

Stability of surface mechanisms with three species and mass-action kinetics

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The linear stability problem for surface mechanisms with free sites and two adsorbed species is investigated under the assumptions of mass action (Langmuir) surface kinetics, fast mass transport to and from the surface, and a conservation condition. The results also apply to enzyme kinetics for systems with a single enzyme occurring in the free form and two combined forms, and with fast mass transport of the substrates and products. Mechanisms are classified according to their stability and the presence or absence of complex eigenvalues, and specific reactions with numerical values of the rate constants and surface concentrations are given to illustrate the results. Some mechanisms, e.g., proportionate reactions, are shown to be stable for all values of the rate constants and stoichiometric coefficients. The two most common types of mechanisms, namely sequential mechanisms and the simple Langmuir–Hinshelwood mechanism (one adsorbate per site), are always stable. The possibility of complex eigenvalues arises for sequential mechanisms (providing a counterexample to a condition for real eigenvalues given previously in the literature). More general Langmuir–Hinshelwood mechanisms can be unstable (e.g., those in which one adsorbate occupies two sites). Some results are generalized to mechanisms with three or more adsorbed species, and global stability is investigated using monotone dynamical systems theory.

KEY WORDS: stability, mass-action, kinetics, adsorbed, enzyme, Langmuir–Hinshelwood

1. Introduction

Here we treat the linear stability problem for mass-action kinetic mechanisms with three species and a single conservation condition, with the conserved moiety (atom or group of atoms) present in each of the three species. In the context of surface reactions, it is the atoms of the surface itself that are conserved, and the three species are two types of molecules adsorbed on the surface and the unoccupied surface sites (free sites). Mass-action kinetics for surface reactions is the same as Langmuir kinetics, provided

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the surface sites are treated as a separate species. Our treatment is also relevant for enzyme systems with a single enzyme (the conserved moiety) in three forms, one of which is the free enzyme. In both the surface and enzyme cases, mass transport in the ambient phase is considered to be fast, so that the concentrations in the ambient phase may be taken as constant. We have previously given a comprehensive analysis of the case of a single adsorbed species [1]. Here we show that of the two most common types of mechanisms, sequential mechanisms are always stable, but Langmuir–Hinshelwood mechanisms can show unstable behavior. We categorize the possible mechanisms in terms of their stability and whether the eigenvalues may be real or complex. We also provide a counterexample to a condition for real eigenvalues given in the literature.

There is an extensive literature on the stability of mass-action mechanisms, with work to 1980 summarized by Clarke [2], and later work mainly by Feinberg, e.g., review articles [3] and [4]. Feinberg's work follows on from the work of Horn and Jackson [5] by classifying mechanisms on the basis of the number of complexes, i.e., "sides" of reactions. However, from an experimental point of view, the number of adsorbed species is more likely to be known than the number of complexes, e.g., some form of spectroscopy may indicate CO(ads) and O(ads). Indeed, three species can be combined to give an infinite number of complexes, e.g., 2CO(ads), CO(ads) + O(ads), CO(ads) + 2O(ads), 2O(ads), etc. Our approach in classifying in terms of number of species will be closer in spirit to that of Beretta et al. [6,7]. As explained below, the presence of one conservation condition covers almost all heterogeneous catalytic mechanisms, and many important cases have two or fewer adsorbed species.

The stability problem proves to be a subproblem in electrochemical impedance spectroscopy (EIS) used to measure rate parameters for electrochemical surface mechanisms. Our larger interest in the impedance problem requires us not only to know when the mechanism is stable (eigenvalues have negative real parts), but also when the eigenvalues are real. Complex eigenvalues lead to an equivalent circuit containing an inductor [1]. We first define some of the concepts and give some example mechanisms from surface chemistry, indicating that some quite important mechanisms are not easily handled by the existing theories. Then we summarize our assumptions and proceed to classify mechanisms and predict their stability.

We always assume mass-action kinetics, i.e., reactions between s species in r elementary reactions with the net rates v_j defined by

$$v_j = k_j \prod_{\text{reactants } i} c_i^{-n_{ij}} - k_{-j} \prod_{\text{products } i} c_i^{n_{ij}}, \quad j = 1, \dots, r, \quad (1)$$

where c_i , $i = 1, \dots, s$, is the concentration of the i th species, k_j and k_{-j} are the forward and backward rate constants and n_{ij} are the stoichiometric coefficients, i.e., the numbers of molecules of type i appearing in reaction j . These are positive for products and negative for reactants; we assume that no species appears as both a reactant and product in the same reaction step. The stoichiometric coefficients are the entries of an $s \times r$ stoichiometric matrix N . In this formulation, each reaction has one column in N , whether it is reversible or not, and the rate v_j is the net rate in the forwards direction, i.e.,

$v_j = v_{jf} - v_{jb}$ where v_{jf} and v_{jb} are the forward and backward rates, respectively. The number of independent reactions is $\text{rank}(\mathbf{N})$. We will use the derivatives $\partial v_j / \partial c_i$, which have one of the following forms, depending on whether or not c_i is the concentration of a reactant or a product, respectively:

$$\frac{\partial v_j}{\partial c_i} = -\frac{n_{ij}v_{jf}}{c_i} \quad \text{for reactant } i; \quad \frac{\partial v_j}{\partial c_i} = -\frac{n_{ij}v_{jb}}{c_i} \quad \text{for product } i. \quad (2)$$

The time evolution of the concentrations is governed by the set of s differential equations:

$$\frac{d\mathbf{c}}{dt} = \mathbf{r}(\mathbf{c}) = \mathbf{N}\mathbf{v}(\mathbf{c}), \quad (3)$$

where c_i and v_j have been collected into vectors \mathbf{c} and \mathbf{v} , and $\mathbf{r} = [r_1, \dots, r_s]^T$ is the vector of the rates of production of the species. At a steady state, the net rates \mathbf{v} must satisfy $\mathbf{N}\mathbf{v} = 0$. A steady state of the system is stable (strictly “locally asymptotically stable”) if the matrix \mathbf{T} of partial derivatives with i, k entry equal to $\partial r_i / \partial c_k$ has all eigenvalues with negative real parts (a zero eigenvalue is allowed for each conservation condition; see below). A mechanism is stable if all steady states are stable (for all possible sets of rate constants). Since these partial derivatives are typically negative, we avoid excessive use of negative signs in the following by considering the eigenvalues of the $s \times s$ matrix $\mathbf{Q} = -\mathbf{T}$, where

$$\mathbf{Q} = \begin{bmatrix} -\frac{\partial r_1}{\partial c_1} & -\frac{\partial r_1}{\partial c_2} & \cdots & -\frac{\partial r_1}{\partial c_s} \\ -\frac{\partial r_2}{\partial c_1} & -\frac{\partial r_2}{\partial c_2} & \cdots & -\frac{\partial r_2}{\partial c_s} \\ \vdots & \vdots & \ddots & \vdots \\ -\frac{\partial r_s}{\partial c_1} & -\frac{\partial r_s}{\partial c_2} & \cdots & -\frac{\partial r_s}{\partial c_s} \end{bmatrix} = \mathbf{N}\mathbf{G} = \mathbf{N} \begin{bmatrix} -\frac{\partial v_1}{\partial c_1} & -\frac{\partial v_1}{\partial c_2} & \cdots & -\frac{\partial v_1}{\partial c_s} \\ -\frac{\partial v_2}{\partial c_1} & -\frac{\partial v_2}{\partial c_2} & \cdots & -\frac{\partial v_2}{\partial c_s} \\ \vdots & \vdots & \ddots & \vdots \\ -\frac{\partial v_r}{\partial c_1} & -\frac{\partial v_r}{\partial c_2} & \cdots & -\frac{\partial v_r}{\partial c_s} \end{bmatrix} \quad (4)$$

with the partial derivatives evaluated at the steady-state concentrations.

We assume throughout that there is at least one conservation condition involving all species, thus there exists at least one positive left null vector \mathbf{f} for \mathbf{N} such that $\mathbf{f}^T \mathbf{N} = 0$. The concentrations may be normalized so that $\mathbf{f}^T \mathbf{c} = 1$; for the surface chemistry case this corresponds to defining concentrations as coverages, i.e., ratios of the number of adsorbed species to the number of atoms on the clean surface. We adopt the conventions that the free sites are the last species, and that they have formula M, i.e., one atom of the clean surface. (M is mnemonic for metal.) Therefore the last entry of \mathbf{f} is one and we write $\mathbf{f} = [\mathbf{h}^T, 1]^T$.

As an example, we use a simple sequential mechanism (SQ) with three species to illustrate these ideas:



Here M is an uncovered active site on the surface. In reaction step 1, a species moves to the surface rapidly and part or all of it adsorbs as MA, e.g., CO(g) adsorbs to give MCO. The concentration of the species in the solution or gas phase is assumed to be effectively constant, so that its concentration may be subsumed into k_1 , i.e., it is an external species, and is not counted among the s species. Step 2 converts this surface species to a different one, possibly losing or gaining some atoms via unwritten external species. In the third step MB desorbs from the surface to give an external product species and releases a surface site. Treating M explicitly as a species allows us to formally equate Langmuir kinetics with mass-action kinetics [1]. Feinberg has likewise applied mass-action results to heterogenous catalysis systems [8].

The stoichiometric matrix for (5) is

$$N = \begin{bmatrix} 1 & 2 & 3 \\ 1 & -1 & 0 \\ 0 & 1 & -1 \\ -1 & 0 & 1 \end{bmatrix} \begin{matrix} \text{MA} \\ \text{MB} \\ \text{M} \end{matrix} \tag{6}$$

and the conservation of M atoms is associated with the vector $f = [1, 1, 1]^T$, where the entries are the numbers of M atom in each of the species MA, MB and M. $\text{Rank}(N) = 2$ here, since the third reaction may be written as the reverse of the second reaction plus the reverse of the first reaction.

2. Theory

We first give some discussion of the general mechanisms considered and the eigenvalues of Q . Later, we specialize the discussion to three species and to specific types of mechanisms. All mechanisms considered satisfy the following assumptions.

- (A1) Each of the internal species appears somewhere in the mechanism. The last species is taken to be the free sites.
- (A2) Mass-action or Langmuir kinetics applies, i.e., the exponents in the rate laws are the absolute values of the corresponding stoichiometric coefficients.
- (A3) All species have positive concentrations at any steady state.

- (A4) All reactions are reversible, i.e., have non-zero forward and backward rates.
- (A5) No species appears on both the reactant and product sides of any reaction, i.e., autocatalytic and autoinhibitory reactions are excluded.
- (A6) There is at least one conservation condition, i.e., \mathbf{N} has at least one positive left null vector \mathbf{f} .

Following Beretta and co-workers [6,7], we define an “elementary matrix” A_j for each step j as the product $\mathbf{n}_j \mathbf{g}_j^T$, i.e., the product of the j th column of \mathbf{N} by the j th row of \mathbf{G} :

$$\begin{aligned}
 A_j = \mathbf{n}_j \mathbf{g}_j^T &= \begin{bmatrix} n_{1j} \\ n_{2j} \\ \vdots \\ n_{sj} \end{bmatrix} \begin{bmatrix} -\frac{\partial v_j}{\partial c_1} & -\frac{\partial v_j}{\partial c_2} & \cdots & -\frac{\partial v_j}{\partial c_s} \end{bmatrix} \\
 &= \begin{bmatrix} n_{1j} \\ n_{2j} \\ \vdots \\ n_{sj} \end{bmatrix} \begin{bmatrix} \frac{n_{1j} v_{jfb}}{c_1} & \frac{n_{2j} v_{jfb}}{c_2} & \cdots & \frac{n_{sj} v_{jfb}}{c_s} \end{bmatrix}. \tag{7}
 \end{aligned}$$

The last form is obtained using equation (2); v_{jfb} means v_{jf} if n_{ij} is negative and v_{jb} if n_{ij} is positive. For example, the elementary matrix for the first step of the SQ mechanism (equation (5)) is:

$$A_1 = \begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix} \begin{bmatrix} \frac{v_{1b}}{c_1} & 0 & -\frac{v_{1f}}{c_3} \end{bmatrix} = \begin{bmatrix} \frac{v_{1b}}{c_1} & 0 & -\frac{v_{1f}}{c_3} \\ 0 & 0 & 0 \\ -\frac{v_{1b}}{c_1} & 0 & \frac{v_{1f}}{c_3} \end{bmatrix}. \tag{8}$$

Since \mathbf{n}_j and \mathbf{g}_j have the same sign pattern, each elementary matrix is symmetrical in signs. The i, i (diagonal) entries are positive when species i is involved in the reaction and zero otherwise. Therefore the elementary matrices are rank one matrices with a positive trace, a single positive eigenvalue and $s - 1$ zero eigenvalues.

We now give statements about the eigenvalues of \mathbf{Q} that apply to all mechanisms that satisfy (A1)–(A5). Since $\mathbf{Q} = \mathbf{N}\mathbf{G}$, the elementary matrices sum to \mathbf{Q} :

$$\mathbf{Q} = \mathbf{N}\mathbf{G} = \sum_{j=1}^r \mathbf{n}_j \mathbf{g}_j^T = \sum_{j=1}^r A_j. \tag{9}$$

Each species i must appear in some reaction and so the i, i entry of some elementary matrix must be positive, leading to a positive i, i entry for \mathbf{Q} , i.e., \mathbf{Q} must have all diagonal entries positive. Therefore $\text{trace}(\mathbf{Q}) > 0$ and at least one eigenvalue must have positive real part.

It is evident from $\mathbf{Q} = \mathbf{N}\mathbf{G}$ that $\mathbf{f} = [\mathbf{h}^T, 1]^T$, the left null vector for \mathbf{N} , is also a left null vector for \mathbf{Q} and therefore \mathbf{Q} is singular, with one (or more) zero eigenvalues. We may factor out the zero eigenvalue associated with \mathbf{f} as follows. First we partition \mathbf{Q} to separate out its last row and column:

$$\mathbf{Q} = \begin{bmatrix} \mathbf{B} & \mathbf{y} \\ \mathbf{x}^T & z \end{bmatrix}. \quad (10)$$

Here \mathbf{B} is an $(s-1) \times (s-1)$ submatrix, \mathbf{x} and \mathbf{y} are vectors and z is a scalar. Applying $[\mathbf{h}^T, 1]^T \mathbf{Q} = \mathbf{0}$ to the partitioned \mathbf{Q} gives $\mathbf{x}^T = -\mathbf{h}^T \mathbf{B}$, $z = -\mathbf{h}^T \mathbf{y}$, thus

$$\mathbf{Q} = \begin{bmatrix} \mathbf{B} & \mathbf{y} \\ -\mathbf{h}^T \mathbf{B} & -\mathbf{h}^T \mathbf{y} \end{bmatrix}. \quad (11)$$

We apply a similarity using the nonsingular matrix $\mathbf{R} = \begin{bmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{h}^T & 1 \end{bmatrix}$:

$$\begin{aligned} \mathbf{R}\mathbf{Q}\mathbf{R}^{-1} &= \begin{bmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{h}^T & 1 \end{bmatrix} \begin{bmatrix} \mathbf{B} & \mathbf{y} \\ -\mathbf{h}^T \mathbf{B} & -\mathbf{h}^T \mathbf{y} \end{bmatrix} \begin{bmatrix} \mathbf{I} & \mathbf{0} \\ -\mathbf{h}^T & 1 \end{bmatrix} \\ &= \begin{bmatrix} \mathbf{B} - \mathbf{y}\mathbf{h}^T & \mathbf{y} \\ \mathbf{0}^T & 0 \end{bmatrix} = \begin{bmatrix} \tilde{\mathbf{Q}} & \mathbf{y} \\ \mathbf{0}^T & 0 \end{bmatrix}, \end{aligned} \quad (12)$$

where

$$\tilde{\mathbf{Q}} = \mathbf{B} - \mathbf{y}\mathbf{h}^T. \quad (13)$$

Therefore \mathbf{Q} has a zero eigenvalue and the eigenvalues of $\tilde{\mathbf{Q}} = \mathbf{B} - \mathbf{y}\mathbf{h}^T$. The significance of $\tilde{\mathbf{Q}}$ may be seen in the formulation of the problem without explicitly using the free site concentration c_s . The free site concentration c_s may be removed by writing it in terms of the other concentrations using the relationship $\mathbf{f}^T \mathbf{c} = 1$ or $c_s = 1 - \mathbf{h}^T \tilde{\mathbf{c}}$ where $\mathbf{c} = [\tilde{\mathbf{c}}^T, c_s]^T$, e.g., $c_s = c_3 = 1 - c_1 - c_2$ for the above example. The differential equation for c_s is a linear combination of the others, $dc_s/dt = -\mathbf{h}^T d\tilde{\mathbf{c}}/dt$, and may be omitted. Thus we reduce the number of variables and differential equations by one, and the problem is then formulated in the conventional Langmuir kinetics form in which the site concentration is not a variable. This formulation no longer has the mass action form, but it is clear from the linear nature of these transformations that its eigenvalues are the same as the non-zero eigenvalues of \mathbf{Q} . The Jacobian matrix of the reduced problem is $-\tilde{\mathbf{Q}}$ as given in equation (13). The zero eigenvalue of \mathbf{Q} results from the existence of the conservation condition and the extraneous differential equation, and is therefore not relevant in considering the stability of the system.

From here on, we specialize to the case of three species ($s = 3$, two adsorbed species and free sites). In this case, there are only a few possibilities for the signs of eigenvalues of \mathbf{Q} . Since \mathbf{Q} is a product of \mathbf{N} and \mathbf{G} , its rank cannot exceed that of \mathbf{N} . There may be one or two conservation conditions, corresponding to $\text{rank}(\mathbf{N}) = 1$ or 2 , respectively. Furthermore, the positive diagonal elements of \mathbf{Q} mean that its rank cannot be zero, and its eigenvalues must have a positive sum. Therefore possible eigenvalue

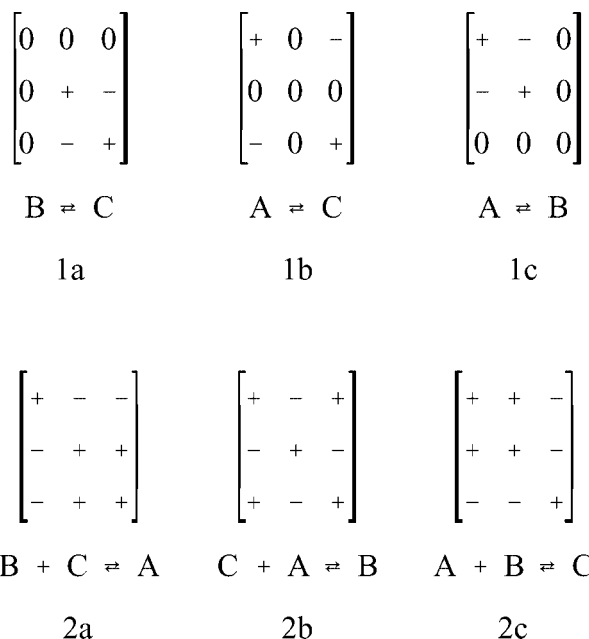


Figure 1. Possible sign patterns for elementary matrices A_j . Combinations of these sum to give Q .

patterns are $\{0, 0, +\}$ when $\det(\tilde{Q}) = 0$, $\{0, +, -\}$ when $\det(\tilde{Q}) < 0$, and $\{0, +, +\}$ or $\{0, x + iy, x - iy\}$, $x > 0$ when $\det(\tilde{Q}) > 0$.

The $\{0, 0, +\}$ pattern arises from $\text{rank}(Q) = 1$, but might also arise if $\text{rank}(Q) = 2$ and $\det(\tilde{Q}) = 0$. In this second case, one of the zero eigenvalues does not arise from a conservation condition (does not have an eigenvector), Q is not diagonalizable, and determination of the stability requires examination of the nonlinearities in the differential equations. We consider this possibility separately for each of the classes of mechanisms considered in sections 2.1–2.3 below. Clearly, determining the sign of $\det(\tilde{Q})$ is the key to assigning the types of eigenvalues. This quantity can be calculated from equation (13), or as the sum of the principal 2×2 minors of Q .

We now classify the possible types of mechanisms and determine the nature of the eigenvalues. In doing so, we will make frequent use of the sign patterns of the six possible types of elementary matrices, as summarized in figure 1. Here, and elsewhere where the exact stoichiometric composition of the species is not important, we will refer to the species as A, B and C. To see that these are the only six possibilities, note that a reaction without any reactants or a reaction without any products cannot be compatible with the conservation assumption A6. Therefore there must be at least one reactant species and at least one product species. We will call a reaction with one species as reactant and another species as product a “type 1 reaction”. There are three possibilities for this, depending on whether the species not appearing is species A (type 1a), species B (type 1b) or species C (type 1c). Since the two

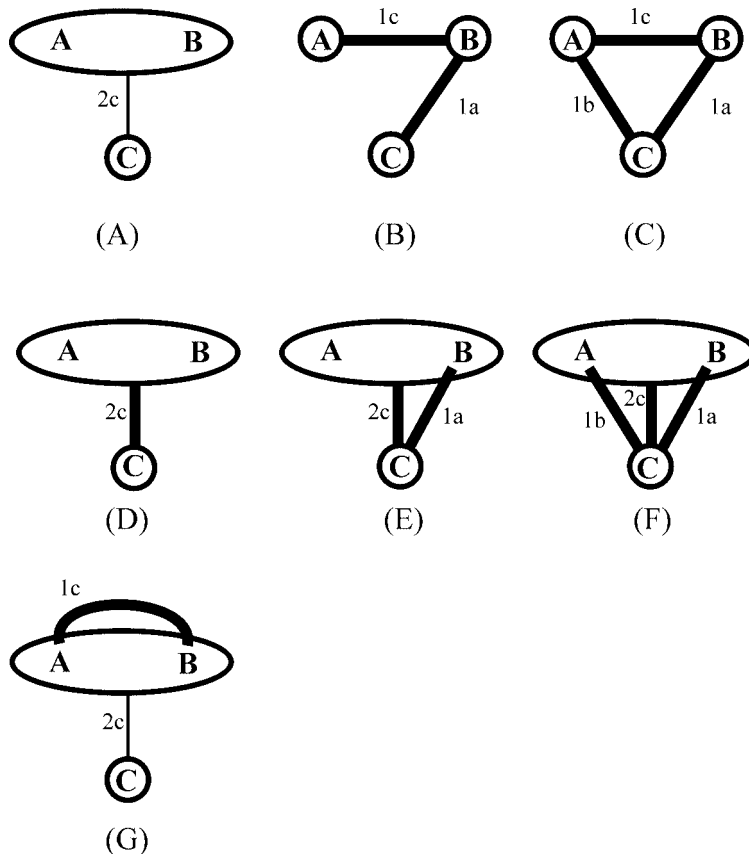


Figure 2. Generalized knot graphs for mechanisms considered. Mechanisms obtained by cyclic permutation of A, B, C and a, b, c are implied. The ellipse around A and B indicates that these species are together on the same side of the reaction. Thin lines indicate proportional reactions; thick lines indicate any number of (non-proportionate) reactions.

species are on opposite sides of the reaction, their stoichiometric coefficients have opposite signs and the elementary matrix has two negative off-diagonal entries and two positive diagonal entries as in the figure. (The sign pattern is independent of the direction the reaction is written, or the values of the stoichiometric coefficients.) The next possibility is for two of the species to be on one side and the third species to be on the other side, giving the three “type 2 reactions”. Since no species can appear on both sides (assumption A5) and there are only three species, this exhausts the possibilities.

Figure 2 shows graphs for the classes of mechanisms considered, similar to the knot graphs of Beretta et al. [6] but generalized to allow more than one reaction per graph edge. Circles or ellipses are the “knots” and contain species present on the same side of a reaction. The lines represent the reactions and link reactant species to product species. When lines terminate on the circles or ellipses, all species within are part of

Table 1

Summary of possible eigenvalues for selected mechanisms. Reaction types as in figure 1; p indicates proportionate, otherwise no restriction on number or proportionality of steps; Commas separate alternative mechanisms. Mechanisms obtained by cyclic permutation of a, b and c are implied. Superscripts refer to example numbers in table 2.

Mechanism	Stable			Unstable
	{0, +, +}	{0, $x + iy$, $x - iy$ }, $x > 0$	{0, 0, +}	{0, -, +}
$p2c$	no	no	always	no
$1a + 1c$	always	no	no	no
$1a + 1b + 1c$	yes	yes ³	no	no
$2c, 1a + 1b + 2c, 1a + 2c$	yes	no	yes ^{1,5,7}	yes ^{2,6,8}
Simple LH (eq. (14) with $m = n = 1$)	always	no	no	no
$p2c + 1c$	yes	*	no	no

* $y = 0$ is found (table 2, example 9), but we do not have an example for $y \neq 0$.

the reaction, but when the lines terminate inside, then only the species at the end of the line is part of the reaction. Thin lines indicate a single reaction or several proportionate reactions and thick lines indicate one or more non-proportionate reactions; the reaction types are labelled according to the notation of figure 1.

Table 1 summarizes the nature of the eigenvalues for the various cases.

2.1. Proportionate reactions only ($\text{rank}(N) = 1$)

If all reactions have proportionate stoichiometries, i.e., the columns of N are all multiples of each other, then $\text{rank}(N) = 1$. Then from $Q = NG$, $Q \neq 0$, it must be that $\text{rank}(Q) = 1$, and since Q has positive trace, it has two zero eigenvalues and one positive eigenvalue. The two left null vectors of N are also left null vectors of Q , and so the system of three differential equations may be reduced down to a single differential equation, whose steady states are always stable.

A mechanism with only one of the type 1 reactions in figure 1 has only two species, violates assumption A1, and leads to a zero diagonal element for Q . Therefore the proportionate reactions must be of type 2a, 2b, or 2c, and Q must have one of the three sign patterns shown in the bottom half of figure 1. The two linearly-independent left null vectors can both be chosen with positive integer entries: Suppose, without loss of generality, that the proportionate reactions are of type 2c (figure 2(A)), and that the columns of N are multiples of $[p, q, -t]^T$ with p, q, t positive integers. Then $[t, 0, p]^T$ is a left null vector which is linearly independent of the positive left null vector f that exists by assumption. Therefore we may take f and $f + [t, 0, p]^T$ as two positive left null vectors. The interpretation of the second positive null vector in chemical terms as a conservation condition may be unclear, e.g., for $MA + MB \rightarrow 2M$, the left null vector $[1, 1, 1]^T$ represents conservation of the M atoms, but the interpretation of the left null vector $[3, 1, 2]^T$ is problematic.

The proof in the appendix shows that this case of proportionate reactions is the only case that gives $\text{rank}(Q) = 1$, i.e., all other mechanisms have $\text{rank}(Q) = 2$. Conse-

quently, for all other mechanisms, there can only be one left null vector and one conservation condition.

2.2. Only one species on each side of a reaction – type 1 reactions only

This case includes any mixtures of type 1 reactions. The elementary matrices have non-positive off-diagonal entries (the Z sign pattern), positive diagonal entries and are symmetric in signs, i.e., have transposed corresponding off-diagonal entries of the same sign, and \mathbf{Q} has the same sign pattern. \mathbf{Q} has a positive left null vector and the Z sign pattern, is a singular M -matrix [9, theorem 5.11, p. 124], and has eigenvalues with non-negative real parts. Zero is a simple eigenvalue if and only if \mathbf{Q} is irreducible. Having established the stability or semistability of \mathbf{Q} , we investigate whether the eigenvalues must be real. There are two subcases, depending on whether the mechanism contains all three types 1a, 1b, and 1c, or only two of these.

2.2.1. One species per side, two reaction types

Without loss of generality we take the two types to be 1a and 1c (figure 2(B)), leading to a single possible sign pattern for \mathbf{Q} :

$$\begin{array}{ccc} \begin{bmatrix} 0 & 0 & 0 \\ 0 & + & - \\ 0 & - & + \end{bmatrix} & + & \begin{bmatrix} + & - & 0 \\ - & + & 0 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} + & - & 0 \\ - & + & - \\ 0 & - & + \end{bmatrix}. \\ \text{1a} & & \text{1c} \qquad \qquad \mathbf{Q} \end{array} \quad (14)$$

This is a real tridiagonal matrix with the product of corresponding off-diagonal entries positive, for which the eigenvalues are known to be real and simple [10, 3.7.1, p. 166]. The $\{0, 0, +\}$ case cannot occur here, because zero would not be a simple eigenvalue. From section 2.2 above, we know that \mathbf{Q} is stable with rank 2, so it must have a zero eigenvalue and two distinct positive eigenvalues.

The real eigenvalues follow from the tree structure of the graph (figure 2(B)) for a tridiagonal matrix, and the argument is similar to that of Beretta et al. [6]. However, the argument has been generalized to any number of reactions linking two species, proportionate or not. Furthermore, it is clear that to have the sign structure of equation (14) all reactions need not be reversible, only each link (edge of the graph) needs a forward and reverse reaction, e.g., the mechanism $\text{MA} \rightarrow \text{MB}$, $2\text{MB} \rightarrow 2\text{MA}$, $\text{MB} \rightarrow \text{M}$, $2\text{M} \rightarrow 2\text{MB}$ would suffice even though all reactions are irreversible.

2.2.2. One species per side, three reaction types

Here we have stable mechanisms with types 1a, 1b and 1c all present (figure 2(C)). The eigenvalues do not have to be real. The SQ mechanism (equation (5)) falls in this category (see equation (8)) and has complex eigenvalues with the rate parameters given in table 2, example 3. This is a counterexample to Solimano and Beretta's assertion that a single cycle with at least one surface (or enzyme) species alone on a reaction side leads to real eigenvalues when the rest of the knot graph is a tree [7]. This same mechanism

at equilibrium has two positive eigenvalues and one zero eigenvalue, so that $\{0, +, +\}$ and $\{0, x + iy, x - iy\}$ with $x > 0$ can both arise for these classes of mechanisms. Furthermore, unlike the case above, equal positive eigenvalues are possible, i.e., $\{0, a, a\}$, $a > 0$, table 2, example 4. The eigenvalues cannot be $\{0, 0, +\}$, i.e., $\det(\tilde{\mathbf{Q}}) \neq 0$. This follows from the irreducibility of \mathbf{Q} in this case (see beginning of section 2.2).

2.3. Mechanisms with type 2 reactions

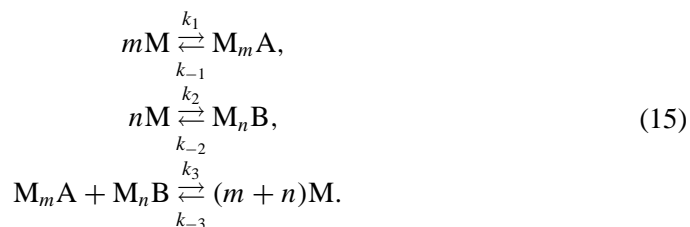
So far all reaction classes considered have been stable, but we will find unstable examples among the mechanisms with type 2 reactions. The case of proportionate reactions of a single type (2a, 2b or 2c) has been dealt with above (section 2.1), and leads always to $\{0, 0, +\}$. Nonproportionate reactions of single type, say type 2c, are next in complexity, and already in this case unstable behavior is possible, table 2, example 2. However, adding 1a and/or type 1b to type 2c reactions does not change the sign pattern, and so we deal with these cases together.

2.3.1. Sign-compatible type 1 and type 2 reactions

Without loss of generality, we assume reactions of type 2c alone, with 1a or with 1a and 1b (figures 2(D)–(F)). These mechanisms are those in which the surface site is alone and present in all reactions. \mathbf{Q} has sign pattern 2c, \mathbf{B} is positive, \mathbf{y} is negative and \mathbf{h} is positive, so $\tilde{\mathbf{Q}} = \mathbf{B} - \mathbf{y}\mathbf{h}^T$ is positive. Since the off-diagonal elements of $\tilde{\mathbf{Q}}$ have the same sign, the eigenvalues must be real. Furthermore, since $\tilde{\mathbf{Q}}$ is positive, the Perron–Frobenius theorem implies that the largest eigenvalue is positive. The possibilities are $\{0, +, +\}$ with unequal positive eigenvalues or $\{0, -, +\}$. Examples of the latter are found, i.e., unstable examples with $\det(\tilde{\mathbf{Q}}) < 0$. As noted, even non-proportionate 2c reactions alone show this behavior, so one might seek stable behavior amongst mixed mechanisms in which the 2c reactions are proportionate. However, unstable cases are found for cases with proportionate 2c plus 1a or plus 1a and 1b, table 2, examples 6 and 8. A continuity argument suggests it is also possible to have $\det(\tilde{\mathbf{Q}}) = 0$, i.e., $\{0, 0, +\}$ as a transition case between $\{0, -, +\}$ and $\{0, +, +\}$, and this proves to be the case, table 2, examples 5 and 7.

2.3.1.1. Langmuir–Hinshelwood mechanisms

Instability is possible in general for sign-compatible mixed type 1/type 2 mechanisms. We now investigate the stability of an important subcase, the classical Langmuir–Hinshelwood (LH) mechanism:



Here molecules A and B adsorb on the surface and then react with each other to give an external product (releasing the reaction sites). An analysis based on sign patterns is insufficient in this case. Explicit evaluation of $\det(\tilde{\mathbf{Q}})$ is aided by developing a new form of \mathbf{Q} . Writing $\mathbf{v}_f = \mathbf{v} + \mathbf{v}_b$ where $\mathbf{v}_b = [v_{1b}, v_{2b}, v_{3b}]^T$ in each elementary matrix and then collecting the back reaction parts of the elementary matrices separately from the parts with v_j shows that \mathbf{QC} can be written as

$$\mathbf{QC} = \mathbf{NV}_b\mathbf{N}^T + \mathbf{NVN}^{T-}, \quad (16)$$

where $\mathbf{C} = \text{diag}(\mathbf{c})$, $\mathbf{V}_b = \text{diag}(\mathbf{v}_b)$, $\mathbf{V} = \text{diag}(\mathbf{v})$, and \mathbf{N}^{T-} is \mathbf{N}^T with its positive elements set to zero. For the LH mechanism at steady state $v_1 = v_2 = v_3$, and the problem may be scaled so that the net rate is unity, $\mathbf{v} = [1, 1, 1]^T$. Substituting values for this example gives:

$$\mathbf{QC} = \begin{bmatrix} a & b & -am - bn \\ b & d & -dn - bm \\ -am - bn & -dn - bm & am^2 + 2bmn + dn^2 \end{bmatrix} + \begin{bmatrix} 1 & 1 & -m \\ 1 & 1 & -n \\ -m - n & -m - n & m^2 + n^2 \end{bmatrix}, \quad (17)$$

where $a = v_{1b} + v_{3b} > 0$, $b = v_{3b} > 0$, $d = v_{2b} + v_{3b} > 0$ and the last row and column of the first term may be deduced from its leading 2×2 submatrix using the fact that $\mathbf{f} = [m, n, 1]^T$ is the left and right null vector of this term. Explicitly evaluating the principal 2×2 minors gives

$$\begin{aligned} |\mathbf{QC}[1, 2]| &= (\delta + \gamma), \\ |\mathbf{QC}[2, 3]| &= (\delta + \gamma + b + 1)m^2 - (1 + d)mn, \\ |\mathbf{QC}[1, 3]| &= (\delta + \gamma + b + 1)n^2 - (1 + a)mn, \end{aligned} \quad (18)$$

where $\delta = ad - b^2 > 0$ and $\gamma = a + d - 2b$. The arithmetic geometric mean inequality and $\delta > 0$ imply $\frac{1}{2}(a + d) \geq (ad)^{1/2} > b$ so that $\gamma > 0$. Therefore $|\mathbf{QC}[1, 2]| > 0$ regardless of the values of m and n .

The ‘‘simple LH’’ mechanism has $m = n = 1$, as frequently assumed in textbooks, e.g., [11]. In this case, $|\mathbf{QC}[2, 3]| = \delta + \gamma + b - d = \delta + a - b = \delta + v_{1b} > 0$, and $|\mathbf{QC}[1, 3]|$ is similarly positive. The sum of the principal 2×2 minors for $\mathbf{Q} = (\mathbf{QC})\mathbf{C}^{-1}$ is

$$\begin{aligned} |\tilde{\mathbf{Q}}| &= \frac{|\mathbf{QC}[1, 2]|}{c_1c_2} + \frac{|\mathbf{QC}[2, 3]|}{c_2c_3} + \frac{|\mathbf{QC}[1, 3]|}{c_1c_3} \\ &= \frac{c_3|\mathbf{QC}[1, 2]| + c_1|\mathbf{QC}[2, 3]| + c_2|\mathbf{QC}[1, 3]|}{c_1c_2c_3} \end{aligned} \quad (19)$$

and this is positive since all the concentrations and QC minors are positive. The simple LH mechanism therefore has eigenvalues $\{0, +, +\}$ and is always stable. (The above shows that this is true also for any case with $m = n$.)

In the more general case of arbitrary m and n , instability may arise. To see this, note that $|QC[2, 3]|$ (equation (18)) may be made negative by choosing n sufficiently large, and similarly $|QC[1, 3]|$ may be made negative by choosing m sufficiently large. However, they cannot both be negative at the same time since their sum is positive:

$$|QC[2, 3]| + |QC[1, 3]| = \delta(m^2 + n^2) + (\gamma + b + 1)(m - n)^2 + \gamma mn. \quad (20)$$

An unstable example can be constructed by taking n large enough to make $|QC[2, 3]|$ negative. This can occur for n as low as 2 for an appropriate choice of rate constants, table 2, example 6.

2.3.2. Sign incompatible type 1 and type 2 cases

Since many of our arguments have relied on sign patterns, it is interesting that a case where the sign pattern is not known *a priori* can nonetheless lead only to stable behavior. This is the case of proportionate 2c reactions plus 1c reactions (figure 2(G)). Addition of enough 1c reaction to 2c to give the leading 2×2 submatrix negative off-diagonal elements gives the sign pattern of section 2.2.2, which is always stable. If this sign pattern does not result, then we consider the signs of the principal 2×2 minors to decide the stability. The proportionate 2c rank 1 matrix Q has all its 2×2 minors zero. If addition of the 1c reaction leads to only one negative off-diagonal element in the leading 2×2 submatrix, then that minor is explicitly positive. If both off-diagonal elements are positive, then they are less than without the 1c reaction, while the diagonal elements are greater, so that the determinant is greater, making it positive. The 1, 3 and 2, 3 principal minors are positive because the 1c reactions increase diagonal elements of these minors without altering the off-diagonal elements. Therefore all principal minors are positive, and only stable behavior is possible. Degenerate positive roots are possible (table 2, example 9), but we have not found an example with complex roots.

Other cases involve at least two types of type 2 reactions, e.g., $2c + 2b$, have minors of indefinite sign, and can show all types of behavior, including instability.

2.4. Reactions at equilibrium

Reactions at equilibrium may be dealt with in a way that crosses the boundaries of the above classification scheme, and the nature of the eigenvalues is further constrained. (By equilibrium we mean the special case of steady state in which the forward and reverse rates are equal for all reactions; in the literature equilibrium is sometimes used instead as a synonym for steady state.) At equilibrium all the elementary matrices times C become symmetric and therefore positive semidefinite. Their sum, QC , is therefore positive semidefinite, and congruent to $C^{-1/2}QC C^{-1/2} = C^{-1/2}QC^{1/2}$, which is similar to Q . Therefore the eigenvalues are real and non-negative, a well-known result [12].

There are some circumstances under which one or more reactions must be at equilibrium under all conditions, no matter what the rate constant values are, e.g., any two-step mechanism must be at equilibrium, since the number of reactions (columns of N) cannot exceed the rank of N , the nullity of N is zero, and the only solution to $N\mathbf{v} = \mathbf{0}$ is $\mathbf{v} = 0$.

There are cases in which one step has a net rate of zero, but the others do not. Even though one step is not participating, and is in some sense at equilibrium, it can allow the mechanism to become unstable. For example, two proportionate 2c reactions are stable, but adding a type 1a reaction with zero net rate can lead to an unstable steady state (table 2, example 8).

3. Discussion and conclusions

The above analysis shows that there are some categories of mechanisms for which the nature of the eigenvalues (aside from the zero one coming from the conservation condition) may be deduced without regard to the values of the rate constants or the stoichiometric coefficients (see also table 1), namely, proportionate reactions (stable and real, section 2.1), two-step mechanisms (stable and real, section 2.4), mechanisms with a single species in all reaction sides, i.e., type 1 (stable, sections 2.2, 2.2.2), type 1 with two species that do not interconvert in any reaction (stable and real, section 2.2.1), mechanisms in which one species is alone in all reactions (real, section 2.3.1), and $p2c + 1c$ mechanisms (stable, section 2.3.2). As may be expected from a continuity argument, mechanisms that can have a complex conjugate pair may have degenerate non-zero eigenvalues as a special case, and mechanisms that can be unstable may also be stable with a (second) zero eigenvalue (without a corresponding eigenvector).

The sequential (equation (5)) and simple Langmuir–Hinshelwood (equation (15), $m = n = 1$) mechanisms are the most common surface mechanisms, and are always stable. McCafferty [13] has given a number of electrochemical mechanisms that proceed by the simple LH mechanism, and analyzed its irreversible variant, concluding that it may be unstable (at a steady state in which c_1 or c_2 is zero). That result does not contradict the present conclusions, since we consider only reversible reactions and exclude zero concentrations. In gas phase and dilute-solution kinetics, third- and higher-order reactions are often rejected because concerted collision of three or more molecules is considered unlikely. However, in surface chemistry the coverages may be of order unity, and such reactions are more probable. In the LH mechanism, the last step is usually considered to be bimolecular, but for m or $n > 2$ the forward reactions of steps 1 and 2 are of higher order. This arises because the probability of finding m free sites together for adsorption of the large molecule A goes as c_3^m , and not because a collision of m molecules is invoked.

Although the possibility of unstable steady states arises in the mechanisms here, this does not imply exotic behavior in the non-linear dynamics. The reduced system has only two differential equations (with Jacobian $-\tilde{Q}$), and \tilde{Q} can only have eigenvalues $\{+, +\}$, $\{+, -\}$, $\{+, 0\}$ or $\{x \pm iy, x > 0\}$. Instability can only arise by one eigenvalue

Table 2
Examples ($f = [1, 1, 1]^T$ except as noted).

Mechanism	N	Rate parameters	Q	Eigenvalues	
1.		$c_1 = c_2 = c_3 = 1/3$ $k_1 = 12; k_2 = 81; k_3 = 108$ $k_{-1} = 3; k_{-2} = k_{-3} = 27$ $v_{1f} = 4/3; v_{2f} = 3; v_{3f} = 4/3$ $v_{1b} = 1/3; v_{2b} = 1; v_{3b} = 1/3$	$\begin{bmatrix} 11 & 22 & -33 \\ 22 & 46 & -74 \\ -33 & -68 & 107 \end{bmatrix}$	0, 0, 164	
2.	$2M \rightleftharpoons MA + MB$ $MA + 2MB \rightleftharpoons 3M$ $4M \rightleftharpoons MA + 3MB$ (2c)	$c_1 = c_2 = c_3 = 1/3$ $k_1 = 21/2; k_2 = 81; k_3 = 243/2$ $k_{-1} = 3/2; k_{-2} = 27; k_{-3} = 81/2$ $v_{1f} = 7/6; v_{2f} = 3; v_{3f} = 3/2$ $v_{1b} = 1/6; v_{2b} = 1; v_{3b} = 1/2$	$\begin{bmatrix} 1 & -1 & 1 \\ 1 & -2 & 3 \\ -2 & 3 & -4 \end{bmatrix}$	$\begin{bmatrix} 11 & 23 & -34 \\ 23 & 50 & -79 \\ -34 & -73 & 113 \end{bmatrix}$	0, 174.052, -0.052
3.		$c_1 = c_2 = c_3 = 1/3$ $k_1 = k_2 = k_3 = 4$ $k_{-1} = k_{-2} = k_{-3} = 1$ $v_{1f} = v_{2f} = v_{3f} = 4/3$ $v_{1b} = v_{2b} = v_{3b} = 1/3$	$\begin{bmatrix} 5 & -1 & -4 \\ -4 & 5 & -1 \\ -1 & -4 & 5 \end{bmatrix}$	0, 7.50 ± 2.60 i	
4.	$M \rightleftharpoons MA$ $MA \rightleftharpoons MB$ $MB \rightleftharpoons M$ (SQ, 1a + 1b + 1c)	$c_1 = c_2 = c_3 = 1/3$ $k_1 = 15/2; k_2 = 9; k_3 = 6$ $k_{-1} = 9/2; k_{-2} = 6; k_{-3} = 3$ $v_{1f} = 5/2; v_{2f} = 3; v_{3f} = 2$ $v_{1b} = 3/2; v_{2b} = 2; v_{3b} = 1$	$\frac{1}{2} \begin{bmatrix} 27 & -12 & -15 \\ -18 & 24 & -6 \\ -9 & -12 & 21 \end{bmatrix}$	0, 18, 18	
5.		$c_1 = 1/2; c_2 = 1/10; c_3 = 3/10$ $v_{1f} = 5/4; v_{2f} = 19/18; v_{3f} = 4/3$ $v_{1b} = 1/4; v_{2b} = 1/18; v_{3b} = 1/3$ $k_1 = 25/6; k_2 = 950/81; k_3 = 80/3$ $k_{-1} = 1/2; k_{-2} = 5/9; k_{-3} = 1000/81$	$\frac{1}{54} \begin{bmatrix} 171 & 720 & -405 \\ 144 & 750 & -560 \\ -459 & -2220 & 1525 \end{bmatrix}$	0, 0, 45.30	
6.	$M \rightleftharpoons MA$ $2M \rightleftharpoons M_2B$ $MA + M_2B \rightleftharpoons 3M$ (LH, 1a + 1b + 2c) $f = [1, 2, 1]^T$	$c_1 = 1/2; c_2 = 1/10; c_3 = 3/10$ $k_1 = 11/3; k_2 = 110/9; k_3 = 22$ $k_{-1} = 1/5; k_{-2} = 1; k_{-3} = 100/27$ $v_{1f} = v_{2f} = v_{3f} = 11/10$ $v_{1b} = v_{2b} = v_{3b} = 1/10$	$\frac{1}{15} \begin{bmatrix} 36 & 165 & -70 \\ 33 & 180 & -125 \\ -102 & -525 & 320 \end{bmatrix}$	0, 36.06, -0.32	

Table 2
(Continued.)

Mechanism	N	Rate parameters	Q	Eigenvalues
7. 10M \rightleftharpoons MA + 9MB 2MA + 18MB \rightleftharpoons 20M MB \rightleftharpoons M (p2c + 1a)	$\begin{bmatrix} 1 & -2 & 0 \\ 9 & -18 & -1 \\ -10 & 20 & 1 \end{bmatrix}$	$c_1 = c_2 = c_3 = 1/3$ $k_1 = 1.96e5; k_2 = 4.64e9; k_3 = 3$ $k_{-1} = 7.87e4; k_{-2} = 1.16e9; k_{-3} = 3$ $v_{1f} = 10/3; v_{2f} = 4/3; v_{3f} = 1$ $v_{1b} = 4/3; v_{2b} = 1/3; v_{3b} = 1$	$\begin{bmatrix} 20 & 180 & -140 \\ 180 & 1623 & -1263 \\ -200 & -1803 & 1403 \end{bmatrix}$	0, 0, 3046
8. (p2c + 1a)		$c_1 = c_2 = c_3 = 1/3$ $k_1 = 1.48e5; k_2 = 5.23e9; k_3 = 3$ $k_{-1} = 2.95e4; k_{-2} = 1.74e9; k_{-3} = 3$ $v_{1f} = 2/5; v_{2f} = 3/2; v_{3f} = 1$ $v_{1b} = v_{2b} = 1/2; v_{3b} = 1$	$\frac{1}{2} \begin{bmatrix} 39 & 351 & -270 \\ 351 & 3165 & -2436 \\ -390 & -3516 & 2706 \end{bmatrix}$	0, 2955.01, -0.0015
9. 2M \rightleftharpoons MA + MB 2MA + 2MB \rightleftharpoons 4M MB \rightleftharpoons MA (p2c + 1c)	$\begin{bmatrix} 1 & -2 & 1 \\ 1 & -2 & -1 \\ -2 & 4 & 0 \end{bmatrix}$	$c_1 = c_2 = c_3 = 1/3$ $k_1 = 27; k_2 = 162; k_3 = 69$ $k_{-1} = 9; k_{-2} = 81; k_{-3} = 69$ $v_{1f} = 3; v_{2f} = 2; v_{3f} = 23$ $v_{1b} = v_{2b} = 1; v_{3b} = 23$	$\begin{bmatrix} 96 & -42 & -42 \\ -42 & 96 & -42 \\ -54 & -54 & 84 \end{bmatrix}$	0, 138, 138
10. 2MA + MB \rightleftharpoons 3M MB + MC \rightleftharpoons 2M M \rightleftharpoons MA M \rightleftharpoons MB (4 species, $f = [1, 1, 1, 1]^T$)	$\begin{bmatrix} -2 & 0 & 1 & 0 \\ -1 & -1 & 0 & 1 \\ 0 & -1 & 0 & 0 \\ 3 & 2 & -1 & -1 \end{bmatrix}$	$c_1 = c_2 = c_3 = c_4 = 1/4$ $k_1 = 12864; k_2 = 160$ $k_3 = 3600; k_4 = 804$ $k_{-1} = 64; k_{-2} = 160$ $k_{-3} = 2000; k_{-4} = 4$ $v_{1f} = 201; v_{2f} = 10; v_{3f} = 900; v_{4f} = 201$ $v_{1b} = 1; v_{2b} = 10; v_{3b} = 500; v_{4b} = 1$	$\frac{1}{2} \begin{bmatrix} 652 & 201 & 0 & -453 \\ 201 & 106 & 5 & -112 \\ 0 & 5 & 5 & -10 \\ -853 & -312 & -10 & 575 \end{bmatrix}$	0, 650.02, 9.49 \pm 2.76 i

crossing through zero, not by a complex conjugate pair crossing the imaginary axis. Therefore Hopf bifurcation to a periodic solution is not possible. Instability is always manifested by a saddle point, and the solution flows away from this point to a stable steady state without showing exotic behavior.

Because these types of unstable steady states have only a transient existence on the way to a stable steady state, they have no implications for EIS, in which a stable steady state is attained before being perturbed. The more critical issue for EIS is to find conditions under which the stable steady state(s) have complex eigenvalues, a sufficient condition for an inductive equivalent circuit.

The issue of whether the eigenvalues are real or complex has been investigated less than the issue of stability. Early it was shown from a thermodynamic point of view that perturbations relax to equilibrium exponentially and therefore the eigenvalues at equilibrium are real [14,15]. First-order mechanisms with detailed balance were also shown to have real eigenvalues [12,16–18]. Hearon extended this result to show that the equilibrium eigenvalues for arbitrary mechanisms were real [12]. There are only a few general cases (without restrictions on the rate constants) where the eigenvalues are known to be real. Tree graphs of various kinds were shown to have real eigenvalues for different classes of mechanism [12,18–20], culminating in the knot graph approach [6]. Knot graphs, in which the vertices (knots) are collections of species that appear together on the same sides of reactions and the edges are reactions, were shown to have real eigenvalues if they are trees, i.e., they have no cycles. (The mechanisms in section 2.2.1 have real eigenvalues for this reason.)

In the case of surface (and enzyme) mechanisms, the conservation of the surface atoms (enzyme) typically leads to cycles in the graphs. For example, most surface mechanisms begin with adsorption of reactants onto previously free reaction sites, and end with release of these reaction sites, leading to a cycles such as in figures 2(C), (E), (F), (G). Solimano and Beretta suggested that the eigenvalues would still be real if removal of one cycle in which one surface/enzyme species appeared alone in one vertex left a tree graph [7]. The SQ mechanism provides a counterexample to this assertion, since there is one cycle containing M alone at one vertex (figure 2), and complex eigenvalues are found, table 2, example 3. Many stability results have been obtained through the use of Lyapunov functions, which give no information about whether the eigenvalues are real or not. For example, complex eigenvalues can occur for deficiency zero mechanisms, as the SQ mechanism shows. Our case of mechanisms with one species alone in all reactions is one of the few cases where the eigenvalues are real without the restriction to a tree graph.

It appears that a classification scheme for four (or more) species will be substantially more complicated, but it is worth considering whether a generalization of mechanisms with sign-compatible type 1 and type 2 reactions can be found that always has real eigenvalues. Unfortunately this is not the case: the 3×3 matrix \mathbf{B} for the mechanism $2A + B \rightleftharpoons 3D$, $B + C \rightleftharpoons 2D$, $D \rightleftharpoons A$, $D \rightleftharpoons B$ is positive definite and totally non-negative, yet \mathbf{Q} still has complex eigenvalues for some values of the rate constants (table 2, example 10).

The results for mechanisms with only type 1 reactions can, however, be generalized for more than three species. In the more general case a type 1 reaction may be defined as one in which the reactants consist of a single species and the products consist of a single but different species. Regardless of the number of species, the positive conservation vector means that Q is a singular M matrix, which is stable or semistable; purely imaginary eigenvalues cannot occur. In the case that Q is irreducible (always true for the three-species cases above), zero is a simple eigenvalue associated with the conservation condition and so the linearized problem is stable. The assumption of reversible reactions leads to matrices that are symmetric in signs. Then it is clear that Q is reducible if and only if it can be permuted to a direct sum of irreducible diagonal blocks, of order two or greater (order one is incompatible with a positive conservation vector). The irreducible blocks correspond to subsystems of differential equations, each with their own positive conservation condition and uncoupled from the other subsystems. All zero eigenvalues are associated with a conservation condition, and the linearized problem is therefore always stable.

The non-linear dynamical behavior for these systems can be deduced from the theory of monotone dynamical systems [21,22]. They obey the Kamke condition [22, p. 32] and are cooperative, which in chemical terms means that the rate of production of a species cannot be decreased by increasing the concentration of any of the other species. No attractive, nonconstant periodic orbits are possible. Since the system is irreducible for $t > 0$, then almost all solutions approach the set of stable steady states [21]. A steady state cannot have any species concentration zero, given that all reactions are assumed to be reversible.

Subclasses of type 1 mechanisms have been dealt with previously in the literature. Networks of unimolecular reactions (without reactions to or from the zero complex) are stable [12,18]. This is because the conservation vector $f = [1, 1, \dots, 1]^T$ applies to such mechanisms. These systems are also referred to as closed compartmental systems [23]. A closed *generalized* compartmental system is one in which each species appears in exactly one complex, and each complex has only one species [23,24]. Thus $2A \rightleftharpoons 3B \rightleftharpoons C \rightleftharpoons A$ is unacceptable because A appears in two complexes ($2A$ and A), but $2A \rightleftharpoons 3B \rightleftharpoons C \rightleftharpoons 2A$ is acceptable. These mechanisms are also stable, again because a conservation vector may be constructed for them. The vector $[p/\mu_1, p/\mu_2, \dots, p/\mu_s]^T$ is suitable, where μ_i is the stoichiometric coefficient for species i in its complex, and p is the least common multiple of the μ_i , e.g., $[3, 2, 6]^T$ for the example just given. These results are more usually approached through deficiency theory, since both compartmental and generalized compartmental systems have deficiency zero [24].

Our result relaxes the requirement that a species appears only in one complex, but requires that a positive conservation vector exists. The construction of a conservation vector from a mechanism written with generic species is non-obvious, but if the chemical identity of the species is specified, a conservation vector is more easily found. In the present work, the surface atoms M guarantee a conservation condition. In other cases, conservation may also be obvious. For example, any mechanism in which all species

contain benzene rings will be conservative if reactions neither create nor destroy such rings, and a vector of the numbers of benzene rings in each species is a conservation vector. A three-species example is $A \rightleftharpoons B$, $2B \rightleftharpoons 2C$, $2C \rightleftharpoons 2A$, which is neither a generalized compartmental system nor does it have deficiency zero, but it is stable from our results, since it is composed only of type 1 reactions ($1a + 1b + 1c$).

The requirement for reversible reactions may be relaxed provided that \mathbf{Q} remains symmetric in signs. A weaker acceptable requirement is “species reversibility”, i.e., a reaction taking B to A exists whenever a reaction taking A to B exists, e.g., $2A \rightarrow 2B$ may be partnered with $B \rightarrow A$.

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Appendix. Proof that $\text{rank}(\mathbf{N}) = \text{rank}(\mathbf{Q})$

We show in lemma A.2 below that $\text{rank}(\mathbf{Q}) = 1$ implies $\text{rank}(\mathbf{N}) = 1$. The rule for the rank of a product applied to $\mathbf{Q} = \mathbf{N}\mathbf{G}$ gives $\text{rank}(\mathbf{Q}) \leq \text{rank}(\mathbf{N})$. Also $\text{rank}(\mathbf{N}) \leq 2$, since \mathbf{N} is $3 \times r$ with at least one left null vector. So $\text{rank}(\mathbf{Q}) = 2$ implies $\text{rank}(\mathbf{N}) = 2$. Therefore in all cases $\text{rank}(\mathbf{N}) = \text{rank}(\mathbf{Q})$.

Lemma A.1. A mix of type 2c reactions has $\det(\mathbf{B}) = 0$ if the reactions are proportionate and $\det(\mathbf{B}) > 0$ otherwise.

Proof. If a type 2c elementary matrix is postmultiplied by \mathbf{C} , then the leading 2×2 submatrix of the product can be written as $v_{jf}\tilde{\mathbf{n}}_j\tilde{\mathbf{n}}_j^T$ or $v_{jb}\tilde{\mathbf{n}}_j\tilde{\mathbf{n}}_j^T$ where $\tilde{\mathbf{n}}_j$ is \mathbf{n}_j without its last entry, because each entry involves the same rate (v_{jf} or v_{jb}). The sum of these positive semidefinite submatrices is the product $\mathbf{B}\tilde{\mathbf{C}}$:

$$\mathbf{B}\tilde{\mathbf{C}} = \sum_{j=1}^r v_{j\text{fb}}\tilde{\mathbf{n}}_j\tilde{\mathbf{n}}_j^T = \tilde{\mathbf{N}}\mathbf{V}_{\text{fb}}\tilde{\mathbf{N}}^T = \tilde{\mathbf{N}}\mathbf{V}_{\text{fb}}^{1/2}(\tilde{\mathbf{N}}\mathbf{V}_{\text{fb}}^{1/2})^T,$$

where the subscript fb denotes f or b as appropriate, $\mathbf{V}_{\text{fb}} = \text{diag}(v_{1\text{fb}}, v_{2\text{fb}}, \dots, v_{r\text{fb}})$, and $\tilde{\mathbf{N}}$ is the first two rows of \mathbf{N} . Let $\mathbf{A} = \tilde{\mathbf{N}}\mathbf{V}_{\text{fb}}^{1/2}$, and recall that \mathbf{V}_{fb} and $\tilde{\mathbf{C}}$ are nonsingular. Then $\text{rank}(\mathbf{B}) = \text{rank}(\mathbf{B}\tilde{\mathbf{C}}) = \text{rank}(\mathbf{A}\mathbf{A}^T) = \text{rank}(\mathbf{A}) = \text{rank}(\tilde{\mathbf{N}}) = \text{rank}(\mathbf{N})$, where the last equality applies since the positive left null vector \mathbf{f} of \mathbf{N} means that the last row of \mathbf{N} is a linear combination of the first two rows. So if the reactions are proportionate ($\text{rank}(\mathbf{N}) = 1$), then $\text{rank}(\mathbf{B}) = 1$, \mathbf{B} is singular and $\det(\mathbf{B}) = 0$. But if $\text{rank}(\mathbf{N}) = 2$, then $\mathbf{B}\tilde{\mathbf{C}}$ is non-singular positive definite and $\det(\mathbf{B}) = \det(\mathbf{B}\tilde{\mathbf{C}})/\det(\tilde{\mathbf{C}}) = \det(\mathbf{B}\tilde{\mathbf{C}})/c_1c_2 > 0$. \square

Lemma A.2. $\text{rank}(\mathbf{Q}) = 1$ implies $\text{rank}(\mathbf{N}) = 1$.

Proof. We show that the only mechanisms with $\text{rank}(\mathbf{Q}) = 1$ are those with proportionate reactions of one of the types 2a, 2b, or 2c, which have $\text{rank}(\mathbf{N}) = 1$. Suppose $\text{rank}(\mathbf{Q}) = 1$. Then no column (or row) can have a zero entry, otherwise a diagonal entry would be zero. For \mathbf{Q} to have a positive left null vector, each column must have two positive entries and a negative entry or two negative entries and a positive entry. Each column must be a multiple of the others, and these conditions only lead to positive diagonal entries of \mathbf{Q} if \mathbf{Q} has one of the three sign patterns of the bottom half of figure 1. Without loss of generality, we permute species so that the leading 2×2 submatrix \mathbf{B} has positive entries, i.e., \mathbf{Q} has a sign pattern looking like 2c in figure 1. For \mathbf{Q} to have this sign pattern, at least one of the component elementary matrices in the sum must be of type 2c, since the others have negative or zero 1, 2 and 2, 1 entries. The others may be present in the sum so long as their 1, 2 and 2, 1 entries are small enough that the positive 1, 2 and 2, 1 entries in the type 2c reactions dominate and make these entries in the sum positive. Addition of a 2×2 leading submatrix with non-negative diagonal entries and non-positive off-diagonal entries (for reactions not of type 2c) to a positive 2×2 submatrix (for the type 2c reactions) increases the diagonal entries and decreases the off-diagonal entries (since they remain positive), so that the determinant must increase. The only way for the determinant to be zero, as required for $\text{rank}(\mathbf{Q}) = 1$ is for there to be only type 2c reactions and furthermore that these 2c reactions are proportionate (from lemma A.1). We conclude that $\text{rank}(\mathbf{Q}) = 1$ can only occur for mechanisms with proportionate reactions of one of the types 2a, 2b or 2c, i.e., $\text{rank}(\mathbf{Q}) = 1$ implies $\text{rank}(\mathbf{N}) = 1$. \square

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