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STABILITY OF O.D.E. SYSTEMS ASSOCIATED WITH FIRST ORDER CHEMICAL KINETICS MECHANISMS WITH AND WITHOUT FINAL PRODUCTS

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Abstract. First order chemical reaction mechanisms are modelled through Ordinary Differential Equations (O.D.E.) systems of the form: $\dot{X} = AX$, being X the chemical species concentrations vector, $\dot{X}$ its time derivative and A the associated system matrix. In previous papers, First Order Chemical Kinetics Mechanisms (F.O.C.K.M.) involving two or three chemical species were considered and in all these cases, solutions show a weak stability (i.e., they are stable but not asymptotically). This fact implies that small errors due to measurements in the initial concentrations will remain bounded, but they do not tend to vanish as the reaction proceeds. In order to know if these results can be extended or not to other chemical mechanisms, a general result is obtained through an inverse modelling approach. For this purpose, theoretical mechanisms with and without final products are proposed, and the corresponding F.O.C.K.M. matrices are studied. As a consequence of the particular structure of the F.O.C.K.M. matrices, the Gershgorin Circles Theorem can be applied to show that all the eigenvalues have real parts negative or zero. Moreover, it is proved as the main result of the paper, that for the null eigenvalue, algebraic and geometric multiplicities (A.M. and G.M.) give the same number. As an application of these results, several conclusions about the stability of the O.D.E. solutions are obtained for this kind of chemical reactions, and its consequences on the propagation of concentrations and/or surface concentrations measurement errors are analyzed.

1. INTRODUCTION

A typical example of a mechanism of chemical reactions involving three different species takes place when a chemical substance A reacts giving a chemical compound B which reacts again to give C, which is the final product of the whole reactions sequence [1]. This is a very common situation in real life, for example, when grape juice is converted into wine, and then it is transformed into vinegar. This sequence of reactions is a particular case of first order chemical kinetics mechanism (F.O.C.K.M), which can be easily represented as follows:

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$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{1.1}$$

where k_1 and k_2 are the corresponding kinetic constants. In the production of wine and vinegar, A is a carbohydrate, B is ethylic alcohol and C is acetic acid. In this mechanism, A is only reactant, C is only final product and B is both reactant and final product. The mathematical model for this F.O.C.K.M. is the following O.D.E. system:

$$\begin{cases} \dfrac{d[A]}{dt} = -k_1[A] \\ \dfrac{d[B]}{dt} = k_1[A] - k_2[B] \\ \dfrac{d[C]}{dt} = k_2[B] \end{cases} \tag{1.2}$$

and its associated matrix is:

$$A = \begin{pmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{pmatrix} \tag{1.3}$$

It is important to note that A has a null column and a possible conjecture is that this is due to the presence of the final product C which does not appear in the right side of the O.D.E. system.

A second observation is that A is a triangular matrix, so its eigenvalues are: $\lambda_1 = -k_1 < 0$, $\lambda_2 = -k_2 < 0$ and $\lambda_3 = 0$, i.e., two of them are negative and the other is zero.

An interesting classical example of F.O.C.K.M. without final products is given by the Mutarotation of Glucose [2] . This is a typical reversible reaction where α-Glucose is converted into β-Glucose and vice versa. This situation could be represented as below:

$$A \xrightarrow{K} B \quad , \quad B \xrightarrow{k} A \tag{1.4}$$

where A and B represent α-Glucose and β-Glucose, and K and k are the corresponding kinetic constants. This situation can be modelled using an O.D.E. system like this:

$$\begin{cases} \dfrac{d[A]}{dt} = -K[A] + k[B] \\ \dfrac{d[B]}{dt} = K[A] - k[B] \end{cases} \tag{1.5}$$

This system can be written easily as $\dot{X} = AX$ being the associated system matrix:

$$A = \begin{pmatrix} -K & k \\ K & -k \end{pmatrix} \tag{1.6}$$

In this case, there are no final products since A and B are reactants of the direct and the opposite reaction, respectively and so, there are no null columns in this matrix. Also, it is important to note that the corresponding eigenvalues are $\lambda_1 = -(K+k) < 0$ and $\lambda_2 = 0$ (see [3] for this result), so again the eigenvalues are negative or zero as in the previous example.

Another interesting example, involving three species without final products comes from the study of the adsorption of Carbon Dioxide (CO_2) on Platinum (Pt) surfaces [3-4-5]. One more time, for this new F.O.C.K.M. all the eigenvalues are negative, except one which is zero.

In all the prior examples, the chemical or electrochemical processes considered were quite different; however in all of them the mathematical models showed certain regularity. In order to propose general results about F.O.C.K.M., several theoretical examples will be considered in the next section.

2. A FEW REMARKS ABOUT THE EIGENVALUES

The first example to be considered in this section is an F.O.C.K.M. without final products, where three different species are involved [6]. This F.O.C.K.M. can be considered as an extension of the Glucose Mutarotation example and can be schematized as follows:

$$A \xrightarrow{k} B \quad , \quad B \xrightarrow{l} C \ , \quad C \xrightarrow{m} A \tag{2.1}$$

The corresponding O.D.E. system is:

$$\begin{cases} \dfrac{d[A]}{dt} = -k[A] + m[C] \\ \dfrac{d[B]}{dt} = k[A] - l[B] \\ \dfrac{d[C]}{dt} = l[B] - m[C] \end{cases} \tag{2.2}$$

And the associated matrix is:

$$A = \begin{pmatrix} -k & 0 & m \\ k & -l & 0 \\ 0 & l & m \end{pmatrix} \tag{2.3}$$

The characteristic equation for this matrix is $p(\lambda) = (-\lambda)(\lambda^2 + \Sigma_1\lambda + \Sigma_2)$ where $\Sigma_1 = k + l + m$ and $\Sigma_2 = kl + km + lm$. For instance, if $k > 0$,$l > 0$ and $m = 0$ then A is a lower matrix and the O.D.E. system has only real simple eigenvalues: $-k$, $-l$ and 0. Now, if $k = l > 0$ and $m = 0$, the F.O.C.K.M. matrix will have a double eigenvalue. Finally, if $k = l = m > 0$ then $\Delta = -3k^2 < 0$ and there will be complex roots. In this last case, the solutions will be linear combinations of $\exp(0t) = 1$, $\exp\left(-\frac{3}{2}kt\right)\cos\left(-\frac{\sqrt{3}}{2}kt\right)$ and $\exp\left(-\frac{3}{2}kt\right)\sin\left(-\frac{\sqrt{3}}{2}kt\right)$.

These solutions will show oscillations which tend to vanish as time tends to infinite. Then, the solutions will be stable, but not asymptotically.

In the second example of this section, an F.O.C.K.M. with final products will be considered [7]. In this case, four species A, B, C and D are involved, such that

all possible reactions between A, B, C take place, while D is just a final product. This mechanism can be schematized as follows:

$$\begin{array}{ccccc} A \xrightarrow{K_{12}} B & , & B & \xrightarrow{K_{21}} A \\ A \xrightarrow{K_{13}} C & , & C & \xrightarrow{K_{31}} A \\ B \xrightarrow{K_{23}} C & , & C & \xrightarrow{K_{32}} B \end{array} \tag{2.4}$$

and

$$A \xrightarrow{K_{14}} D \tag{2.5}$$

The corresponding O.D.E. system is:

$$\frac{d}{dt}\begin{pmatrix}[A]\\[B]\\[C]\\[D]\end{pmatrix} = \begin{pmatrix} -K_{12}-K_{13}-K_{14} & K_{21} & K_{31} & 0 \\ K_{12} & -K_{21}-K_{23} & K_{32} & 0 \\ K_{13} & K_{23} & -K_{31}-K_{32} & 0 \\ K_{14} & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix}[A]\\[B]\\[C]\\[D]\end{pmatrix} \tag{2.6}$$

It can be noted that this system has a null column, that can be expected since D is only a final product and so, it does not appear in the right side of the differential equations given in (2.6). The characteristic equation corresponding to (2.6) is:

$$p(\lambda) = (-\lambda) det \begin{pmatrix} -S_1-\lambda & K_{21} & K_{31} \\ K_{12} & -S_2-\lambda & K_{32} \\ K_{13} & K_{23} & -S_3-\lambda \end{pmatrix} = 0 \tag{2.7}$$

where $S_1 = K_{12}+K_{13}+K_{14}$, $S_2 = K_{21}+K_{23}$ and $S_3 = K_{31}+K_{32}$

This equation can have a double null eigenvalue if and only if:

$$det \begin{pmatrix} -S_1 & K_{21} & K_{31} \\ K_{12} & -S_2 & K_{32} \\ K_{13} & K_{23} & -S_3 \end{pmatrix} = 0 \tag{2.8}$$

or after some algebraic manipulations:

$$K_{14}\left(K_{21}K_{31}+K_{21}K_{32}+K_{23}K_{31}\right) = 0 \tag{2.9}$$

It is not necessary to have two null columns in order to get a double null eigenvalue. For instance, if $K_{21} = K_{31} = 0$ then (2.9) is satisfied and the corresponding F.O.C.K.M. matrix will be:

$$A = \begin{pmatrix} -S_1 & 0 & 0 & 0 \\ K_{12} & -K_{23} & K_{32} & 0 \\ K_{13} & K_{23} & -K_{32} & 0 \\ K_{14} & 0 & 0 & 0 \end{pmatrix} \tag{2.10}$$

being $S_1 = K_{12}+K_{13}+K_{14}$ as mentioned before.

In this case the characteristic polynomial is $p(\lambda) = \lambda^2(S_1+\lambda)\left[\lambda+(K_{23}+K_{32})\right]$ and this mathematical model corresponds to the following F.O.C.K.M.:

$$A \xrightarrow{K_{12}} B \ , \ A \xrightarrow{K_{13}} C \ , \ B \xrightarrow{K_{23}} C \ , \ C \xrightarrow{K_{32}} B \ , \ A \xrightarrow{K_{14}} D \tag{2.11}$$

In this mechanism, A is only reactant, D is only final product and B and C are linked by reversible reactions like in the mutarotation example. Due to this, the system will have two negative eigenvalues and a null double eigenvalue (i.e., $A.M._{\lambda=0} = 2$).

It is important to point out that in this example appeared a double null eigenvalue without having in the mechanism more than one final product (and only one null column in the corresponding F.O.C.K.M. matrix). As a last remark, it can be observed that in all the previous examples —with and without final products— it is possible to get a plethora of solutions with real simple eigenvalues, complex eigenvalues, double eigenvalues, etc. Nevertheless, in all cases there was a null eigenvalue (simple, double, etc.) and all the other eigenvalues had negative real parts. This general result will be commented with more details in the next section.

3. SOME PREVIOUS RESULTS

A general form for mathematical models of F.O.C.K.M. was developed and it appears in a book chapter recently published in New York [8]. In this book it was proved that the corresponding O.D.E. system can be written as:

$$\frac{d}{dt}\begin{pmatrix}[E_1]\\ [E_2]\\ \vdots \\ [E_n]\end{pmatrix} = \begin{pmatrix}-S_1 & K_{21} & \cdots & K_{n1}\\ K_{12} & -S_2 & \cdots & K_{n2}\\ \vdots & \vdots & \ddots & \vdots \\ K_{1n} & K_{2n} & \cdots & -S_n\end{pmatrix}\begin{pmatrix}[E_1]\\ [E_2]\\ \vdots \\ [E_n]\end{pmatrix} \tag{3.1}$$

and the associated matrix is:

$$A = \begin{pmatrix}-S_1 & K_{21} & \cdots & K_{n1}\\ K_{12} & -S_2 & \cdots & K_{n2}\\ \vdots & \vdots & \ddots & \vdots \\ K_{1n} & K_{2n} & \cdots & -S_n\end{pmatrix} \tag{3.2}$$

All the non-diagonal entries of this matrix are non-negative and the diagonal elements are $-S_i = -\sum_{j\neq i} K_{ij}$, so all the matrix columns add to zero. To summarize, the characteristics that define these F.O.C.K.M. matrices, are the following:

- A is a $n \times n$ matrix with real entries a_{ij}.
- The non-diagonal entries are always non-negative numbers: $a_{ij} \geq 0 \ \ \forall \ \ i \neq j$
- The diagonal elements are $-S_i$, being S_i the sum of the non-diagonal entries in the i-th column.

Due to this particular structure, three important results can be obtained for this general form:

- $\lambda = 0$ is an eigenvalue of A.
- $\mathrm{Re}(\lambda_i) \leq 0 \ \ \forall \ \ i = 1, 2, \ldots, n$
- $\mathrm{Re}(\lambda_k) = 0 \Leftrightarrow \lambda_k = 0$

The first one is a consequence of the fact that all the matrix columns add to zero and the last two properties can be obtained by applying the Gershgorin circle theorem [9] to the general F.O.C.K.M. matrix [8].

From the O.D.E. solutions point of view, the non-zero eigenvalues give linear combinations of functions like:

$$\exp(\lambda t)\ ,\ t\exp(\lambda t)\ ,\ t^2\exp(\lambda t)\ ,\ \ldots\ ,\ t^p\exp(\lambda t) \tag{3.3}$$

depending on the algebraic multiplicity (A.M.) and the corresponding geometric multiplicity (G.M.) of the eigenvalue λ . Therefore, taking into account that $\exp(\lambda t) = e^{at}(\cos bt + i\sin bt)$, being $a < 0$, it follows that $\exp(\lambda t) \longrightarrow 0$ when $t \to +\infty$ and the same happens with all the other functions:

$$t\exp(\lambda t)\ ,\ t^2\exp(\lambda t)\ ,\ \ldots\ ,\ t^p\exp(\lambda t) \tag{3.4}$$

Then, all the O.D.E. solutions associated with an eigenvalue $\lambda \neq 0$ tend to vanish with time, independently of corresponding A.M. and/or G.M.

The O.D.E. solutions corresponding to the null eigenvalue are linear combinations of these functions: $\left\{e^{0t}, te^{0t}, \ldots, t^q e^{0t}\right\}$, or the equivalent: $\{1, t, \ldots, t^q\}$. Then, the solutions due to the null eigenvalue are polynomial functions which grade q depends on both the A.M. and the G.M., corresponding to $\lambda = 0$ and it follows straightforward that only if $q = 0$ the polynomial solutions remain bounded when t tends to infinite.

To sum up all the previous results, it can be stated that only the null eigenvalue —and particularly, its A.M. and G.M.— is relevant to make predictions about the stability of the O.D.E. system solutions.

All these results were proved for the F.O.C.K.M. general matrix, so they happen both in mechanisms with final products (like wine-vinegar example) or without final products (like mutarotation example) and these results are true for reversible or irreversible reactions, independently of the number of chemical species involved.

4. TWO GENERAL RESULTS

As it was mentioned before, the general form for F.O.C.K.M. mathematical models has the following form:

$$\frac{d}{dt}\begin{pmatrix}[E_1]\\ [E_2]\\ \vdots\\ [E_n]\end{pmatrix} = \begin{pmatrix}-S_1 & K_{21} & \cdots & K_{n1}\\ K_{12} & -S_2 & \cdots & K_{n2}\\ \vdots & \vdots & \ddots & \vdots\\ K_{1n} & K_{2n} & \cdots & -S_n\end{pmatrix}\begin{pmatrix}[E_1]\\ [E_2]\\ \vdots\\ [E_n]\end{pmatrix} \tag{4.1}$$

In this O.D.E. system, the diagonal elements are $-S_i = -\sum_{j\neq i} K_{ij}$, so all the matrix columns add to zero, then it can be stated that $\dfrac{d}{dt}\left([E_1] + [E_2] + \ldots + [E_n]\right) = 0$ and so, the sum of variables $[E_1] + [E_2] + \ldots + [E_n]$ is a constant κ.

As a consequence of this fact, it follows that for every $[E_i]$ with $1 \leq i \leq n$, the inequalities $0 \leq [E_i] \leq [E_1] + [E_2] + \ldots + [E_n] = \kappa$ are satisfied and all the $[E_i]$ must be bounded for every time $t \geq 0$.

In examples like (2.11) it was observed that the null eigenvalue can have an algebraic multiplicity greater than one. If in one of those cases, the inequality $G.M._{\lambda=0} < A.M._{\lambda=0}$ is satisfied, then solutions of the O.D.E. system will contain linear combinations of $\left\{e^{0t}, te^{0t}, \ldots, t^q e^{0t}\right\}$, or the equivalent: $\{1, t, \ldots, t^q\}$ which are unbounded for $t \geq 0$. This fact contradicts the previous statement about $[E_i]$ which must be bounded for every time $t \geq 0$.

Consequently, a first general result can be stated: $G.M._{\lambda=0} = A.M._{\lambda=0}$ and this result is valid for every $n \times n$ F.O.C.K.M. matrix.

A second general result can be obtained from the following statements mentioned in the previous section: $\mathrm{Re}(\lambda_i) \leq 0 \ \ \forall \ \ i = 1, 2, \ldots, n$ and $\mathrm{Re}(\lambda_k) = 0 \Leftrightarrow \lambda_k = 0$. These results combined with the previous one (i.e., $G.M._{\lambda=0} = A.M._{\lambda=0}$), gives a second general result: the solutions of the O.D.E. system are stable but not asymptotically.

5. CONCLUSION

In previous papers, a general form for matrices associated with F.O.C.K.M. problems was obtained. As a consequence of this structure, several properties were proved. Particularly, for a general $n \times n$ matrix A , corresponding to a given F.O.C.K.M., the following statements were demonstrated:

- $\det(A) = 0$
- if λ is an eigenvalue of A, then $\mathrm{Re}(\lambda) \leq 0$
- $\mathrm{Re}(\lambda) = 0$ if and only if $\lambda_k = 0$

In this paper it was proved that if n chemical substances are considered, the corresponding F.O.C.K.M. matrix verifies that $G.M._{\lambda=0} = A.M._{\lambda=0}$ and this algebraic result has an analytical corollary: the O.D.E. solutions for F.O.C.K.M. systems are always stable, but not asymptotically.

This weak stability has an important chemical consequence, since it implies that small errors in the initial concentrations measurements will remain bounded as the reactions take place, but they will not tend to disappear when $t \to +\infty$.

It is important to remark that other qualitative results can be obtained by an inverse modelling approach (i.e., proposing a theoretical F.O.C.K.M. that fits with a given matrix and/or O.D.E. system). This methodology was used in several previous articles, book chapters, etc. [3-6-7-8-10-11-12-13-14]. For instance, it is possible to analyse the form of the solutions [3-6], the existence and number of inflexion points in curves of $[E_i]$ vs. t [3], the A.M. and G.M. of the null eigenvalue [6-7-8-14], among other conclusions with important mathematical and chemical consequences.

Finally, the study of stability properties and qualitative results, for any number of reactants and for any kind of chemical reactions like second and third order reactions represents a challenging problem and an opportunity for further research in this area.

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