

# How catalytic mechanisms reveal themselves in multiple steady-state data: I. Basic principles

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## Abstract

Multiple steady states are often observed in isothermal continuous flow stirred tank reactors (CFSTRs) involving heterogeneous catalysis. At least, when certain physical conditions prevail, even fragmentary multiple steady-state data can be used to help determine the operative catalytic mechanism. This article describes theory that can ascertain both whether a given candidate mechanism has the capacity to support multiple steady states and, more importantly, whether the mechanism has the capacity to support a particular pair of steady states observed experimentally. In this article, hypothetical examples are used to illustrate the scope, purpose and methodology of this theory. The examples also demonstrate the way in which even partial multiple steady-state data provide a basis for highly refined discrimination between very similar mechanisms. In a companion article, actual multiple steady-state data are used to discriminate between proposed mechanisms for ethylene hydrogenation on rhodium. A public computer program is available that will allow the user to apply the theory described in this article without knowledge of any underlying theory. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Multiple steady states; Mechanism discrimination

## 1. Introduction

It has been observed that catalytic continuous flow stirred tank reactors (CFSTRs) often demonstrate complex behavior such as multiple steady states [1–3]. This is to say that for many catalytic CFSTRs, different start-up procedures can produce two or more distinct steady states under otherwise identical operating conditions. Often, the presence of multiple steady states is

attributed to heat interactions in the CFSTR; however, even when heat effects are eliminated by running the reactor isothermally, the interplay of the reactions themselves are sometimes enough to produce multiple steady states. If isothermal multiple steady-state data can be obtained, such data can provide clues to which reactions are actually taking place. This article describes how, through chemical reaction network theory, multiple steady-state data can be used to discriminate in a very refined way between candidates for the operative catalytic mechanism.

Isothermal multiple steady-state data, even fragmentary data, provide several opportunities for mechanism discrimination. First, if multiple

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steady states are observed, then, in order for a candidate mechanism to be viable, it must have the qualitative ability to support multiple steady states. However, there is a sharper requirement than just this capacity to support multiple steady states. Even when a mechanism can support multiple steady states, it will usually be able to support only certain pairs of steady states. Thus, the possible pairs of steady states for a mechanism provide a type of “signature” for that mechanism. A viable candidate mechanism must not only be able to support multiple steady states, but also multiple steady states *consistent with the available data*. It turns out that even partial multiple steady-state data can be enough to discriminate sharply between rival candidate mechanisms.

Ethylene hydrogenation serves as an example both of how multiple steady-state data can be used as a discrimination tool and of why such tools are necessary. There is no general consensus about the way in which ethylene hydrogenation occurs on various catalytic surfaces. Table 1 contains just a few of those mechanisms that have been proposed for ethylene hydrogenation.

In these mechanisms the symbol S represents an empty catalytic site. As usual, the symbol H – S represents H adsorbed onto an individual catalytic site, the symbol C<sub>2</sub>H<sub>3</sub> – S represents C<sub>2</sub>H<sub>3</sub> adsorbed onto an individual catalytic site,

and the symbol C<sub>2</sub>H<sub>4</sub> – S<sub>2</sub> represents C<sub>2</sub>H<sub>4</sub> that has adsorbed not onto a single site, but onto two sites simultaneously. The other symbols in these mechanisms are defined similarly. In all three of these mechanisms it is assumed that when C<sub>2</sub>H<sub>6</sub> is formed, it enters the gas phase immediately.

The three mechanisms in Table 1 are just a sample of the large number of distinct mechanisms that have been proposed for ethylene hydrogenation. A good discrimination tool needs to be general enough to handle all of the different types of mechanisms that can be proposed, but subtle enough to distinguish between very similar mechanisms. The theory discussed in this article is one such tool. Partial multiple steady-state data have been found for ethylene hydrogenation over rhodium in an isothermal CFSTR [6]. Granted certain assumptions, it turns out that these fragmentary data provide enough information to discriminate greatly between candidate mechanisms using chemical reaction network theory. In a companion article, these data are used to discriminate between a large number of candidate mechanisms for ethylene hydrogenation, including some involving multiple pathways.

The purpose of this article is to describe some of the types of results that can be obtained using chemical reaction network theory. The

Table 1  
Some proposed mechanisms for ethylene hydrogenation

$\begin{aligned} \text{H}_2 + 2\text{S} &\rightleftharpoons 2\text{H} - \text{S} \\ \text{C}_2\text{H}_4 + 2\text{S} &\rightleftharpoons \text{C}_2\text{H}_3 - \text{S} + \text{H} - \text{S} \\ \text{C}_2\text{H}_4 + 2\text{H} - \text{S} &\rightarrow \text{C}_2\text{H}_6 + 2\text{S} \end{aligned}$	Eley–Rideal reaction mechanism proposed by Mullins and Rumschitzki [2,3]	(M1)
$\begin{aligned} \text{H}_2 + 2\text{S} &\rightleftharpoons 2\text{H} - \text{S} \\ \text{C}_2\text{H}_4 + 2\text{S} &\rightleftharpoons \text{C}_2\text{H}_4 - \text{S}_2 \\ \text{C}_2\text{H}_4 - \text{S}_2 + \text{H} - \text{S} &\rightleftharpoons \text{C}_2\text{H}_5 - \text{S} + 2\text{S} \\ \text{C}_2\text{H}_5 - \text{S} + \text{H} - \text{S} &\rightarrow \text{C}_2\text{H}_6 + 2\text{S} \end{aligned}$	Langmuir–Hinshelwood reaction mechanism: variation of the Horiuti–Polanyi [4] reaction mechanism	(M2)
$\begin{aligned} \text{C}_2\text{H}_4 + 2\text{S} &\rightleftharpoons \text{C}_2\text{H}_4 - \text{S}_2 \\ \text{C}_2\text{H}_4 - \text{S}_2 + \text{H}_2 &\rightleftharpoons \text{C}_2\text{H}_5 - \text{S} + \text{H} - \text{S} \\ \text{C}_2\text{H}_5 - \text{S} + 2\text{S} &\rightleftharpoons \text{C}_2\text{H}_4 - \text{S}_2 + \text{H} - \text{S} \\ \text{C}_2\text{H}_5 - \text{S} + \text{H} - \text{S} &\rightarrow \text{C}_2\text{H}_6 + 2\text{S} \end{aligned}$	Twigg–Rideal [5] mechanism	(M3)

theory described in this article is algorithmic in nature and can be applied in a straightforward and precise manner either by hand or by computer. If one wishes to apply reaction network theory by hand, then detailed procedures can be found in Refs. [7–10]. (Proofs for these procedures can be found in Refs. [7,11,12].) However, use of a computer reduces both the chance of error and the computation time. In fact, all of the results in this article were found by use of an easily applied and freely available public stand-alone program called the CHEMICAL REACTION NETWORK TOOLBOX [13]<sup>1</sup>, suitable for use on DOS- or WINDOWS-based personal computers. This toolbox will determine whether a given reaction network has the capacity to support multiple steady states and will test the network against multiple steady-state data. The program can be used without knowledge of any underlying theory. Indeed, our emphasis here is entirely on applications. Readers interested in details of the theory or in its by-hand algorithmic implementation should see the aforementioned references.

For the rest of this article, generic mechanisms will be used to demonstrate the principles and uses of chemical reaction network theory. Although this article focuses on catalytic CFSTRs, the theory can be used for a wide range of reactors from catalytic CFSTRs to homogeneous CFSTRs to batch reactors. Section 2 describes some basic principles of chemical reaction network theory and includes some of the earliest and most powerful results of the theory. Section 3 focuses on how the theory can be used to discriminate between single pathway catalytic mechanisms. Section 4 motivates the necessity of considering multiple-pathway mechanisms and then explains how recent advances in chemical reaction network theory [7] can be used to analyze such mechanisms.

## 2. Chemical reaction network theory background

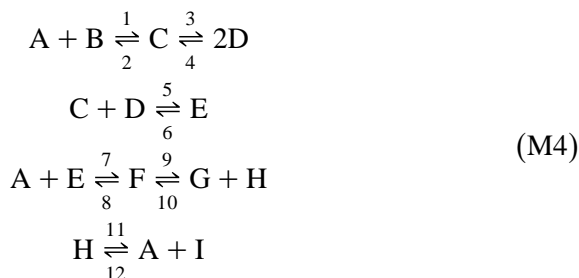
When a catalytic mechanism is poorly understood, rate constants for the postulated elementary reactions are likely to be known only roughly, if they are known at all. Without values for the rate constants the analysis of candidate mechanisms must initially be at least partially qualitative in nature. One goal of chemical reaction network theory is to determine whether a reaction network has even the qualitative capacity to exhibit behavior observed in the laboratory. That is, we ask if there exists any set of positive rate constants for the postulated network such that the corresponding differential equations produce the behavior observed. A positive response indicates that the network has the qualitative capacity to produce the observed behavior; it does not guarantee that a particular set of rate constants will produce such behavior. In this way, observations of multiple steady states in the laboratory can deny the feasibility of mechanisms that cannot support multiple steady states. On the other hand, a failure to observe multiple steady states in the laboratory does not preclude the feasibility of mechanisms that have the capacity to support multiple steady states.

In order to derive the differential equations that correspond to a given reaction mechanism, it is necessary to state what assumptions are in force. First, all mechanisms in this article are assumed to be governed by mass action kinetics. Second, all reactors are assumed to operate at a fixed and spatially uniform temperature. Third, in the reactors under consideration, both the gas phase and the catalyst surface are each presumed to be spatially uniform in composition; in this way we will be able to talk about the gas phase concentration of a species or the surface concentration of a species unambiguously. Finally, the gas phase is presumed to be sufficiently rich in an inert carrier (such as argon) that, to good approximation, its density can be considered independent of composition.

<sup>1</sup>The toolbox is available at <http://www.che.eng.ohio-state.edu/~feinberg/crnt>.

Readers should, of course, be aware that departures these from these assumptions are common even in carefully controlled catalytic experiments. In particular, heterogeneity in the catalytic surface and the formation of islands by adsorbants are serious complications in any attempt to arrive at a fundamental understanding of catalytic behavior. Nevertheless, we find it quite striking that, under more ideal circumstances, even fragmentary multiple steady-state data carry such a wealth of information.

In order to talk about the philosophy of reaction network theory, it is easier to start by considering a single-phase batch reactor. Consider an isothermal, well-mixed, constant volume, batch reactor in which the following (numbered) reactions are occurring:



Formulated in the usual way, the differential equations for this batch reactor are as follows:

$$\begin{aligned}
 \dot{c}_A &= -k_1 c_A c_B + k_2 c_C - k_7 c_A c_E + k_8 c_F \\
 &\quad + k_{11} c_H - k_{12} c_A c_I \\
 \dot{c}_B &= -k_1 c_A c_B + k_2 c_C \\
 \dot{c}_C &= k_1 c_A c_B - k_2 c_C - k_3 c_C + k_4 c_D^2 - k_5 c_C c_D \\
 &\quad + k_6 c_E \\
 \dot{c}_D &= 2k_3 c_C - 2k_4 c_D^2 - k_5 c_C c_D + k_6 c_E \\
 \dot{c}_E &= k_5 c_C c_D - k_6 c_E - k_7 c_A c_E + k_8 c_F \\
 \dot{c}_F &= k_7 c_A c_E - k_8 c_F - k_9 c_F + k_{10} c_G c_H \\
 \dot{c}_G &= k_9 c_F - k_{10} c_G c_H \\
 \dot{c}_H &= k_9 c_F - k_{10} c_G c_H - k_{11} c_H + k_{12} c_A c_I \\
 \dot{c}_I &= k_{11} c_H - k_{12} c_A c_I
 \end{aligned} \quad (1)$$

where  $c_A, \dots, c_I$  are the species concentrations,  $k_1, \dots, k_{12}$  are the rate constants, and the over-dot indicates differentiation with respect to time.

Note that this is a system of nine coupled non-linear differential equations with 12 unknown positive parameters. Normally such a system would be extremely difficult to analyze. However, these differential equations fall within a very special class, those that come from reaction networks. It turns out that the differential equations produced by reaction networks have some very special properties. In fact, chemical reaction network theory was developed precisely to draw relationships between the structure of a reaction network and the properties of its corresponding differential equations.

Chemical reaction network theory has many facets now. The part of the theory that is most relevant to this article is theory that relies on a classification of reaction networks by means of a non-negative integer index called the *deficiency*. That is, there are networks of deficiency zero, of deficiency one, of deficiency two, and so on. The deficiency can be quickly calculated [8], but its calculation will not be essential to an understanding of this article. For now it suffices to say that the deficiency depends solely on the reactions in the network and not on any rate constants. Moreover, the deficiency is not a measure of the size of the reaction network; there are deficiency zero reaction networks with thousands of species and reactions and deficiency one reaction networks with only a few species and reactions.

An early major result of chemical reaction network theory was the Deficiency Zero Theorem [8]. In rough terms, the theorem states that no reaction network with a deficiency of zero can support complex behavior. If a reaction network has a deficiency of zero, then it cannot support multiple steady states, unstable steady states or sustained oscillations, no matter what (positive) values the rate constants take.

The Deficiency Zero Theorem is a prototypical example of a reaction network theory result. Just by calculating the deficiency of a reaction network, it may be possible to determine a lot of qualitative information about reactor behavior without having to look at the governing

differential equations or even knowing values for the rate constants. For example, it turns out that reaction network (M4) has a deficiency of zero. Thus, no matter what positive values the rate constants  $k_1, \dots, k_{12}$  take, the differential Eq. (1) cannot support multiple steady states. In addition, any steady state of the differential equations will be asymptotically stable. By using the Deficiency Zero Theorem, all of this information can be obtained quickly without having to analyze the differential equations. Our batch reactor example was a relatively simple one, but it should be noted that the Deficiency Zero Theorem applies to the differential equations of far more complex reactors as well.

### 3. Catalytic mechanism discrimination: a hypothetical example

Let us now consider a hypothetical isothermal catalytic CFSTR whose overall reaction is  $A + B \rightarrow C$ .

The feed stream of this reactor contains A and B, and the effluent stream contains A, B and C. The feed stream also contains enough inert carrier such that the volumetric flow rate of the feed and effluent streams can be considered equal. With some appropriate choice of units, we suppose that the residence time for the reactor is 1.0 and that the concentrations of A and B in the feed stream are  $c_A^f = 0.8$  and  $c_B^f = 1.0$ , respectively.

Suppose that, under identical operating conditions, two steady states have been observed for

Table 2  
Steady-state data

	$c_A$	$c_B$	$c_C$
<i>Gas Phase Data</i>			
Steady State #1	0.4	0.6	0.4
Steady State #2	0.1	0.3	0.7
<i>Surface Data</i>			
More A adsorbed on the surface in Steady State #2 than in Steady State #1			

Table 3

Candidate mechanisms

$A + S \rightleftharpoons AS$ $B + S \rightleftharpoons BS$ $AS + BS \rightarrow C + 2S$	Langmuir–Hinshelwood mechanism (M5)
$A + S \rightleftharpoons AS$ $B + S \rightleftharpoons BS$ $A + BS \rightarrow C + S$	Eley–Rideal mechanism (M6)
$A + 2S \rightleftharpoons AS_2$ $B + S \rightleftharpoons BS$ $AS_2 + BS \rightarrow C + 3S$	Langmuir–Hinshelwood mechanism (M7)

the reactor and that, by analyzing the effluent stream, the concentrations of the gas phase species have been measured for the two steady states. In addition, suppose that it has been determined that there is more A on the catalytic surface in the second steady state than in the first. (By using an electrochemical technique, for example, Yue was able to determine the relative concentrations of hydrogen on a rhodium surface during ethylene hydrogenation [6]). These hypothetical multiple steady-state data are given in Table 2.

For this example, let us consider the catalytic mechanisms proposed in Table 3. The CFSTR differential equations that govern mechanism (M5), taken with mass action kinetics, are:

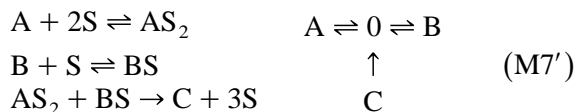
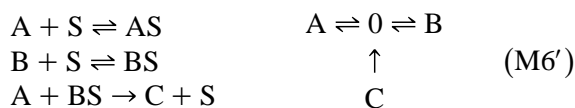
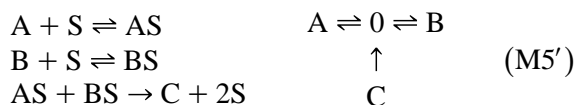
$$\begin{aligned} \dot{c}_A &= (1/\tau) \cdot (c_A^f - c_A) - k_1 c_A c_S + k_2 c_{AS} \\ \dot{c}_B &= (1/\tau) \cdot (c_B^f - c_B) - k_3 c_B c_S + k_4 c_{BS} \\ \dot{c}_C &= -(1/\tau) \cdot c_C + k_5 c_{AS} c_{BS} \\ \dot{c}_S &= -k_1 c_A c_S + k_2 c_{AS} - k_3 c_B c_S + k_4 c_{BS} \\ &\quad + 2k_5 c_{AS} c_{BS} \\ \dot{c}_{AS} &= k_1 c_A c_S - k_2 c_{AS} - k_5 c_{AS} c_{BS} \\ \dot{c}_{BS} &= k_3 c_B c_S - k_4 c_{BS} - k_5 c_{AS} c_{BS} \end{aligned} \quad (2)$$

where  $k_1, \dots, k_5$  are the rate constants for the reactions in (M5) and  $\tau$  is the residence time for the reactor. The ultimate question we are asking

is: given our feed and residence time, does there exist a set of rate constants such that the differential Eq. (2) support a pair of steady states consistent with the data in Table 2.

The reactions in the mechanisms of Table 3 reflect only the (proposed) reactions occurring *within* the CFSTR. In chemical reaction network theory, it is necessary when modeling CFSTRs to add additional *pseudo-reactions* to the proposed mechanisms in order to account for changes in concentration due to the feed and effluent streams [8]. In order to account for A and B in the feed, the pseudo-reactions  $0 \rightarrow A$  (“zero reacts to A”) and  $0 \rightarrow B$  are added to each mechanism. In order to account for A, B and C in the effluent, the pseudo-reactions  $A \rightarrow 0$ ,  $B \rightarrow 0$  and  $C \rightarrow 0$  are added to each mechanism. {Considered as a first order reaction with rate constant  $1/\tau$ , the reaction  $A \rightarrow 0$  can be viewed as giving rise to the term  $-c_A/\tau$  in Eq. (2). Similarly, the reaction  $0 \rightarrow A$ , considered as a zeroth order reaction with rate constant  $c_A^f/\tau$ , gives rise to the term  $c_A^f/\tau$  in Eq. (2).}<sup>2</sup>

From the viewpoint of reaction network theory, then, one considers for mechanisms (M5), (M6) and (M7) the augmented reaction networks shown below:



For each augmented reaction network we can calculate a deficiency. (Again, the procedure for

calculating the deficiency is not given in this article, but can be found in Ref. [8]. In fact, the CHEMICAL REACTION NETWORK TOOLBOX will do the calculation and report the result.) All three networks have a deficiency of one. Thus, the Deficiency Zero Theorem does not apply. For these networks it is necessary to use another part of reaction network theory: deficiency one theory [9,11,12].

In order to motivate the kind of results deficiency one theory gives, it is useful to look first at an (imperfect) analogy using batch reactors. Consider an isothermal homogeneous (well-stirred) constant volume batch reactor containing A, B, C and D in which the following reactions are occurring:



Suppose that, when the reactor is allowed to come to equilibrium, the molar concentrations of A, B, C and D are  $c_A^*$ ,  $c_B^*$ ,  $c_C^*$  and  $c_D^*$ , respectively. The reactor is then opened, more A is added, and a second equilibrium is reached (at the same temperature). The molar concentrations for this new equilibrium are  $c_A^{**}$ ,  $c_B^{**}$ ,  $c_C^{**}$  and  $c_D^{**}$ . The question is: given the reactions of (M8), what pairs of steady states are possible for this reactor? This question can be answered by looking at the governing differential equations:

$$\begin{aligned} \dot{c}_A &= -\alpha c_A c_B + \beta c_C \\ \dot{c}_B &= -\alpha c_A c_B + \beta c_C \\ \dot{c}_C &= \alpha c_A c_B - (\beta + \gamma) c_C + \delta c_D^2 \\ \dot{c}_D &= 2\gamma c_C - 2\delta c_D^2 \end{aligned} \quad (3)$$

By setting the time derivatives to zero, it can be seen that any equilibrium composition must satisfy the following conditions:

$$(\alpha/\beta)c_A c_B = c_C = (\delta/\gamma)c_D^2. \quad (4)$$

Now, let the numbers  $\mu_A$ ,  $\mu_B$ ,  $\mu_C$  and  $\mu_D$  be defined from the two equilibrium compositions by the following equation:

$$\mu_\theta = \ln(c_\theta^{**}/c_\theta^*), \quad \theta = A, B, C, D. \quad (5)$$

<sup>2</sup> Certain technical considerations associated with CFSTRs are discussed in [3,6,7].

From Eq. (4), it follows that these  $\mu$ 's, defined by Eq. (5), must satisfy the conditions:

$$\mu_A + \mu_B = \mu_C = 2\mu_D. \quad (6)$$

Thus, any pair of equilibrium compositions for reaction network (M8) must satisfy the conditions of Eq. (6). These conditions are independent of any of the rate constants for the reactions in the network. If two compositions do not satisfy the conditions of Eq. (6), then those two compositions are not simultaneously consistent with reaction network (M8), taken with mass action kinetics, no matter what the values of the rate constants are. These conditions form a type of “signature” for the reaction network. Thus, there is a direct connection between the reaction network and the possible equilibrium pairs, and *this connection is independent of the rate constant values.*

The form of Eq. (6) is suggestive of equations that govern thermodynamic equilibria. It should, however, be noted that Eq. (6) was derived using only the kinetics of the system. It is the differential equations governing a reactor, and not the thermodynamics, that are the foci of this analysis, for ultimately we shall be interested in open reactors operating under conditions different from those prevailing in this batch reactor example. In particular, we shall be interested in catalytic CFSTRs governed by differential equations such as those in Eq. (2).

Before returning to our catalytic example, it will be useful to note the form of the “signature” (6) as it relates to the reaction network (M8). In reaction network theory, *complexes* are the objects that appear at the heads and tails of reactions [8]. The complexes for reaction network (M8) are A + B, C and 2D. Just as we have associated the species A, B, C and D with the variables  $\mu_A$ ,  $\mu_B$ ,  $\mu_C$  and  $\mu_D$ , we can associate the complexes with linear combinations of the  $\mu$ 's in the obvious way; that is, the complexes A + B, C and 2D are associated with  $\mu_A + \mu_B$ ,  $\mu_C$  and  $2\mu_D$ , respectively. Note that the “signature” (6) can be formed by joining these linear forms by equality signs. In a similar

manner, deficiency one theory indicates how deficiency one reaction networks give rise to their own “signatures”. However these signatures usually connect forms such as  $\mu_A + \mu_B$ ,  $\mu_C$ , and  $2\mu_D$ , not with equality signs but, rather, with *inequality* signs.

At this point, let us return to the catalytic example. Initially, we will focus on reaction network (M5'). Reaction network (M5') has six species:

$$\{A, B, C, S, AS, BS\}$$

and ten complexes:

$$\{A + S, AS, B + S, BS, AS + BS, C + 2S, A, B, C, 0\}.$$

The complex “0”, called the *zero complex*, is a complex that is devoid of any species.

By analogy to the batch reactor example, suppose that our catalytic CFSTR admits two steady states:

$$\{c_A^*, c_B^*, c_C^*, c_S^*, c_{AS}^*, c_{BS}^*\}$$

and

$$\{c_A^{**}, c_B^{**}, c_C^{**}, c_S^{**}, c_{AS}^{**}, c_{BS}^{**}\}. \quad (7)$$

We define  $\mu_A$ ,  $\mu_B$ , ...,  $\mu_{BS}$  by the equation:

$$\mu_\theta = \ln(c_\theta^{**}/c_\theta^*), \quad \theta = A, B, \dots, BS. \quad (8)$$

Similarly, we associate with the ten complexes the following linear combinations of the  $\mu$ 's:

$$\{\mu_A + \mu_S, \mu_{AS}, \mu_B + \mu_S, \mu_{BS}, \mu_{AS} + \mu_{BS}, \mu_C + 2\mu_S, \mu_A, \mu_B, \mu_C, 0\}. \quad (9)$$

Note that the linear combination associated with the zero complex is “0”.

Unlike our batch reactor example, deficiency one theory produces two signatures for network (M5') by connecting the linear forms in Eq. (9) by inequality and equality signs. The two distinct<sup>3</sup> signatures produced for reaction network

<sup>3</sup> For every signature of a reaction network there is an equivalent signature that is formed by reversing all of the inequality signs. These new signatures correspond to reversing the roles of the two steady states in Eq. (8). These equivalent signatures are rarely written explicitly, but they must still be considered when testing a signature against multiple steady-state data.

Table 4  
Deficiency one theory signatures

Network		Signature(s)
A + S $\rightleftharpoons$ AS B + S $\rightleftharpoons$ BS AS + BS $\rightarrow$ C + 2S	A $\rightleftharpoons$ 0 $\rightleftharpoons$ B ↑ (M5') C	$\{\mu_A, \mu_B\} < 0 < \mu_C = \mu_{AS} + \mu_{BS}$ $\mu_{AS} > \mu_A + \mu_S > \mu_{AS} + \mu_{BS} > \mu_B + \mu_S > \mu_{BS}$ or $\{\mu_A, \mu_B\} < 0 < \mu_C = \mu_{AS} + \mu_{BS}$ $\mu_{AS} < \mu_A + \mu_S < \mu_{AS} + \mu_{BS} < \mu_B + \mu_S < \mu_{BS}$
A + S $\rightleftharpoons$ AS B + S $\rightleftharpoons$ BS A + BS $\rightarrow$ C + S	A $\rightleftharpoons$ 0 $\rightleftharpoons$ B ↑ (M6') C	$\{\mu_A, \mu_B\} < 0 < \mu_C = \mu_A + \mu_{BS}$ $\mu_A + \mu_{BS} < \mu_B + \mu_S < \mu_{BS}$ $\mu_{AS} = \mu_A + \mu_S$
A + 2S $\rightleftharpoons$ AS <sub>2</sub> B + S $\rightleftharpoons$ BS AS <sub>2</sub> + BS $\rightarrow$ C + 3S	A $\rightleftharpoons$ 0 $\rightleftharpoons$ B ↑ (M7') C	$\{\mu_A, \mu_B\} < 0 < \mu_C = \mu_{AS_2} + \mu_{BS}$ $\mu_{AS_2} > \mu_A + 2\mu_S > \mu_{AS_2} + \mu_{BS} > \mu_B + \mu_S > \mu_{BS}$ or $\{\mu_A, \mu_B\} < 0 < \mu_C = \mu_{AS_2} + \mu_{BS}$ $\mu_{AS_2} < \mu_A + 2\mu_S < \mu_{AS_2} + \mu_{BS} < \mu_B + \mu_S < \mu_{BS}$

(M5'), as found by the CHEMICAL REACTION NETWORK TOOLBOX, are:

$$\{\mu_A, \mu_B\} < 0 < \mu_C = \mu_{AS} + \mu_{BS}$$

$$\mu_{AS} > \mu_A + \mu_S > \mu_{AS} + \mu_{BS} > \mu_B + \mu_S > \mu_{BS} \quad (10)$$

and

$$\{\mu_A, \mu_B\} < 0 < \mu_C = \mu_{AS} + \mu_{BS}$$

$$\mu_{AS} < \mu_A + \mu_S < \mu_{AS} + \mu_{BS} < \mu_B + \mu_S < \mu_{BS} \quad (11)$$

In these signatures, the notation  $\{\mu_A, \mu_B\} < 0$  indicates that both  $\mu_A$  and  $\mu_B$  are less than zero. The procedure for finding these signatures can be found in Ref. [9].

Deficiency one theory makes the following statement about reaction network (M5') and its signatures: *in order for there to exist parameter values* (e.g., positive rate constants, a positive residence time, and a fixed feed composition)

*such that the CFSTR differential Eqs. (2) admit the steady states (7), it is necessary and sufficient that the set of  $\mu$ 's defined by Eq. (8) satisfy at least one of the two signatures, (10) or (11), for the network.* For another reaction network, deficiency one theory may produce different signatures, but their relationship to the possible pairs of steady states that the network can support remains the same. If there is no set of rate constants for a reaction network such that the corresponding differential equations admit multiple steady states, then, the theory will indicate this fact (and will produce no signatures).

By finding signatures, deficiency one theory indicates that reaction network (M5') has the capacity to support multiple steady states. Now let us ask whether the network can account for the hypothetical data in Table 2. First, using the gas phase data, we can calculate the values of  $\mu_A$ ,  $\mu_B$  and  $\mu_C$  as follows:

$$\mu_A = \ln(0.1/0.4) \approx -1.386$$

$$\mu_B = \ln(0.3/0.6) \approx -0.693$$

$$\mu_C = \ln(0.7/0.4) \approx 0.560. \quad (12)$$



In addition, from the surface data it is possible to infer that:

$$\mu_{AS} = \ln(c_{AS}^{**}/c_{AS}^*) > 0. \quad (13)$$

Finally, although we have no direct information on  $\mu_S$  or  $\mu_{BS}$ , the site conservation equation  $c_{AS}^* + c_{BS}^* + c_S^* = c_{AS}^{**} + c_{BS}^{**} + c_S^{**}$  allows us to say that  $\mu_S$ ,  $\mu_{AS}$ , and  $\mu_{BS}$  cannot all have the same sign<sup>4</sup>. Thus, site conservation, taken with Eq. (13), leads to the restriction:

$$\text{either } \mu_S \text{ or } \mu_{BS} \text{ is negative.} \quad (14)$$

It turns out that neither of the signatures of reaction network (M5') has a solution that is consistent with the conditions (12–14). Thus, while there exist rate constants such that reaction network (M5') supports multiple steady states, no rate constants exist such that the network supports multiple steady states *consistent with the data in Table 2*.

Deficiency one theory can be used to find signatures for reaction network (M6') and (M7') as well. The theory produces one signature for reaction network (M6') and two signatures for reaction network (M7'). The signatures for all three reaction networks are summarized in Table 4.

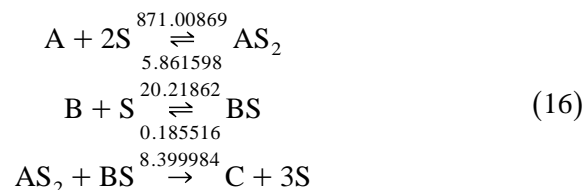
The signature for network (M6') has no solution compatible with the data restrictions (12–14). Thus, reaction network (M6') is inconsistent with the data provided. No matter what rate constants are chosen for the reactions in networks (M5') or (M6'), neither network could produce multiple steady states consistent with the data given in Table 2.

Although the data restrictions (12–14) are not compatible with the second signature of reaction network (M7'), they are compatible with the first signature. A set of  $\mu$ 's can be found that is consistent with both the first signa-

ture and the data restrictions. The following  $\mu$ 's are an example of one such solution:

$$\begin{aligned} \mu_A &= -1.386 & \mu_S &= 1.066 \\ \mu_B &= -0.693 & \mu_{AS_2} &= 0.933 \\ \mu_C &= 0.560 & \mu_{BS} &= -0.373 \end{aligned} \quad (15)$$

Deficiency one theory therefore indicates that it is possible to find rate constants for reaction network (M7') such that the network's corresponding differential equations support multiple steady states consistent with the data in Table 2 (and site conservation). The theory also provides a way to find such rate constants and their corresponding steady states. One set of rate constants, generated using the CHEMICAL REACTION NETWORK TOOLBOX, is given below:



These rate constants give rise to the following steady states:

Steady State #1	Steady State #2	
$c_A = 0.4$	$c_A = 0.1$	
$c_B = 0.6$	$c_B = 0.3$	
$c_C = 0.4$	$c_C = 0.7$	. (17)
$c_S = 0.045833$	$c_S = 0.133116$	
$c_{AS_2} = 0.056628$	$c_{AS_2} = 0.143911$	
$c_{BS} = 0.840911$	$c_{BS} = 0.579062$	

Note that these steady states are consistent with the data in Table 2 and satisfy site conservation. (Both steady states satisfy  $c_S + 2c_{AS_2} + c_{BS} = 1$ .) There is no reason to believe that the rate constants generated bear any relation to actual rate constants. Rather, they serve to indicate by construction that the mechanism is, in principle, compatible with the hypothetical data.

Thus, by using deficiency one theory and the multiple steady-state data in Table 2, it is possible to discriminate among mechanisms (M5),

<sup>4</sup> Similar sign restrictions on the  $\mu$ 's apply for many different types of reactors. Deficiency one theory includes a procedure for finding these restrictions [9].

(M6) and (M7). While mechanism (M7) has the qualitative capacity to explain the data, the viability of mechanisms (M5) and (M6) can be denied. Although the data in Table 1 are fragmentary, they are restrictive enough to eliminate two of the three proposed mechanisms in this example<sup>5</sup>.

#### 4. Multiple pathway mechanisms: a new mechanism discrimination example

Suppose now that the hypothetical CFSTR from Section 3 is run with a new catalyst and a different feed. Again, the feed stream contains A, B, and enough inert carrier so that the volumetric flow rates of the feed and effluent streams can be considered equal; the effluent stream contains A, B, C, and inert. The residence time for the reactor is again 1.0, but the concentrations of A and B in the feed stream are now  $c_A^f = 2.0$  and  $c_B^f = 1.9$ , respectively.

Suppose that we have again measured the gas phase concentrations by examining the effluent stream. In addition, suppose that once more we have determined for which steady state there is more A on the catalytic surface. The new hypothetical data are given in Table 5.

We can now test reaction networks (M5'), (M6') and (M7') against these new data. The new restrictions on the  $\mu$ 's are as follows:

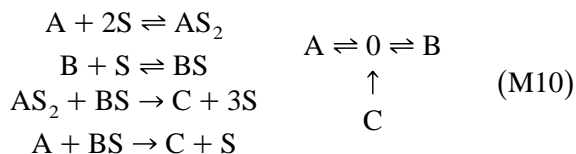
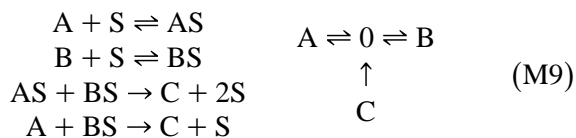
$$\begin{aligned}\mu_A &= \ln(0.4/1.0) \approx -0.916 \\ \mu_B &= \ln(0.3/0.9) \approx -1.099 \\ \mu_C &= \ln(1.6/1.0) \approx 0.470 \\ \mu_{AS} &= \ln(c_{AS}^{**}/c_{AS}^*) < 0 \\ \text{either } \mu_S &\text{ or } \mu_{BS} \text{ is positive}\end{aligned}\quad (18)$$

It turns out that the data restrictions (18) are not compatible with any of the signatures in Table 4. Thus, none of the proposed reaction networks can account for the multiple steady-

Table 5  
New steady-state data

	$c_A$	$c_B$	$c_C$
<i>Gas Phase Data</i>			
Steady State #1	1.0	0.9	1.0
Steady State #2	0.4	0.3	1.6
<i>Surface Data</i>			
More A adsorbed on surface in Steady State #1 than in Steady State #2			

state data in Table 5. At this point we might consider some new catalytic mechanisms. One method for creating new mechanisms is to modify existing mechanisms; an example of such an analysis can be found in Ref. [3]. Another method for creating new mechanisms is to combine single pathway mechanisms to form multiple-pathway mechanisms. For example, reaction networks (M5'), (M6') and (M7') could be combined to give the following new reaction networks:



Reaction network (M9) is a combination of reaction networks (M5') and (M6'). Reaction network (M10) is a combination of reactions (M6') and (M7'). Both reaction networks are dual pathway networks and have a deficiency of two<sup>6</sup>. Deficiency one theory cannot be used for either network. Until recently, such reaction networks fell outside of the scope of reaction network theory and could not be analyzed properly.

<sup>5</sup> It is interesting to note that, even without the surface data restrictions, the gas phase data (taken with site conservation) are restrictive enough to deny the feasibility of mechanism (M6).

<sup>6</sup> There is a weak correspondence between the deficiency of a catalytic CFSTR reaction network and the number of catalytic pathways in the original mechanism. The deficiency of a catalytic network usually equals the number of pathways.

The advanced deficiency theory [7], a recent addition to reaction network theory, has the capability to analyze any network that falls outside the scope of deficiency one theory. Similar to deficiency one theory, the advanced deficiency theory also produces for a network signatures containing the  $\mu$ 's. These  $\mu$ 's are again related by Eq. (8) to the pairs of steady states that a reaction network can support. If multiple steady-state data are available, the signatures can again be used to determine if a network has the capacity to support multiple steady states consistent with the data. As with deficiency one theory, the advanced deficiency theory will determine if a network does not have the qualita-

tive capacity to support multiple steady states, in which case no signatures are produced.

The most significant difference between the signatures produced by deficiency one theory and the signatures produced by advanced deficiency theory is that advanced deficiency signatures will sometimes include a few non-linear equalities. *For most catalytic CFSTRs, however, the signatures will be completely linear.* (There are straightforward tests on a reaction network that can be used to determine whether such non-linearities occur.) In addition, even when a reaction network's signatures are non-linear, the linear part of the signature is often restrictive enough to produce definitive an-

Table 6  
Advanced deficiency theory signatures

Network		Signature(s)
A + S $\rightleftharpoons$ AS	A $\rightleftharpoons$ 0 $\rightleftharpoons$ B	{ $\mu_A, \mu_B$ } < 0 < $\mu_C$
B + S $\rightleftharpoons$ BS	↑ (M9)	$\mu_{BS} < \mu_B + \mu_S < \mu_C$
AS + BS $\rightarrow$ C + 2S	C	$\mu_{BS} + \mu_A < \mu_C < \mu_{AS} + \mu_{BS} < \mu_A + \mu_S < \mu_{AS}$
A + BS $\rightarrow$ C + S		or
		{ $\mu_A, \mu_B$ } < 0 < $\mu_C < \mu_B + \mu_S < \mu_{BS}$
		$\mu_{AS} < \mu_A + \mu_S < \mu_{AS} + \mu_{BS}$
		$\mu_{AS} + \mu_{BS} < \mu_C < \mu_A + \mu_{BS}$
		or
		{ $\mu_A, \mu_B$ } < 0 < $\mu_C < \mu_B + \mu_S < \mu_{BS}$
		$\mu_{AS} < \mu_A + \mu_S < \mu_{AS} + \mu_{BS}$
		$\mu_A + \mu_{BS} < \mu_C < \mu_{AS} + \mu_{BS}$
		or
		{ $\mu_A, \mu_B$ } < 0 < $\mu_C < \mu_B + \mu_S < \mu_{BS}$
		$\mu_{AS} < \mu_A + \mu_S < \mu_{AS} + \mu_{BS}$
		$\mu_{AS} + \mu_{BS} = \mu_C = \mu_A + \mu_{BS}$
A + 2S $\rightleftharpoons$ AS <sub>2</sub>	A $\rightleftharpoons$ 0 $\rightleftharpoons$ B	{ $\mu_A, \mu_B$ } < 0 < $\mu_C$
B + S $\rightleftharpoons$ BS	↑ (M10)	$\mu_{BS} < \mu_B + \mu_S < \mu_C$
AS <sub>2</sub> + BS $\rightarrow$ C + 3S	C	$\mu_{BS} + \mu_A < \mu_C < \mu_{AS_2} + \mu_{BS} < \mu_A + 2\mu_S < \mu_{AS_2}$
A + BS $\rightarrow$ C + S		or
		{ $\mu_A, \mu_B$ } < 0 < $\mu_C < \mu_B + \mu_S < \mu_{BS}$
		$\mu_{AS_2} < \mu_A + 2\mu_S < \mu_{AS_2} + \mu_{BS}$
		$\mu_{AS_2} + \mu_{BS} < \mu_C < \mu_A + \mu_{BS}$
		or
		{ $\mu_A, \mu_B$ } < 0 < $\mu_C < \mu_B + \mu_S < \mu_{BS}$
		$\mu_{AS_2} < \mu_A + 2\mu_S < \mu_{AS_2} + \mu_{BS}$
		$\mu_A + \mu_{BS} < \mu_C < \mu_{AS_2} + \mu_{BS}$
		or
		{ $\mu_A, \mu_B$ } < 0 < $\mu_C < \mu_B + \mu_S < \mu_{BS}$
		$\mu_{AS_2} < \mu_A + 2\mu_S < \mu_{AS_2} + \mu_{BS}$
		$\mu_{AS_2} + \mu_{BS} = \mu_C = \mu_A + \mu_{BS}$

swers. (Examples of such networks can be found in a companion article [14], where ethylene hydrogenation on rhodium is used as a case study.)

Again, reaction networks (M9) and (M10) both have a deficiency of two. Advanced deficiency theory can be used to find signatures for each network. In this case, the signatures produced by the theory are strictly linear; they are summarized in Table 6. As with deficiency one theory, these signatures were also found using the CHEMICAL REACTION NETWORK TOOLBOX. The algorithm for finding these signatures by hand can be found in Ref. [7].

Again, the fact that the advanced deficiency theory has found signatures for the networks indicates that both networks have the qualitative capacity to support multiple steady states. At this point we need to test the signatures against the data restrictions (18) imposed on the  $\mu$ 's. The third signature of reaction network (M9) is compatible with these data restrictions. Thus, positive rate constants exist such that reaction network (M9) supports multiple steady states consistent with the data in Table 5. However, none of the signatures of reaction network (M10) is compatible with the data restrictions. Thus, no set of (positive) rate constants exists such that the differential equations corresponding to reaction network (M10) admit multiple steady states consistent with the data.

Note that reaction network (M9) is consistent with the data in Table 5 even though it is a combination of two reaction networks that are not consistent with the data. Thus, it is possible to combine two “non-viable” single-pathway mechanisms to produce a viable multiple-pathway mechanism. However, as seen by reaction network (M10), not all such multiple-pathway mechanisms will be viable. In this way, advanced deficiency theory acts as a discrimination tool similar to deficiency one theory. It is interesting to note that it is the simpler of the two mechanisms (the one containing only bimolecular reactions) that has the capacity to explain the data in this example.

## 5. Conclusion

Multiple steady states can be observed in many isothermal catalytic CFSTRs. If multiple steady-state data are obtained, then, at least when certain physical conditions prevail, such data provide information about the underlying catalytic mechanism. It turns out that, through use of reaction network theory, even fragmentary data provide a means to discriminate between candidate mechanisms in a very refined way. With the recent addition of the advanced deficiency theory one can now use reaction network theory to analyze a greater range of mechanisms, including multiple-pathway mechanisms. The theory in this article can be applied either by hand [7–9] or by computer [13]. In a companion article, this theory is used to discriminate between candidate mechanisms for ethylene hydrogenation over a rhodium surface using multiple steady-state data obtained in the laboratory.

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