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multiple steady states in ammonia synthesis

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Highlights for the submitted paper "Absence of evidence is not evidence of absence: multiple steady states in the ammonia synthesis", by J. Martín Méndez González and Manuel Díaz de León Cabrero.
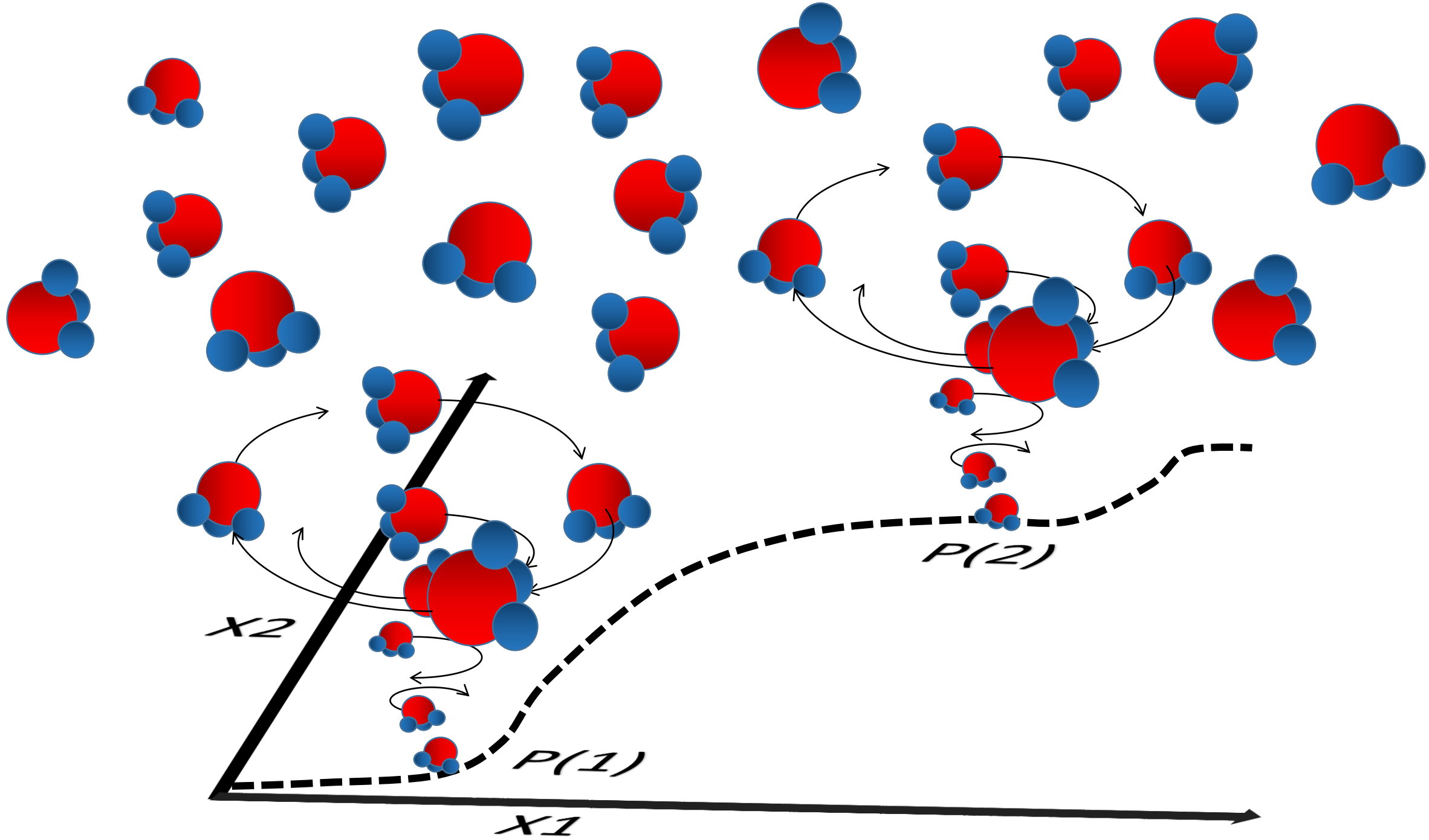
- Bistability in two experimentally accepted ammonia synthesis mechanisms.
- Two surface catalytic sites responsible for bistability in ammonia synthesis.
- Deficiency analysis reveals unexplored dynamical scenarios in ammonia synthesis.

Absence of evidence is not evidence of absence:

multiple steady states in ammonia synthesis

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1

5   **Abstract**

6   Using a Chemical Reaction Network (CRN) Theory approach, three

7   well-accepted mechanisms of ammonia synthesis over iron catalyst taking

8   place within an isothermal Continuous Flow Stirred Tank Reactor (CF-

9   STR) are analysed. Together with its deficiency analysis, the CRN Theory

10   provides a suitable framework to assert whether a particular reaction net-

11   work has the capacity to support multiple steady states using the reaction

12   mechanism structure alone. Through deficiency analysis, we argued that

13   the presence of two surface catalytic sites during absorption-desorption of

14   nitrogen (microscale) is causative of bistability (macroscale) in two of the

15   three ammonia synthesis mechanisms here considered.

16

17   **Keywords:** Ammonia synthesis, Chemical Reaction Network Theory,

18   Bistability, Deficiency analysis, Mathematical modelling, Reactor engi-

19   neering.

2

1   Introduction

It is known in chemical kinetics that more than one proposed reaction mechanism can stand for the same dynamics [1, 2]. That is, two or more proposed chemical kinetic mechanisms explain the experimental observations, therefore we can only disprove mechanisms. Moreover, the experimentally validated reaction mechanisms do not necessarily share the same number of chemical species or reactions. This is particularly well illustrated in heterogeneous catalytic reactions, where several mechanisms are proposed to explain the adsorption phenomena (*e.g.* number of active sites, half-life adsorbed chemical species) taking place at the catalytic surface [3]. Additionally, heterogeneous catalytic Continuous Flow Stirred Tanks Reactors (CFSTRs) have been proven to exhibit complex dynamics such as oscillations, chaotic behaviour and multiple steady states under isothermal conditions [4]. Often, even simple catalytic reactions following Langmuir-Hinshelwood kinetics, operating in an isothermal CFSTR, exhibit multiplicity of steady states [5, 6, 7]. In this sense, the capacity for a given candidate reaction mechanism to support two or more observed experimental steady states in the laboratory can be used to deny the feasibility of some mechanisms [5]. On the other hand, absence of experimental evidence of multiple steady states for a candidate reaction mechanism is not evidence of the incapacity of the candidate (or validated) mechanism to support multiple steady states [6]. An example of this last situation is ammonia synthesis.

The ammonia synthesis reaction is frequently used as a traditional example in chemical kinetics textbooks due to its industrial importance and simplic-

3

ity [8, 9, 10, 11]. Detailed surface catalytic studies of ammonia synthesis over iron catalyst have been reported without the existence of multiple steady states under isothermal conditions [12, 13, 14]. Nevertheless, it is possible to determine, for the ammonia synthesis, whether the propounded chemical reaction mechanisms are capable of exhibiting multiple steady states using the structure of the mechanism alone: this approach utilizes Chemical Reaction Network (CRN) Theory.

CRN Theory and its deficiency oriented analyses are able to draw rapid conclusions concerning the existence or not of multiple positive steady states among candidate reaction mechanisms [5, 6, 7, 15]. If multiple steady states exist, then the CRN Theory provides an algorithm to derive kinetic constants[1], feed, and effluent rates such that the corresponding isothermal CFSTR Ordinary Differential Equations (ODEs) support multiple positive steady states. We stress the fact that the existence of multiple positive steady states comes from the structure of the proposed reaction network alone [15], and not from the interplay of thermal effects and reaction kinetics as analysed for the ammonia synthesis in [16].

In this contribution we present theoretical evidence, using a CRN Theory approach, for the possible existence of multiple steady states for the ammonia synthesis reaction in an isothermal CFSTR [2]. We also argue that the existence

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[1]Such kinetic constants does not necessarily bear any relation to experimental rate constants. See [6] for details.

[2]The CRN Theory can be used also for batch operation conditions, see [15] for further details.

4

⁶³ of two surface catalytic sites (microscale) are responsible for multiple steady

⁶⁴ states (macroscale) under an isothermal CFSTR operation, in two of three ex-

⁶⁵ perimentally accepted ammonia synthesis mechanisms. Further, through the

⁶⁶ CRN Theory approach, we intend to revive interest in classical catalytic mecha-

⁶⁷ nisms such as ammonia synthesis, to spur experimental studies of the potential

⁶⁸ dynamical scenarios that lie in wait within the structure of reaction mechanisms

⁶⁹ which are so crucial to the industrial and engineering chemistry community.

⁷⁰ The present contribution is organised as follows: In section 2 three experi-

⁷¹ mentally accepted ammonia synthesis mechanisms are presented for isothermal

⁷² CFSTR operation. Section 3 presents the CRN Theory formalism and its de-

⁷³ ficiency analysis terminology. Results obtained from the deficiency analysis

⁷⁴ applied to ammonia synthesis mechanisms (1), (2), and (3) are presented in sec-

⁷⁵ tion 4. The impact of the number of adjacent surface catalytic sites considered

⁷⁶ in the ammonia synthesis mechanisms on their CFSTR dynamics are discussed

⁷⁷ in section 5. Some conclusions are drawn in section 6.

⁷⁸ 2 Ammonia synthesis reaction mechanisms

⁷⁹ Along this work, we consider three experimentally validated chemical reaction

⁸⁰ mechanisms for the ammonia synthesis reaction over iron catalyst, that follows

⁸¹ the overall reaction:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \tag{1}$$

5

82 Firstly, the mechanism reported by Stoltze [12] is composed by the set of re-

83 actions displayed as mechanism (1) in Figure 1. The symbol S represents an

84 active catalytic site and $N_2 - S$, $N - S$, $H - S$, $NH - S$, $NH_2 - S$, $NH_3 - S$

85 are the adsorbed chemical species on the catalyst's surface. The reaction mech-

86 anism suggests that the adsorption of a nitrogen diatomic molecule takes place

87 in a single site, while a nearby vacant catalytic site is needed for each nitrogen

88 atom to be adsorbed in a single site. Meanwhile, a hydrogen diatomic molecule

89 is adsorbed, each hydrogen atom in a single site, implying that the two hydro-

90 gen atoms can transform in hydrogen adsorbed species only by interacting with

91 two neighbouring sites. The ammonia molecule formation takes place from the

92 interaction of the adsorbed species. This mechanism requires clusters of three

93 neighbouring catalytic sites at least to occur (the mechanistics and occurrence

94 of surface adsorbed species are beyond the scope of this analysis).

6

Mechanism (1)

$$N_2 + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2 - S$$

$$N_2 - S + S \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 2N - S$$

$$H_2 + 2S \underset{k_6}{\overset{k_5}{\rightleftharpoons}} 2H - S$$

$$N - S + H - S \underset{k_8}{\overset{k_7}{\rightleftharpoons}} NH - S + S$$

$$NH - S + H - S \underset{k_{10}}{\overset{k_9}{\rightleftharpoons}} NH_2 - S + S$$

$$NH_2 - S + H - S \underset{k_{12}}{\overset{k_{11}}{\rightleftharpoons}} NH_3 - S + S$$

$$NH_3 - S \underset{k_{14}}{\overset{k_{13}}{\rightleftharpoons}} NH_3 + S$$

$$N_2 \underset{k_{15}}{\overset{k_{16}}{\rightleftharpoons}} \emptyset \underset{k_{18}}{\overset{k_{17}}{\rightleftharpoons}} H_2$$

$$k_{19} \uparrow$$

$$NH_3$$

Mechanism (2)

$$N_2 + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2 - S$$

$$N_2 - S \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 2N - S$$

$$H_2 + 2S \underset{k_6}{\overset{k_5}{\rightleftharpoons}} 2H - S$$

$$N - S + H - S \underset{k_8}{\overset{k_7}{\rightleftharpoons}} NH - S + S$$

$$NH - S + H - S \underset{k_{10}}{\overset{k_9}{\rightleftharpoons}} NH_2 - S + S$$

$$NH_2 - S + H - S \underset{k_{12}}{\overset{k_{11}}{\rightleftharpoons}} NH_3 - S + S$$

$$NH_3 - S \underset{k_{14}}{\overset{k_{13}}{\rightleftharpoons}} NH_3 + S$$

$$N_2 \underset{k_{15}}{\overset{k_{16}}{\rightleftharpoons}} \emptyset \underset{k_{18}}{\overset{k_{17}}{\rightleftharpoons}} H_2$$

$$k_{19} \uparrow$$

$$NH_3$$

Mechanism (3)

$$N_2 + 2S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2N - S$$

$$H_2 + 2S \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 2H - S$$

$$N - S + H - S \underset{k_6}{\overset{k_5}{\rightleftharpoons}} NH - S + S$$

$$NH - S + H - S \underset{k_8}{\overset{k_7}{\rightleftharpoons}} NH_2 - S + S$$

$$NH_2 - S + H - S \underset{k_{10}}{\overset{k_9}{\rightleftharpoons}} NH_3 - S + S$$

$$NH_3 - S \underset{k_{12}}{\overset{k_{11}}{\rightleftharpoons}} NH_3 + S$$

$$N_2 \underset{k_{13}}{\overset{k_{14}}{\rightleftharpoons}} \emptyset \underset{k_{16}}{\overset{k_{15}}{\rightleftharpoons}} H_2$$
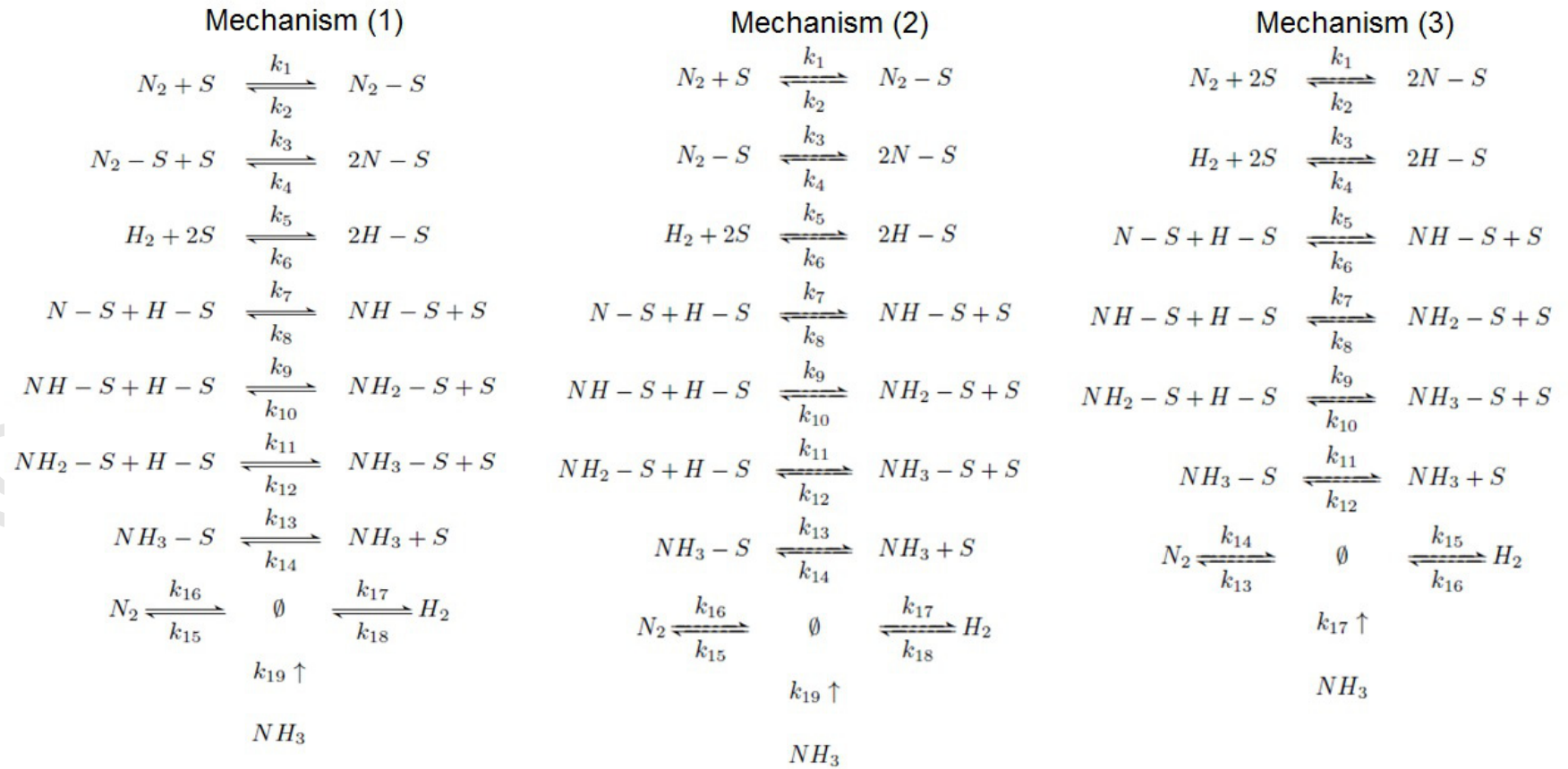
$$k_{17} \uparrow$$

$$NH_3$$

Figure 1: Ammonia synthesis mechanisms modelled as isothermal CFSTR. Mechanism (1) proposed by Stoltze [12], mechanism (2) reviewed by Aparicio and Dumesic in [13], and mechanism (3) reported by Dumesic in [14].

95 Additionally, the continuous inflow of N_2 and H_2 into the reactor need to be

96 taken under consideration, as well as their outflow from the reaction chamber

97 containing NH_3 and unreacted reactants N_2, H_2. The pseudo-reactions that

98 account for these flows within the CRN Theory (see section 3) formalism [6, 15]

99 are displayed in Figure 1 as reactions 16 to 19, for mechanism (1).

100 The symbol $\emptyset$ is the zero complex, which represents the surroundings of the

101 reactor. The pseudo-reaction $\emptyset \xrightarrow{k} A$ states that chemical species A is being

102 fed into the reactor at a continuous rate $k = x_A^f/\tau$, where τ is the residence

103 time in the reactor, and x_A^f is the concentration of chemical species A in the

104 feed stream. The opposite arrow direction, $A \xrightarrow{k'} \emptyset$, represents the continuous

105 outflow of species A from the reactor at a rate $k' = -x_A/\tau$.

106 The second ammonia synthesis mechanism was suggested in the thorough

107 review of ammonia synthesis kinetics by Aparicio and Dumesic [13]; it is shown

108 in Figure 1 as mechanism (2). Again, active sites and chemical species and their

109 adsorbed versions are defined exactly as in mechanism (1). Note that reaction

110 mechanisms (1) and (2) have the same number of reactions.

111 However, one important difference in reaction mechanism (2) is that the

112 nitrogen diatomic molecules are adsorbed in one active site and then dissoci-

113 ate into two nitrogen adsorbed atomic species, while the hydrogen diatomic

114 molecules are adsorbed in pairs of adjacent catalytic sites (since it is required

115 for the sites to be adjacent in order to perform a single step adsorption of two

116 atoms, each in a catalytic site). Nitrogen dissociation is probed to be the rate-

117 determining step in the process and more complex than depicted by this single

8

118 step (for a wider approach of this matter literature is at hand [13]). Finally,

119 ammonia forms, as before, when all adsorbed species interact. Thus, mecha-

120 nism (2) requires clusters of neighbouring catalytic sites at least to occur.

121   The third ammonia synthesis mechanism reported by Dumesic [14] is a

122 slightly modified version of mechanism (2). According to mechanism (3) in

123 Figure 1, it is proposed that all diatomic molecules (nitrogen and hydrogen) are

124 adsorbed in pair of adjacent catalytic sites and that such adsorption processes

125 are single stepwise. This implies that the reaction mechanism requires clusters

126 of four neighbouring catalytic sites at least to occur, and such clusters must be

127 formed by pairs of adjacent vacant catalytic sites, given the constraint that such

128 adsorption processes must occur in a single step manner.

129   Despite all three mechanisms being very similar, their potential dynamical

130 scenarios are different. CRN Theory, along with its deficiency oriented analysis,

131 is sharp enough to reveal that minor structural subtleties at the microscale level

132 can have a macroscale impact on the CFSTR dynamics, *i.e.*, the behaviour of

133 their associated ODEs. That is, deficiency analysis shows that the presence

134 of adjacent active catalytic sites in two mechanisms can induce the existence

135 of multiple steady states under isothermal operation of the CFSTR. The next

136 section briefly reviews CRN Theory and its deficiency analysis.

9

3 Chemical reaction network theory and deficiency analysis

CRN Theory is a graph theoretical approach that classifies any chemical reaction mechanism using a non-negative integer called *deficiency*, $\delta \geq 0$ [15]. This integer relates the structure of a reaction mechanism with the existence or not of multiple positive steady states for the corresponding system of CFSTR ODEs. The dynamical information the deficiency provides is embraced by the Deficiency Zero Theorem (DZT), Deficiency One Theorem (DOT) along with the Deficiency One Algorithm (DOA), and the Advanced Deficiency Algorithm (ADA). Before reviewing them, some terminology inherent to CRN Theory approach is required.

The *complexes* of a mechanism are the linear combinations of chemical species that appear before and after the reaction arrow [15]. Complexes are restricted to appear just once in the graphical representation of the mechanism under study, including the zero complex, $\emptyset$. Thus, from a graph theoretical point of view, complexes are the vertices of the graph associated with a mechanism. Additionally, a mechanism can be composed of more than one graph, that is, there might exist sub-graphs whose union yields the whole mechanism. Such pieces are termed *linkage classes*. Formally, a linkage class is a group of complexes that are connected by reaction arrows, *i.e.* the number of separate "pieces" of which the mechanism is composed.

10

₁₅₈ The mathematical definition of the deficiency is:

$$\delta = |\mathcal{C}| - |\mathcal{L}| - rank(N) \tag{2}$$

₁₅₉ where $|\mathcal{C}|$ is the number of complexes (including the zero complex, $\emptyset$), $|\mathcal{L}|$ is the

₁₆₀ number of *linkage classes*, and the last term in Eq. (2) is the rank of the stoichio-

₁₆₁ metric matrix, $N \in \mathbb{R}^{s \times r}$, formed by s rows of chemical species and r columns

₁₆₂ of reactions. It might be the case that N does not have full row-rank, *i.e.*, there

₁₆₃ exist *stoichiometric compatibility classes* or conservation relations that solutions

₁₆₄ of the associated CFSTRs ODEs need to fulfill [15]. In heterogeneous catalytic

₁₆₅ reactions, these compatibility classes are the site concentration balance for the

₁₆₆ catalyst surface under study [5, 6, 7].

₁₆₇ If the deficiency $\delta = 0$ for a particular reaction mechanism, then, regardless

₁₆₈ of the positive rate constants, the set of CFSTR ODEs derived from the mech-

₁₆₉ anism and endowed with mass action kinetics, cannot admit multiple positive

₁₇₀ steady states or sustained oscillations [15]. On the other hand, if $\delta = 1$ and

₁₇₁ the reaction mechanism satisfies some additional conditions, DOT can address

₁₇₂ the existence and uniqueness of positive steady states [5, 15], meanwhile the

₁₇₃ DOA can decide whether a mechanism can or cannot admit multiple steady

₁₇₄ states by solving systems of equalities and inequalities which are guaranteed

₁₇₅ to be linear [5, 15, 17]. Furthermore, if $\delta > 1$, the ADA [5] might have to

₁₇₆ consider nonlinear inequalities to decide about multistationarity of the reaction

₁₇₇ mechanism.

₁₇₈ The DOT and ADA are implemented in the CRN Toolbox [17]. If multiple

₁₇₉ positive steady states are possible for a reaction mechanism, then, a set of kinetic

11

180 constants for which the CFSTR ODEs admits a pair of positive steady states is

181 provided by the CRN Toolbox. It is beyond the scope of this work to provide

182 a thorough description of DOT and the ADA; the interested reader is referred

183 to [5]. Thus, we stress the fact that reaction mechanism structure already

184 conveys a wealth of dynamical information without having to numerically solve

185 their induced CFSTR ODEs or compute the associated thermodynamics.

186   Before proceeding, it is pertinent at this point to state the assumptions on

187 which the forthcoming analysis is based. Hereafter, we assume the following:

188   • All reactions in the mechanisms are elementary and described by mass
189   action kinetics.

190   • The CFSTR operates at constant temperature and is well mixed.

191   • The concentration of chemical species is considered uniform in the gas
192   phase and on the catalyst surface. Mass transfer is negligible.

193   • No reaction takes place in the gas phase, only on the catalyst surface.

194   • In the feed, there is a large quantity of an inert gas as a carrier, *e.g.* argon,
195   such that the effluent volumetric rates are considered the same.

196 Now, we have all the elements to apply the CRN Theory approach to the am-

197 monia synthesis CRNs.

12

4 Results

Table 1 summarizes the output of the computer implementation of deficiency analysis [17] for mechanisms (1), (2), and (3).

Table 1: Ammonia synthesis reaction mechanisms and their capacity for isothermal CFSTR multiple positive steady states.

Reaction mechanism	$|\mathcal{C}|$	$|\mathcal{L}|$	$rank(N)$	δ	Multiple Steady Sates?
Stoltze, mechanism (1)	18	8	9	1	Yes
Aparicio & Dumesic, mechanism (2)	17	7	10	0	No
Dumesic, mechanism (3)	16	7	8	1	Yes

According to DZT, we can state that, for mechanism (2), " the corresponding differential equations cannot admit a steady state at which all species concentrations are positive (some species will be absent at the steady state), nor can the differential equations admit a cyclic composition trajectory that passes through a composition for which all species concentrations are positive" [17]. This result is not easy to visualise by the traditional methodology in chemical engineering textbooks which sets a system of nonlinear coupled CFSTR ODEs to zero and then find the steady states which satisfy the resulting multivariate polynomials (see the complexity of the associated mass action CFSTR ODEs in the Appendix). Not to mention the fact that, most of the time, kinetic rate constant values are unknown *a priori* in experimental surface chemical kinetics.

On the other hand, mechanisms (1) and (3) have a deficiency of one. According with the DOA [5, 18, 17], the reaction mechanisms do have the capacity for multiple steady states. That is, there are kinetic rate constants that give

13

215   rise to two or more positive steady states supported by the nonlinear mass ac-

216   tion CFSTR ODEs. Therefore, depending upon the start-up reactor conditions,

217   the lower or higher steady state will be reached. Seeking completeness, sets of

218   kinetic rate constants that exhibit multiple steady states, along with the mass

219   action CFSTR ODEs for mechanisms (1) and (3), are reported in the Appendix.

220   Figure 2 shows the typical S-shape for three steady states for network (1)

221   (two stable, one unstable) as the feed concentration of N_2 (k_{15}) and H_2 (k_{17})

222   are varied, respectively. Upper panel in Fig. 2 indicates that, for values of k_{15}

223   of < 25 and > 33, there is a unique steady state composition within (and at the

224   effluent) of the CFSTR. However, for intermediate values of k_{15}, there are three

225   steady states, two of them stable (upper and lower branch) and one unstable

226   (middle branch). Note that, for the steady state value of NH_3 within the re-

227   actor, its equilibrium concentration increases almost linearly up to a maximum

228   (≈ 63) as feed of N_2 is increased, until the flow rate of N_2 exceeds a value of

229   ≈ 30. At that point, the steady state concentration of NH_3 drops abruptly to

230   a value of ≈ 15. If k_{15} in reduced in small decrements then NH_3 increments

231   until the flow rate of N_2 is below 25, at which point it increases sharply from

232   ≈ 28 to 50. Note that these switch-like transitions take place between a narrow

233   region of N_2 feed concentrations, thus, when performing experimental kinetic

234   studies for mechanism (1) and feeding N_2 as the limiting reagent, these discon-

235   tinuities might be interpreted as failed attempts to reach "the" steady state in

236   the laboratory.

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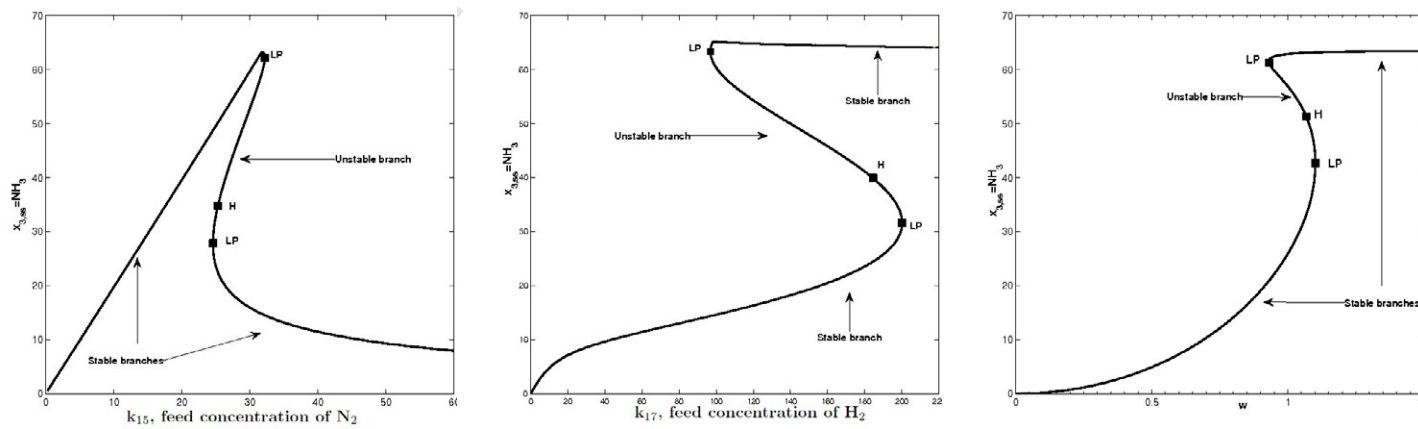
Figure 2: Bifurcation diagrams for mechanism (1). The ammonia locus of equilibria, $x_{3,ss} = NH_3$, when flow rate of H_2 is fixed (left panel), N_2 is fixed (middle panel), and when varying the total concentration of catalytic sites, w (right panel). Limit Points (LP) indicate a stability change of the equilibrium branch. Neutral Saddle (H) is a point where two eigenvalues of opposite signs vanish. The numerical bifurcation analysis was performed using *Matcont* [19].

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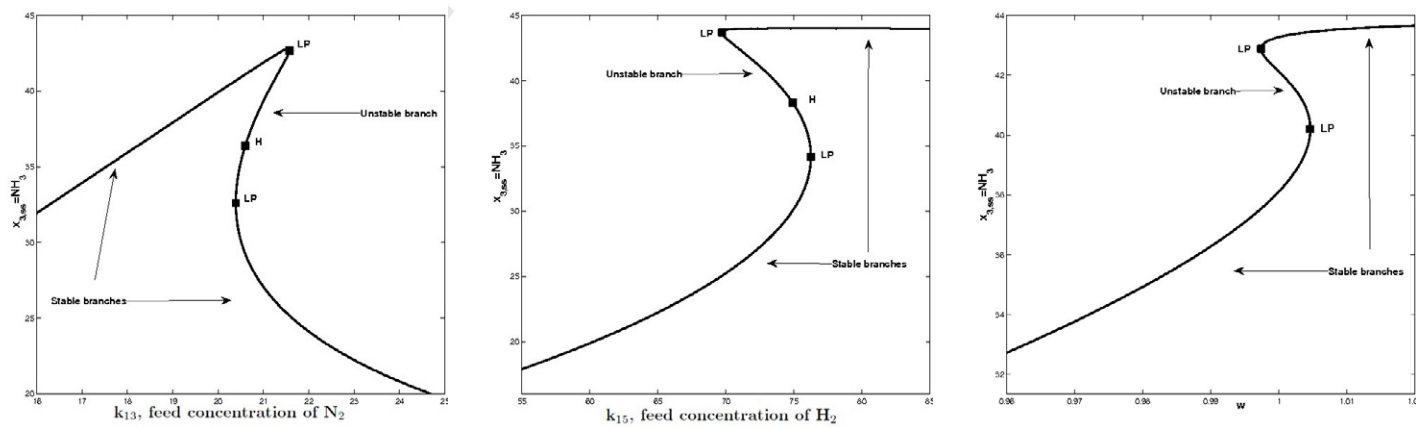
Figure 3: The ammonia locus of equilibria, $x_{3,ss} = NH_3$, when flow rate of H_2 is fixed (left panel), N_2 is fixed (middle panel), and when varying the total concentration of catalytic sites, w (right panel). Limit Points (LP) indicate a stability change of the equilibrium branch. Neutral Saddle (H) is a point where two eigenvalues of opposite signs vanish. The numerical bifurcation analysis was performed using *Matcont* [19].

On the other hand, if the flow rate of N_2 is fixed and the supply rate of H_2 is increased in small steps (see middle panel in Fig. 2), NH_3 steady state concentration increases slowly until the feed concentration surpasses a value of 200. At this point, a sudden jump to a higher NH_3 steady state concentration takes place (from ≈ 33 to ≈ 64). Additionally, between a flow rate, k_{17}, of 100 and 200, three steady states (two stable, one unstable) are found, which can be reached depending on the start-up reactor conditions. Outside these extremes, only one steady state is encountered (upper or lower branch). Compared with the bistable region engendered when the supply rate of N_2 (i.e. k_{15}) is manipulated, H_2 supply rate shows a broader range for bistability to occur.

Bistability phenomena can also be observed when the amount of active sites in the catalyst increase. In a hypothetical situation, an operator might conduct a series of experiments in which samples of the same batch of catalyst with a total number of catalytic sites of $w = 1.5$ (keep in mind that w is not a normalized quantity) is tested for ammonia synthesis reactivity. The operator will selectively block a certain amount of active sites (as commonly done with cations over acidic sites when working with zeolites). This blocking technique allows for a real comparison between catalyst samples when varying w, without changing the morphology. Each sample will be loaded in the reactor and ammonia synthesis reaction will be conducted until steady state is reached. The series begins with the sample containing the lowest number of unblocked active sites. The operator will observe an increase in ammonia conversion at steady state, as the number of available active sites is increased. When w approximates

17

₂₆₀ unity, the operator will observe the system saddling down into a concentration

₂₆₁ of NH_3 around 30 or reaching a upper limit of NH_3 above 60. Interestingly,

₂₆₂ the operator might reach any of the possible two outcomes, and possibly dis-

₂₆₃ miss any of the two as an operative mistake. Further experiments will lead

₂₆₄ the operator to the highest NH_3 possible concentration (above 60), that is for

₂₆₅ $w > 1$. At this moment, the operator will conclude that the ammonia might

₂₆₆ increase in a sigmoidal manner, unaware of the bistability phenomena exhibited

₂₆₇ by the reaction system. This situation, the presence of multiple steady states

₂₆₈ that might go unnoticed, can be assumed as "operator's bad technique" or in-

₂₆₉ explicable " turnoffs"of the reactor during experimentation. Thus, the operator

₂₇₀ will report the findings and miss the more nuanced behaviour.

₂₇₁ The geometry of bifurcation diagrams for mechanism (3) is similar to those

₂₇₂ presented for mechanism (1), thus observations concerning the expected dynam-

₂₇₃ ical behaviour also applies for mechanism (3) (see Fig. 3). However, we do stress

₂₇₄ the fact that the bistable regions are narrower for both N_2 and H_2 supply rates

₂₇₅ in mechanism (3) than those exhibited by mechanism (1).
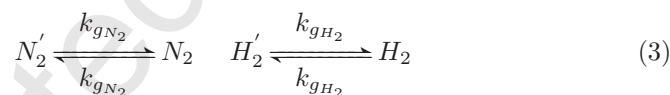
5 Discussion

₂₇₇ In this contribution we have analysed, using a deficiency oriented analysis, three

₂₇₈ closely related mechanisms for ammonia synthesis [12, 13, 14]. Under the as-

₂₇₉ sumptions of mass action kinetics and isothermal conditions, mechanisms (1)

₂₈₀ and (3), taking place within a CFSTR, can support the existence of multiple

18

²⁸¹ positive steady states. On the contrary, the dynamics of reaction mechanism (2)

²⁸² will behave in a dull way; that is, existence of multiple steady states or chemical

²⁸³ composition oscillations is precluded. Further, a steady state at which all chem-

²⁸⁴ ical species are positive is not possible; some of them shall be absent. A possible

²⁸⁵ reason to these differences, *i.e.* existence or not of multiple steady states, lies

²⁸⁶ on the adsorption-desorption kinetics of N_2 and the interaction of neighbouring

²⁸⁷ surface catalytic sites, which is the only difference among mechanisms (1), (2),

²⁸⁸ and (3). All authors agreed that this step is rate determining[3] [12, 13, 14].

²⁸⁹ For instance, reaction mechanism (1) considers the interaction of adsorbed N_2

²⁹⁰ with a neighbouring or adjacent catalytic site to produce two adsorbed atoms

²⁹¹ of N (that is $N_2 - S + S \rightleftharpoons 2N - S$). The propounded process of adsorption

²⁹² might consist of one or two steps. This observation was proposed as a one step

²⁹³ process by Dumesic [14], that is $N_2 + 2S \rightleftharpoons 2N - S$ (cf. mechanism (3)). Nev-

²⁹⁴ ertheless, in the review article by Aparicio and Dumesic [13], only one catalytic

²⁹⁵ site is considered for adsorption-desorption (a two step process): $N_2 \rightleftharpoons 2N - S$.

²⁹⁶ Therefore, it can be inferred that the presence of the second catalytic site enables

²⁹⁷ the existence of multiple steady states in mechanisms (1) and (3). It is remark-

²⁹⁸ able how microscale events might impact the macroscale dynamics (bistability),

²⁹⁹ specifically the existence of neighbouring catalytic sites.

³⁰⁰ However, let us recall that all three reaction mechanisms were experimen-

³⁰¹ tally validated. Thus, if bistability is reported in the future for the ammonia
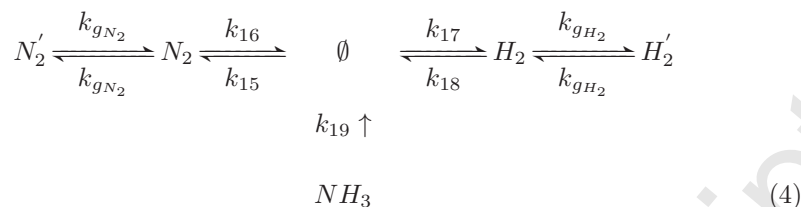
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[3]Mechanism (2) is a bit less realistic due to the fact that mass is not conserved in the second step. Nevertheless, it was included because it was used as a core mechanism to develop others [13].

19

302 synthesis, reaction mechanism (2) shall be discarded or properly modified to

303 account for it. Concerning the latter option, a possible modification is to con-

304 sider a mass transfer limitation under reaction conditions. It is known that

305 the presence of mass transfer limitations in isothermal catalytic reactions would

306 admit multiplicity of steady states [4]. CRN Theory allows to model the mass

307 transfer effect of the chemical species between the bulk of the gas phase and

308 the interface formed above the fluid phase and the solid catalytic surface using

309 first order reactions [20, 21]. This kind of mass transfer limitation is defined

310 as *external* mass transfer limitation [9]. On the contrary, the effect of *internal*

311 mass transfer limitation due to the transport of chemical species at the catalyst

312 surface to the interior of the porous catalyst cannot be embraced by the CRN

313 Theory [21]. Then, if external mass transfer is considered for reaction mecha-

314 nism (2), it is necessary to add the following reactions for chemical species N_2

315 and H_2:

$$N_2^{'} \underset{k_{g_{N_2}}}{\overset{k_{g_{N_2}}}{\rightleftharpoons}} N_2 \quad H_2^{'} \underset{k_{g_{H_2}}}{\overset{k_{g_{H_2}}}{\rightleftharpoons}} H_2 \qquad (3)$$

316 where $N_2^{'}$ represents the species on the catalyst surface and $k_{g_{N_2}}$ is regarded

317 as the mass transfer coefficient associated with transport of N_2 from the bulk

318 to the fluid-solid interface and vice versa. In this sense, $N_2^{'}$ is considered as a

319 different species along with its concentration. The same concepts applies for

320 species $H_2^{'}$. In this manner, assuming an external mass transfer limitation for

321 reaction mechanism (2) leads to a modification of the linkage class that contains

20

322 the inflow-outflow of chemical species as follows:

$$N_2' \underset{k_{g_{N_2}}}{\overset{k_{g_{N_2}}}{\rightleftharpoons}} N_2 \underset{k_{15}}{\overset{k_{16}}{\rightleftharpoons}} \quad \emptyset \quad \underset{k_{18}}{\overset{k_{17}}{\rightleftharpoons}} H_2 \underset{k_{g_{H_2}}}{\overset{k_{g_{H_2}}}{\rightleftharpoons}} H_2'$$

$$k_{19} \uparrow$$

$$NH_3 \tag{4}$$

323 The mass transfer consideration thus increases by two the number of chemical

324 species and complexes, and by four the number of chemical reactions. Applying

325 the deficiency analysis, it turns out that reaction mechanism (2) remains to be

326 a deficiency of zero as in the previous analysis (cf. section 4). Using Eq. (2),

327 we can see that $\delta = (17 + 2) - 7 - (10 + 2) = 0$. Again, no balance of catalytic

328 sites is obtained directly from the (full rank) modified stoichiometric matrix of

329 mechanism (2) under an external mass transfer limitation assumption. It seems

330 that additional structural conditions need to be satisfied to support multiple

331 steady states for reaction mechanism (2).

332 Since the capacity to support multiple steady states is not a sufficient con-

333 dition to validate mechanisms [5, 6, 7, 21], further tests would be necessary to

334 validate reaction mechanisms (1) and (3) in the presence of two or more steady

335 states gathered from experimental data. It might be the case that both mecha-

336 nisms support the pair of steady states recorded from experiments by measuring

337 N_2, H_2, and NH_3 concentrations. Under such circumstances, it would be nec-

338 essary to measure the surface species concentrations or consider external mass

339 transport effects to discriminate among candidate mechanisms [21]. If such situ-

340 ation becomes necessary, then, reaction mechanism (2) would not have a chance

21

341 to be tested because, under a CFSTR operation, it does not induce a balance
342 of catalytic sites, which plays a paramount role on the screening of candidate
343 reaction mechanisms [5, 6, 7, 21]. As a consequence, current ammonia synthe-
344 sis mechanisms remain valid until the weight of further experimental evidence
345 settles this apparent dispute.

6 Conclusions

347 We have shown, using a CRN Theory approach, that two of three experimentally
348 validated ammonia synthesis mechanisms can support multiple steady states un-
349 der isothermal CFSTR operation. This result was found using the structure of
350 the ammonia mechanism alone. We argued that multiplicity of steady states
351 are caused by the existence of a second adjacent catalytic site. Additionally,
352 the CRN Theory approach is an easy-to-use theory, with a friendly implemen-
353 tation in a computational tool [17], increasing its potential resources among the
354 industrial and engineering chemistry community to spur their curiosity about
355 other kinds of dynamical behaviour (bistability, oscillations) latent within classic
356 reaction mechanisms.

357 It is necessary to stress the fact that, based on the network structure alone
358 and prior to performing experimental kinetic studies, deficiency oriented analysis
359 provides very quickly such a wealth of information despite the subtle differences
360 among the ammonia synthesis mechanisms studied along this contribution. We
361 think that the sharpness of CRN Theory formalism to elucidate interesting

22

362 dynamical features still to be found within well accepted heterogeneous catalytic

363 reactions shall serve to revive the interest on simple and long revised mechanisms

364 as the ammonia synthesis. As properly stated by Feinberg [22]: "There is, then,

365 a lesson to be learnt from the fact that ... a *single* overall reaction can give to

366 multiple steady states in a simple isothermal CFSTR setting: when catalysis is

367 at work, we should be cautious about our traditional expectation that isothermal

368 systems behave in dynamically dull ways."

23

Appendix

Here we provide the mass action CFSTR ODEs for reaction mechanisms (1), (2), and (3), jointly with kinetic rate constants for which multiple steady states are possible. Overdot in $\dot{x}_i$ is used to denote the derivative with respect to time, t, and the argument t of the variables $x_i(t)$ is omitted seeking brevity. Nomenclature for chemical species concentrations in reaction mechanisms (1)-(3) is resumed in Table 2.

A set of kinetic rate constants, provided by the CRN Toolbox [17], for which the associated mass action CFSTR (A.1) ODEs of reaction mechanism (1) and (3) admits multiple positive steady states are reported in Table 3.

24

379 **6.1 Mass action CFSTR ODEs for mechanism (1).**

$$\dot{x}_1 = -k_1 x_1 x_4 + k_2 x_5 + k_{15} - k_{16} x_1$$

$$\dot{x}_2 = -k_5 x_2 x_4^2 + k_6 x_7^2 + k_{17} - k_{18} x_2$$

$$\dot{x}_3 = k_{13} x_{10} - k_{14} x_3 x_4 - k_{19} x_3$$

$$\dot{x}_4 = -k_1 x_1 x_4 + k_2 x_5 - k_3 x_4 x_5 + k_4 x_6^2 - 2k_5 x_2 x_4^2 + 2k_6 x_7^2$$
$$+ k_7 x_6 x_7 - k_8 x_4 x_8 + k_9 x_7 x_8 - k_{10} x_4 x_9 + k_{11} x_7 x_9 - k_{12} x_4 x_{10}$$
$$+ k_{13} x_{10} - k_{14} x_3 x_4$$

$$\dot{x}_5 = k_1 x_1 x_4 - k_2 x_5 - k_3 x_4 x_5 + k_4 x_6^2$$

$$\dot{x}_6 = 2k_3 x_4 x_5 - 2k_4 x_6^2 - k_7 x_6 x_7 + k_8 x_4 x_8$$

$$\dot{x}_7 = 2k_5 x_2 x_4^2 - 2k_6 x_7^2 - k_7 x_6 x_7 + k_8 x_4 x_8 - k_9 x_7 x_8 + k_{10} x_4 x_9 - k_{11} x_7 x_9 + k_{12} x_4 x_{10}$$

$$\dot{x}_8 = k_7 x_6 x_7 - k_8 x_4 x_8 - k_9 x_7 x_8 + k_{10} x_4 x_9$$

$$\dot{x}_9 = k_9 x_7 x_8 - k_{10} x_4 x_9 - k_{11} x_7 x_9 + k_{12} x_4 x_{10}$$

$$\dot{x}_{10} = k_{11} x_7 x_9 - k_{12} x_4 x_{10} - k_{13} x_{10} + k_{14} x_3 x_4 \qquad (A.1)$$

380 The set of CFSTR ODEs (A.1) is restricted to the following balance of catalytic

381 sites derived from the stoichiometric matrix of reaction mechanism (1):

$$x_4 + x_5 + x_6 + x_7 + x_8 + x_9 + x_{10} = w, \quad w \in \mathbb{R}_+ \qquad (A.2)$$

25

382 **6.2 Mass action CFSTR ODEs for reaction mechanism (2).**

383 Stoichiometric matrix, N, for CFSTR reaction mechanism (2) is full rank (cf.

384 Table 1), therefore no balance of catalytic sites is obtained.

$$\dot{x}_1 = -k_1 x_1 x_4 + k_2 x_5 + k_{15} - k_{16} x_1$$

$$\dot{x}_2 = -k_5 x_2 x_4^2 + k_6 x_7^2 + k_{17} - k_{18} x_2$$

$$\dot{x}_3 = k_{13} x_{10} - k_{14} x_3 x_4 - k_{19} x_3$$

$$\dot{x}_4 = -k_1 x_1 x_4 + k_2 x_5 - 2k_5 x_2 x_4^2 + 2k_6 x_7^2 + k_7 x_6 x_7 - k_8 x_4 x_8 + k_9 x_7 x_8 - k_{10} x_4 x_9$$
$$+ k_{11} x_7 x_9 - k_{12} x_4 x_{10} + k_{13} x_{10} - k_{14} x_3 x_4$$

$$\dot{x}_5 = k_1 x_1 x_4 - k_2 x_5 - k_3 x_5 + k_4 x_6^2$$

$$\dot{x}_6 = 2k_3 x_5 - 2k_4 x_6^2 - k_7 x_6 x_7 + k_8 x_4 x_8$$

$$\dot{x}_7 = 2k_5 x_2 x_4^2 - 2k_6 x_7^2 - k_7 x_6 x_7 + k_8 x_4 x_8 - k_9 x_7 x_8 + k_{10} x_4 x_9$$
$$- k_{11} x_7 x_9 + k_{12} x_4 x_{10}$$

$$\dot{x}_8 = k_7 x_6 x_7 - k_8 x_4 x_8 - k_9 x_7 x_8 + k_{10} x_4 x_9$$

$$\dot{x}_9 = k_9 x_7 x_8 - k_{10} x_4 x_9 - k_{11} x_7 x_9 + k_{12} x_4 x_{10}$$

$$\dot{x}_{10} = k_{11} x_7 x_9 - k_{12} x_4 x_{10} - k_{13} x_{10} + k_{14} x_3 x_4 \tag{A.3}$$

26

6.3 Mass action CFSTR ODEs for reaction mechanism (3).

$$\dot{x}_1 \;=\; -k_1 x_1 x_4^2 + k_2 x_5^2 + k_{13} - k_{14} x_1$$

$$\dot{x}_2 \;=\; -k_3 x_2 x_4^2 + k_4 x_6^2 + k_{15} - k_{16} x_2$$

$$\dot{x}_3 \;=\; k_{11} x_9 - k_{12} x_3 x_4 - k_{17} x_3$$

$$\dot{x}_4 \;=\; -2k_1 x_1 x_4^2 + 2k_2 x_5^2 - 2k_3 x_2 x_4^2 + 2k_4 x_6^2 + k_5 x_5 x_6 - k_6 x_4 x_7 + k_7 x_6 x_7 - k_8 x_4 x_8$$

$$+ k_9 x_6 x_8 - k_{10} x_4 x_9 + k_{11} x_9 - k_{12} x_3 x_4$$

$$\dot{x}_5 \;=\; 2k_1 x_1 x_4^2 - 2k_2 x_5^2 - k_5 x_5 x_6 + k_6 x_4 x_7$$

$$\dot{x}_6 \;=\; 2k_3 x_2 x_4^2 - 2k_4 x_6^2 - k_5 x_5 x_6 + k_6 x_4 x_7 - k_7 x_6 x_7 + k_8 x_4 x_8 - k_9 x_6 x_8 + k_{10} x_4 x_9$$

$$\dot{x}_7 \;=\; k_5 x_5 x_6 - k_6 x_4 x_7 - k_7 x_6 x_7 + k_8 x_4 x_8$$

$$\dot{x}_8 \;=\; k_7 x_6 x_7 - k_8 x_4 x_8 - k_9 x_6 x_8 + k_{10} x_4 x_9$$

$$\dot{x}_9 \;=\; k_9 x_6 x_8 - k_{10} x_4 x_9 - k_{11} x_9 + k_{12} x_3 x_4 \tag{A.4}$$

The set of CFSTR ODEs (A.4) is restricted to the following balance of catalytic

sites derived from the stoichiometric matrix of reaction mechanism (3):

$$x_4 + x_5 + x_6 + x_7 + x_8 + x_9 = w, \quad w \in \mathbb{R}_+ \tag{A.5}$$

27

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29

₄₂₄ **Tables**

Table 2: Nomenclature of chemical species concentrations.

	Reaction mechanisms (1) and (2)	Reaction mechanism (3)
x_1	N_2	N_2
x_2	H_2	H_2
x_3	NH_3	NH_3
x_4	S	S
x_5	$N_2 - S$	$N - S$
x_6	$N - S$	$H - S$
x_7	$H - S$	$NH - S$
x_8	$NH - S$	$NH_2 - S$
x_9	$NH_2 - S$	$NH_3 - S$
x_{10}	$NH_3 - S$	

30

Table 3: Kinetic constants for which reaction mechanisms (1) and (3) admits multiple positive steady states.

	Reaction mechanism (1)	Reaction mechanism (3)
k_1	2442.1859	32931.037
k_2	568.67178	1468.3425
k_3	1041538	59003.075
k_4	1834221.3	71321.381
k_5	1317002.3	26717.6
k_6	130593.75	12379.338
k_7	850876.47	2067.2867
k_8	115774.77	1307.0836
k_9	2189.2721	2304.0028
k_{10}	1827.7018	3723.3095
k_{11}	4441.4964	7543.971
k_{12}	12173.19	209.99692
k_{13}	65416.555	22.060441
k_{14}	1334.6836	1
k_{15}	32.723891	68.08732
k_{16}	1	1
k_{17}	95.303688	1
k_{18}	1	-
k_{19}	1	-

31