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Steady state equivalence in speciation: Reaction networks in acid–base aqueous solutions

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ABSTRACT

Acidity levels affect water chemistry and the Chemical Reaction Networks (CRN) encountered within it. In other words, pH is an external factor that influences speciation, precluding or promoting the appearance of certain chemical species as shown by distribution diagrams. Therefore, there is not a unique CRN for the entire pH spectrum. Moreover, it might be the case that an operative CRN for a given pH interval also supports the steady states values engendered by a second CRN which is operative for a distinct pH interval. In this sense, the first CRN is steady state equivalent with respect to the second CRN. Due to their importance for pH regulation in water chemistry and similarity in their speciation diagrams, we consider the well-known phosphoric acid-calcium carbonate system as a case study to show how steady state equivalence allows us to find relationships between reactions in speciation.

1. Introduction

It is known in chemical reactor design that more than one proposed Chemical Reaction Network (CRN) may lead to the same dynamics (Hill, 1972). That is, two or more candidate CRNs can stand for the same experimental reality, a fact known as the fundamental dogma of chemical kinetics (Craciun and Pantea, 2008). These valid CRNs do not necessarily share the same number of chemical species or reactions. Nevertheless, the Ordinary Differential Equations (ODEs) induced by the reaction networks, and endowed with Mass Action Kinetics (MAK) or another type of kinetics, are able to support the same experimental behaviour. Then, we can argue that despite their differences in dimension and kinetic structure, the CRNs are equivalent. The topic of determining conditions where CRNs of different reaction structure exhibit the same solutions has gained attention in the last years (Craciun and Pantea, 2008; Szederkényi and Hangos, 2011; Evans et al., 2004; Schnell et al., 2006; Johnston and Siegel, 2011; Szederkényi et al., 2011; Méndez and Femat, 2012). Other results has been obtained using a Lyapunov based approach to build theoretical relationships between the structure of CRN and the number of steady states the CRN can display along with the stability properties of the solutions (Gorban' et al., 1986; Bykov et al., 1991).

In relation to the equivalence among CRNs, water chemistry can be viewed as a variant of the fundamental dogma of chemical kinetics: several CRNs can occur within an aqueous environment as the pH varies (Snoeyink and Jenkins, 1980; Langmuir, 1997). According to acid-base fundamental studies, distribution diagrams reveal how chemical species (*e.g* ions) appear or disappear under distinct pH conditions. Thus, there might be pH intervals where a particular CRN is valid whereas for other pH values another CRN will be dominant: a spectrum of CRNs for the whole pH range. Such possible scenario would imply that the set of ODEs induced by the CRNs change their dimension and structure along with the pH changes. For example, typical water chemistry equilibrium distribution diagrams suggest the existence of pH intervals where more than one chemical species have the same concentration for more than one CRN. These overlapping concentration regions suggest the existence of CRNs that can support more than one steady state for some pH values.

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In other words, it might be possible that one CRN (operative for some pH range) is capable to display a pair of steady states whereas a second CRN, which is operative for a different pH region, supports also the same pair of steady states. If such scenario takes place, we shall denote both CRNs as *steady state equivalent*. We note that steady state equivalence requires that the steady state solutions of two (or more) MAK ODEs systems induced by their corresponding CRNs reach the same steady states departing from the same initial conditions. The existence of multiple steady states supported by two or more CRNs does not imply steady state equivalence necessarily.

The Chemical Reaction Network Theory (CRNT) is a theoretical formalism incisive enough to decide whether or not a set of MAK ODEs induced by CRNs that stand for the same global reaction are steady state equivalent given a particular pair of steady states (Ellison and Feinberg, 2000; Ellison et al., 2000; Feinberg, 1987, 1988; Ellison, 1998). For example, if a CRN support a particular pair of steady states, then the algorithm presented by Ellison (Ellison, 1998) and its computational implementation (Feinberg and Ellison, 1995) will provide a set of kinetic rate constants (hardly known at the beginning of kinetic studies or toiled obtained from experiments) such that the MAK ODEs derived from the candidate CRN support the given pair of steady states. Another strength of the CRNT is its capacity to provide definite answers to the question of whether a candidate CRN can support the measured steady states in the presence of fragmentary data, that is, when the complete set of chemical species is not available for measurement (a typical situation in chemical kinetic studies).

Thus, taking advantage of the CRNT capabilities, we present a twofold contribution: Firstly, due to their importance for pH regulation in water chemistry and similarity in their speciation diagrams (Snoeyink and Jenkins, 1980), we consider the well-known phosphoric acid–calcium carbonate system (Langmuir, 1997; Snoeyink and Jenkins, 1980) to posit five CRNs and their MAK ODEs for the pH interval [0–14]. The CRNs were propounded based on the computed distribution diagram obtained by HySS (Alderighi et al., 1999) (see Fig. 1), with parameters reported by (Langmuir, 1997; Snoeyink and Jenkins, 1980). Secondly, among the proposed CRNs we identified those that can admit multiplicity of steady states depending on the pH interval. Next, we found kinetic rate constants that allow a CRN, defined for a specific pH interval, to support the same steady states encountered in a different pH interval in a second CRN. In this sense, both CRNs shall be considered as steady state equivalent.

This contribution is organised as follows: The mathematical framework is presented in Section 2. In Section 3, we propose a set of chemical reaction mechanisms for the phosphoric acid–calcium carbonate system. We exploit the CRN Theory in Section 4 to reveal multiple steady states in two phosphoric acid–calcium carbonate CRNs. Then, we present the kinetic rate constants that lead the steady state equivalents between two acid–calcium carbonate CRNs. These findings are discussed in Section 5.

2. Theoretical framework

The aim of this section is to provide the mathematical framework on which the five CRNs for the phosphoric acid–calcium carbonate system are modelled, particularly when the CRNs are endowed with MAK.

2.1. Chemical reaction network theory

The *deficiency* is a non-negative integer ($\delta \geq 0$) that relates the structure of the CRN with the existence of (multiple) positive steady states for the corresponding MAK ODEs (Feinberg, 1987). The dynamical information the deficiency provides is embraced by the Deficiency Zero Theorem (DZT), the Deficiency One Theorem (DOT), and the Advanced Deficiency One Algorithm (ADOA) (Feinberg, 1987, 1988; Ellison, 1998). Before reviewing them, some terminology inherent to the CRNT formalism is presented.

The *complexes* of a CRN are the linear combinations of chemical species that appear before and after the reaction arrow (Feinberg, 1987). Complexes are restricted to appear just once in the graphical representation of the CRN under study, including the zero complex, $\emptyset$, which stands for the surroundings or those chemical species that are present in excess within the aqueous solution (Feinberg, 1987). From a graph theoretical point of view, the complexes are the vertices of the CRN graph. A CRN graph may be composed by more than one subgraph, whose union results in the whole CRN. Such subgraphs are termed *linkage classes* by (Feinberg, 1987).

The deficiency is computed as follows (Feinberg, 1987):

$$\delta = |\mathcal{C}| - |\mathcal{L}| - rank(N) \tag{1}$$

where $|\mathcal{C}|$ is the number of complexes (including the zero complex, $\emptyset$), $|\mathcal{L}|$ is the number of *linkage classes* and the rank of the stoichiometric matrix, $N \in \mathbb{R}^{s\times r}$, where s is the number of chemical species and r is the number of reactions.

We can distinguish three possible outcomes of the deficiency analysis. When $\delta = 0$, then, no matter what values the kinetic rate constants might take, the MAK ODEs associated to the CRN cannot admit multiple (positive) steady states nor sustained oscillations (Feinberg, 1987, 1995b). On the other hand, if $\delta = 1$, and some structural conditions are satisfied by the CRN, then the DOT can decide whether or not the

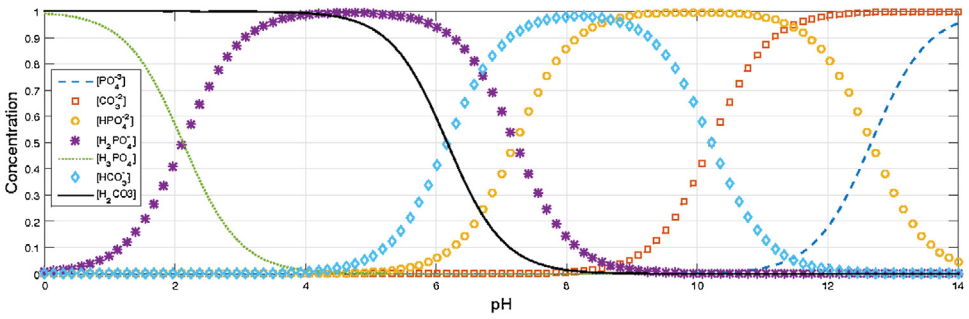

Fig. 1 – Distribution diagram for the phosphoric acid–calcium carbonate system obtained from HySS software (Alderighi et al., 1999). Concentration in molar units (M).