number of roots at fixed W.*

Proof By Lemma 1, system (10) is regular (see 3.2).

Lemma 3 *If $\nu_j = 0, \quad j = 1, ..., k$ and $\nu_i \neq 0, \quad i = k+1, ..., n$ then non-trivial zero of system (16) has no more than k zero coordinates*

Proof is omitted due to space limitations.

Lemma 4 *(Cayley trick for system (20))*

$$R(w_1, ..., w_n) = \Delta_A(w_n(\mathbf{x}) + \sum_{i=1}^{n-1} y_i w_i(\mathbf{x})), \tag{21}$$

where Δ_A is the A-discriminant (see [4, p. 271]) of polynomial

$$f = w_n(\mathbf{x}) + \sum_{i=1}^{n-1} y_i w_i(\mathbf{x}), \tag{22}$$

where $x_1, ..., x_{n-1}, y_1, ..., y_{n-1} \in (\mathbf{C}^*)^{2n-2}$.

Proof Let $x^* = (x_1^*, ..., x_{n-1}^*)^T$ be a common root of $(w_1, ..., w_n)$. Condition $\partial f / \partial x_k$ can be written as

$$\gamma_{nk} w_n^+ + \sum_{i=1}^{n-1} y_i \gamma_{ik} w_i^+ = 0, \tag{23}$$

where $w_i^+ = b_i \prod_{j=1}^{n-1} (x_j^*)^{\alpha_{ij}} = b_{-i} \prod_{j=1}^{n-1} (x_j^*)^{\beta_{ij}}$.

We can always solve system (23) for $\mathbf{y}$. The solution is $y_j^* = \nu_j w_n^+ / (\nu_n w_j^+) \neq 0 \quad j = 1, ..., n-1$. Conversely, if (x^*, y^*) is a point, where polynomial (22) vanishes with all its partial derivatives, then $w_s(\mathbf{x}^*) = 0, \quad s = 1, ..., n$.

Lemma 5 *Let A be a finite subset in the integral lattice $\mathbf{Z}^{2n-2}$ whose elements ω are associated with the monomials $x_1^{\omega_1}, ..., x_{n-1}^{\omega_{n-1}} y_1^{\omega_n}, ..., x_{n-1}^{\omega_{2n-2}}$ of polynomial (22) with indefinite coefficients. Then $A \subset \mathbf{Z}^{2n-2}$ is a circuit and it generates $\mathbf{Z}^{2n-2}$ as an affine lattice.*

Proof Subset A is a circuit if A is affinely dependent but any proper subset of A is affinely independent [4]. We have:

1. Due to (12), unique up to scaling vector of $2n$ integers $m = (\nu_1, -\nu_1, ..., \nu_n, -\nu_n)$, has the property
$\sum_\omega m_\omega \cdot \omega = 0, \quad \sum_\omega m_\omega = 0.$
2. $\nu_s \neq 0, \quad s = 1, ..., n.$
3. $\#(A) = 2n$, i.e. A generates $\mathbf{Z}^{2n-2}$ as affine lattice.

3.4 Coefficients of the Resultant

For sufficiently small $|W|$ the following formula is valid (see [1], [2])

$$dlnR(W)/dW = -\sum_{k=1}^{n} \nu_k \sum_{j_k=1}^{M_k} 1/(w_k(\mathbf{z_{j_k}}(W)) - \nu_k W), \tag{24}$$

where $\mathbf{z_{j_k}}(W)$ is a zero of the subsystem obtained from (10), (11) by removing equation (10) with index k . These subsystems have a finite number of zeroes in the assumptions of the *Base case*. Let

$$d_k = d^k lnR(W)/dW^k|_{W=0}, \tag{25}$$

Then

$$B_k = (1/k!)\sum_{j=1}^{k} B_{k-j} d_j/(j-1)!, \quad k = 1, ..., L. \tag{26}$$

First coefficient is defined by formula $B_1/B_0 = -\sum_{k=1}^{n} \nu_k \sum_{j_k=1}^{M_k} 1/w_k(\mathbf{z_{j_k}}(0))$.

3.5 Symbolic Algorithm

A different set of formulas for computing d_s directly from the coefficients of system (10), (11) was obtained in [2, chapter 14] from the multidimensional residues theory. This method requires the calculation of such polynomial matrix $A = (a_{jk}(\mathbf{z}))_{j,k=1}^{n}$ that homogeneous polynomials $a_{jk}(\mathbf{z})$ satisfy the linear relations

$$z_j^{L+1} = \sum_{k=1}^{n} a_{jk}(\mathbf{z}) w_k(\mathbf{z}), \quad j = 1, ..., n, \tag{27}$$

where $L = l_1 + ... + l_n - n$. Such a sequence of polynomials a_{jk} exists according to Macaulay theorem [6]. We can calculate the coefficients B_k in two steps. First part of algorithm calculates matrix A as follows

1. Find the Groebner basis G for the ideal generated by polynomials $w_1(\mathbf{z}), ..., w_n(\mathbf{z})$. [1] Simultaneously we are generating the linear representation of the Groebner basis polynomials in terms of the original polynomials $g_i = \sum_{j=1}^{n} X_{ij}(z_1, ..., z_n) w_j, i = 1, ..., dim(G)$; X_{ij} are polynomials.

2. Reduce the monomials $z_j^{L+1}, \quad j = 1, ..., n$ modulo G. Simultaneously we are generating the linear representation $z_j^{L+1} = \sum_{i=1}^{dimG} h_{ik}(z_1, ..., z_n) g_i$; h_{ik} are polynomials.

3. $a_{jk}(\mathbf{z}) = \sum_{i=1}^{dimG} h_{ik} X_{ij}$

Second part of the algorithm finds d_s by explicit formulas and calculates B_i by (26) (see [2, chapter 19] for details of REDUCE implementation).

3.6 Example

The kinetic polynomial corresponding to the two-stage mechanism

$A_2 + 2Z \rightleftharpoons 2AZ$

$B + Z \rightleftharpoons BZ$

of heterogeneous catalytic reaction $A_2 + 2B \rightleftharpoons 2AB$ is

$R(W) = 4(b_1 - b_{-1})W^2 - (4b_{-1}b_{-2} + 4b_1b_2 + (b_2 + b_{-2})^2)W + b_1b_2^2 - b_{-1}b_{-2}^2$

Stoichiometric numbers here are $\nu_1 = 1$ and $\nu_2 = 2$, so the constant term is the cyclic characteristic (see Theorem 1).

4 Root count

Let $l_s = max(||\alpha^s||, ||\beta^s||)$ be the *reaction order* of sth stage. Let N be the number of isolated roots of our system.

Proposition 1 $N \leq \prod_{s=1}^{n} l_s$.

Proof This estimate follows from Bezout theorem applied to system (8), (9).

Estimate of Proposition 1 can be improved. Consider first the single-route system. Let us call the reaction "μ", such that $l_\mu = min(l_1, ..., l_n)$ and $\nu_\mu \neq 0$ the *minor reaction.*

Proposition 2 $N \leq L_\mu = \prod_{s \neq \mu}^{n} l_s$.

[1] Although we have applied the pure lexicographic ordering, the type of ordering could be selected different way

Proof This estimate follows from Bezout theorem applied to the *reduced form* of system (10),(11)

$$\begin{aligned} \nu_\mu w_i(\mathbf{z}) - \nu_i w_\mu(\mathbf{z}) = 0, \quad & i \neq \mu, \\ 1 - \sum_i z_i = \quad & 0, \qquad (28) \\ W - w_\mu(\mathbf{z})/\nu_\mu = \quad & 0. \qquad (29) \end{aligned}$$

The estimate of Proposition 2 is non-trivial if reaction order of minor reaction exceeds 1.

For multi-route mechanism we can consider the following procedure.

1. Arrange the reactions of the mechanism in the order of non-increasing $l_i \geq l_{i+1}, \quad i = 1, ..., n-1$.

2. Select a stoichiometric basis. Move all reactions, which do not have non-zero stoichiometric numbers to the "buffer" subset.

3. Find the reaction step with the smallest l_i and the non-zero stoichiometric coefficient $\nu_{ij} \neq 0$. Make the path "j" the rightmost (i.e. swap columns j and P).

4. Eliminate all elements of the row "i" to the left of ν_{iP} .

5. Consider the next reaction index "$i-1$". If all $\nu_{i-1,j}, \quad j < P$ are zero , add this reaction to the "buffer" subset. Otherwise, swap columns j and $P-1$, and perform step 4. Repeat step 5 for remaining reactions. As a result of this procedure, the original stoichiometric basis will be transformed to

$$\mathcal{N}_\mu = \begin{pmatrix} * & * & * \\ \times & \times & \times \\ 0 & \times & \times \\ 0 & 0 & \times \\ 0 & \bullet & \bullet \end{pmatrix} \begin{matrix} top & l_1 \geq l_2 \\ \mu & l_\mu \geq \dots \\ base & \vdots \\ \mu + P - 1 & l_{\mu+P-1} \\ buffer & \end{matrix} \qquad (30)$$

In terms of the basis $\mathcal{N}_\mu$ we have

Proposition 3 $N \leq L_\mu = \prod_{i \neq \mu, \dots, \mu+P-1}^{n} l_i$

This root count corresponds to the system (8), (9) in *reduced form*

$$\begin{aligned} w_I(\mathbf{z}) - \mathcal{N}_I \mathcal{N}_{II}^{-1} w_{II}(\mathbf{z}) = 0, \\ w_{III}(\mathbf{z}) - \mathcal{N}_{III} \mathcal{N}_{II}^{-1} w_{II}(\mathbf{z}) = 0, \qquad (31) \\ \mathbf{L}(\mathbf{z}) = 0, \\ \mathbf{W} - \mathcal{N}_{II}^{-1} w_{II}(\mathbf{z}) = 0, \qquad (32) \end{aligned}$$

where indices I, II, II correspond to the "top", "base", and "buffer" blocks of matrix (30). Propositions 2, 3 show that at least P reactions can be omitted from Bezout count of Proposition 1.

5 Numeric solution

While symbolic algorithms (for instance, methods based on Groebner bases) are important in the analysis of our systems, they do not allow effective numerical implementation. The obstacle is the approximate, floating-point setup of practical problems. Matrix methods [5] represent an attractive alternative for the numeric solution of polynomial systems. We consider below the matrix algorithm for solution of our systems based on classic Macaulay matrices.

5.1 Macaulay matrices

Classic homogeneous elimination theory deals with homogeneous forms in several variables. Let $f_0, ..., f_k$ be $k+1$ homogeneous forms in $k+1$ variables $z_0, ..., z_k$ of order $l_0, ..., l_k$. Let $\mathcal{M} = l_0 + ... + l_n - n$. Let us multiply form f_j by some monomial $z_\omega, ||\omega|| = \mathcal{M} - l_j$. We can associate the result of this multiplication with the $\mathcal{M}$-vector f_j^ω in the basis that consists of all monomials

of degree $\mathcal{M}$. We can collect all possible f_j^ω (row) vectors into the matrix, namely the *Macaulay* matrix M_0 . Macaulay defined the resultant R as the GCD of all $\mathcal{M}$ -minors of matrix M_0 . Furthermore, he proved that the resultant is a multiple of the determinant of the square $\mathcal{M} \times \mathcal{M}$ matrix M_1 . This matrix can be obtained as follows.

Let us partition all monomials of degree $\mathcal{M}$ to $k+1$ sets, so that each monomial in the set j divides $z_j^{l_j}$ but it does not divide $z_i^{l_i}, \quad i < j, \quad j = 1, ..., k$. Let $H_j^\omega = z^\omega / z_j^{l_j}$ where z^ω is a monomial of the set j . Multiplication of monomials H_j^ω by forms $f_j, \quad j = 0, ..., k$ results in the system of $\mathcal{M}$ linear homogeneous equations in $\mathcal{M}$ unknowns (monomials z^ω): $M_1 z^\omega = 0$. Matrix M_1 is generically non-singular. Vanishing of $D = detM_1$ is a necessary condition for non-trivial solution of the homogeneous system. Original system of non-homogeneous polynomials $f_j(z_1, ..., z_k) = 0, \quad j = 0, ..., k$ can be transformed to the homogeneous system by projectivization (see 3.3).

Classic theory has been developed for forms, while we are dealing with their specializations, where many (most) coefficients are zero. It is important to have the criteria of applicability of general theory to our systems. For instance, classic theory does not allow recovering resultant from matrix M_0 if $rkM_0 < \mathcal{M}$. We show below that regular systems possess the necessary non-singularity properties.

5.2 Regular system case

Theorem 2 *Let the system $f_i(z_1, ..., z_n) = 0, \quad i = 1, ..., n$, where f_j are homogeneous polynomials of degree l_j in $\mathbf{C}^n$, has a unique root in the origin. Let M_0 be the Macaulay matrix corresponding to this system. Then $rkM_0 = \mathcal{M}$, where $\mathcal{M} = l_1 + ... + l_n - n + 1$.*

Proof By Macaulay theorem [7], there exist such homogeneous polynomials $a_{ki}(\mathbf{z})$ that $deg \quad a_{ki}(\mathbf{z}) = \mathcal{M} - l_j$ and

$$m_k \equiv \sum_{i=1}^{n} a_{ki}(\mathbf{z}) f_i(\mathbf{z}), \tag{33}$$

where m_k is any monomial $z^\omega, \quad ||\omega|| = \mathcal{M}$. Then $m_k \equiv \sum_{q=1}^{Q} y_q^k B_q$, where $B_q =< \mathbf{b_q}, \mathbf{m} >$ is a homogeneous polynomial of degree $\mathcal{M}$; $\mathbf{m} = (m_1, ..., m_\mathcal{M})$ and each vector $\mathbf{b_q}$ can be associated with the column of matrix M_0^T . Each column of this matrix is a vector of coefficients of polynomial $z^\omega f_i, \quad ||\omega|| = \mathcal{M} - l_i$ in the monomial basis $\mathbf{m}$. Thus,

$$m_k \equiv \sum_{q=1}^{Q} y_q^k \sum_{i=1}^{\mathcal{M}} b_{qi} m_i = \sum_{i=1}^{\mathcal{M}} (\sum_{q=1}^{Q} b_{qi} y_q^k) m_i \tag{34}$$

It follows from (34) that vector $\mathbf{y^k} = (y_1^k, ..., y_Q^k)^T$ should satisfy the linear system $M_0^T \mathbf{y^k} = \mathbf{e_k}$ where $\mathbf{e_k}$ is the standard basis vector. We have the following matrix equation

$$E_\mathcal{M} = M_0^T Y \tag{35}$$

where Y is the matrix composed of Q vectors $\mathbf{y^k}$ and $E_\mathcal{M}$ is the identity matrix. From (35) $rkE_\mathcal{M} = \mathcal{M} \leq rkM_0^T \leq \mathcal{M}$ and $rkM_0 = \mathcal{M}$.

Consider the system of polynomial equations $f_i(z_1, ..., z_n) = 0, \quad i = 1, ..., n$. Let us add to it an equation $u - \phi(z_1, ..., z_n) = 0$ where $\phi(z_1, ..., z_n)$ is a homogeneous polynomial of degree l_u and u is an additional variable. Let us call the augmented system, the *u-extension*. Projectivization of the u-extension of the *regular system* (see 3.2) is the system in variables $\mathbf{Z} = (Z_0, ..., Z_n)$

$$\begin{aligned} P_i(Z_1, ..., Z_N) + Z_0^{l_i - deg Q_i} Q_i(Z_0, ..., Z_n) = 0, \\ Z_0^{l_u} u - \phi(Z_1, ..., Z_n) = 0, \end{aligned} \tag{36}$$

Lemma 6 *System (36) does not have roots in $\mathbf{CP}^n$ at generic values of parameter u .*

Proof Let system (36) has zero with $Z_0 \neq 0$. It means that in original (affine) coordinates our regular system has a continuum of zeroes on the hypersurface $u = \phi(\mathbf{z})$, which is impossible (see 3.2). Otherwise, if $Z_0 = 0$, then the only root of system (36) is $\mathbf{0}$.

Proposition 4 *Macaulay matrix M_0 of system (36) has full column rank.*

Proof Proposition follows from Lemma 6 and Theorem 2.
For our QSSA system we have the following

Proposition 5 *In the assumptions of the Base case, the Macaulay matrix M_0 of the projectivization of the u-extension of system (28) has the full column rank.*

Proof By Lemma 14.2 (see [2, p.141]), the specialization of system (28) at $b_\mu = 0, b_{-\mu} = 0$ is regular system.
We can extend the proposition 5 to multi-route systems.

Proposition 6 *If the system that consists of leftmost terms of all equations (31) has a unique zero in the origin, then matrix M_0 of the projectivization of the u-extension of system (31) has full column rank.*

5.3 The matrix method

Macaulay resultant matrix M_1 has $L_n = \prod_{i=1}^{n-1} l_i$ rows corresponding to the last equation of the system (with respect to the construction described in 5.1). For instance, in the case of u-extension of the reduced form (see (28), (31)), there are L_μ rows corresponding to the u-equation (u-rows). According to definition of Macaulay matrix M_1 , each coefficient u is located in a unique column and row. Coefficient u will be the leftmost in the u-row if we order the monomials lexicographically ($Z_0 \succ Z_1 \succ \ldots \succ Z_n$). Reordering rows and columns of the matrix M_1 , we can obtain the following "wedge" configuration with number L_μ of u-rows

$$M_1^W = \begin{pmatrix} \bullet & \bullet & \bullet & \bullet & \ldots & \bullet \\ \bullet & \bullet & \bullet & \bullet & \ldots & \bullet \\ u & * & * & * & \ldots & * \\ 0 & u & * & * & \ldots & * \\ 0 & 0 & u & * & \ldots & * \end{pmatrix} \tag{37}$$

Proposition 4 guarantees the existence of the non-zero $\mathcal{M}$ - minor of matrix M_0 for regular system. We can build this minor row by row, starting with linearly independent u-rows of some matrix M_1 (37) and sequentially inserting rows from matrix M_0 that are linearly independent on the previously inserted rows (or doing nothing if initial matrix (37) was non-singular). Thus, we can always build the non-singular matrix with number $L \geq L_n$ of u-rows, having the same format as matrix (37).

Let $D(u)$ be the determinant of this matrix. Condition

$$D(u) = 0 \tag{38}$$

is necessary for the existence of the non-trivial zero of system (36). The non-trivial zero $\mathbf{Z} = (Z_0, ..., Z_n) \in \mathbf{CP}^n$ is associated with the zero $\mathbf{z} = (z_1, ..., z_n) \in \mathbf{C}^n$ of the original system as $\mathbf{z} \to \mathbf{Z} = (1, z_1, ..., z_n)$. As $D(u)$ is not identically zero, condition (38) is equivalent to the existence of the non-zero vector $\mathbf{v} = (v_1, ..., v_\mathcal{M})^T$ such that

$$M_1^W \mathbf{v} = 0. \tag{39}$$

Proposition 7 *Problem (39) can be reduced to the algebraic eigenproblem of size L .*

We can represent the matrix M_1^W as a sum of two $\mathcal{M} \times \mathcal{M}$ matrices $M_1^W = A + uB$, where $B = \begin{pmatrix} 0 & 0 \\ E_L & 0 \end{pmatrix}$; E_L is an identity matrix of size L (i.e. we are dealing with the (regular) pencil of

matrices). As matrix M_1^W is generically non-singular, we can always find a constant c: $detA_1 \neq 0$, $A_1 = A + cB$. Let $\omega = u - c$, then $B_1^W = A_1 + \omega B$, $A_1^{-1}M_1^W = E_{\mathcal{M}} + A_1^{-1}B$.

Let us partition matrix A_1^{-1} into the blocks compatible with the blocks of matrix B :

$A_1^{-1} = \begin{pmatrix} K_1 & K_2 \\ K_3 & K_4 \end{pmatrix}$ where K_2 is $L \times L$ matrix. Then

$A_1^{-1}B = \begin{pmatrix} K_2 & 0 \\ K_4 & 0 \end{pmatrix}$ Introducing $\lambda = -1/\omega$, and, partitioning the vector $\mathbf{v}$ as $\mathbf{v} = (\mathbf{x}, \mathbf{y})^T$, we can split (39) as

$$K_2\mathbf{x} = \lambda\mathbf{x}, \tag{40}$$

$$\mathbf{y} = (1/\lambda)K_4\mathbf{x}. \tag{41}$$

Problem (40) is an algebraic eigenproblem of the size L. To find u, satisfying system (39), we have to solve eigenproblem (40) and substitute the result into the formula $u = c - 1/\lambda$. Note, that regular systems cannot have infinite zeros, so spurious infinite solutions, corresponding $\lambda = 0$ can be ignored. Replacing vector $\mathbf{v}$ in (39) with the vector of monomials $\mathbf{m} = (m_1, ..., m_{\mathcal{M}})^T$ ordered as columns of matrix (37), we can interpret each equation of system (39) as a corresponding equation of system (36) F_j multiplied by some monomial of degree $l - degf_j$ i.e. $M_1^W\mathbf{m} = 0$ is the necessary condition for $\mathbf{m}$ to be associated with the zero of the original system.

It follows from (40), (41) that vector $\mathbf{v}$ is unique up to a constant factor if the eigenvalue is not (geometrically) multiple. In this case, we can recover all coordinates of the zero of the system by dividing the elements of vector $\mathbf{v}$, corresponding to monomials $Z_0^{l-1}Z_1, ..., Z_0^{l-1}Z_n$, by the element corresponding to monomial Z_0^l. If all eigenvalues of interest have geometric multiplicity one (which is usually the case), we can find all the roots. As we rely on necessary conditions, the practical algorithm must implement the verification of calculated roots.

5.4 Example

The K_2 matrix for two-stage mechanism (see 3.6) is

$$\frac{\begin{pmatrix} (b_{-2}+b_2)^2 + 4b_1b_2 + 2b_2(b_1+b_{-1}) & 2(b_1-b_{-1})(b_{-2}+b_2) \\ (b_{-2}+b_2)(b_2+2b_{-1}) & 2b_2(b_1-b_{-1}) \end{pmatrix}}{2(b_1b_2^2 - b_{-1}b_{-2}^2)}$$

6 Implementation

We have tested the numeric algorithm, following from Proposition 7, on a MATLAB prototype. Method allowed robust calculation of all zeroes of polynomial systems corresponding to the QSSA models, including those with multiple steady states, as shown in Fig. 1. All 8 steady states were found for the model

$$\begin{aligned} 2k_1z^2 - 2k_{-1}x^2 - k_4xy + k_{-4}zu - k_2x + k_{-3}z &= 0, \\ 2k_2z^2 - 2k_{-2}y^2 - k_4xy + k_{-4}zu - k_5yu &= 0, \\ k_4xy - k_{-4}zu - k_5yu - 2k_6u^2 &= 0, \\ x + y + z + u - 1 &= 0 \end{aligned} \tag{42}$$

of hydrogen catalytic oxidation (see [2]). Corresponding Macaulay matrix M_1 is presented in Fig. 2.

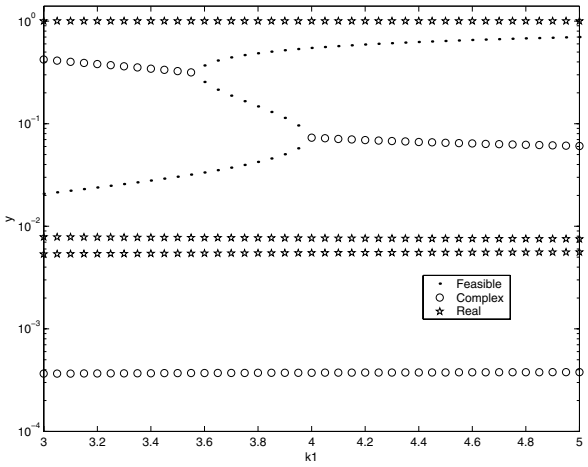

Fig. 1. All steady states of hydrogen oxidation model: the y (adsorbed hydrogen) vs $k1$ plot; $k_{-1} = 0.001$, $k_{-2} = 0.0005$, $k_{-3} = 0.636$, $k_{-4} = 0.01$, $k_2 = 3.91$, $k_3 = 1$, $k_4 = 25$ $k_5 = 1$ $k_6 = 0.0002$

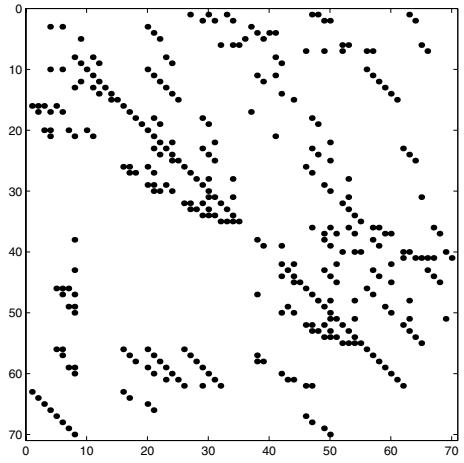

Fig. 2. Macaulay matrix of model (42)

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