

**STABILITY OF O.D.E. SOLUTIONS CORRESPONDING TO  
CHEMICAL MECHANISMS BASED-ON UNIMOLECULAR FIRST  
ORDER REACTIONS**

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(Communicated by Murat TOSUN)

ABSTRACT. The most simple unimolecular first order chemical reaction mechanism that involves two species, can be exemplified by the Mutarotation of Glucose [1]. The corresponding mathematical model is an O.D.E. linear system which solutions are stable, but not asymptotically [2]. When three chemical compounds are considered, the mechanism can vary from a simple two reactions sequence to a complicated one as the adsorption of Carbon Dioxide ( $CO_2$ ) over Platinum ( $Pt$ ) surfaces [2]. Although in these examples the mechanisms are very different, in both cases the O.D.E. system has two negative eigenvalues and the other one is zero. Once again, solutions show a weak stability which 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 this paper, a general result for reversible reactions is stated through an inverse modelling approach [3] [4], proposing theoretical mechanisms and showing algebraically that all the eigenvalues are negative, except one, which is zero. From this fact, the conclusions about the stability of the solutions are obtained and their consequences on the propagation of measurements errors are analysed.

1. INTRODUCTION

A first order chemical reaction proceeds at a rate that depends linearly only on one reactant concentration. The differential equation describing this first order kinetics is:

$$(1.1) \quad \frac{d[A]}{dt} = -k[A]$$

being  $[A]$  the concentration of the reactant  $A$ ,  $t$  is time and  $k$  is the kinetic constant.

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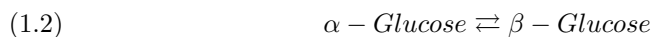
*Date:* Received: December 19, 2014; Accepted: May 20, 2015.

*2010 Mathematics Subject Classification.* 15A18, 34A30, 34D20.

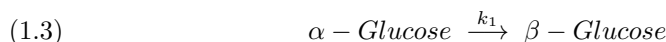
*Key words and phrases.* Chemical mechanisms, O.D.E. linear systems, Solutions stability.

This article is the written version of author's plenary talk delivered on August 25-28, 2014 at 3rd International Eurasian Conference on Mathematical Sciences and Applications IECMSA-2014 at Vienna, Austria.

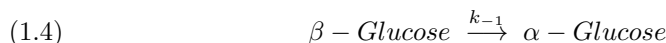
If two chemical species are involved, instead of an O.D.E., we will have an O.D.E. linear system. For instance, in the mutarotation of Glucose we have:



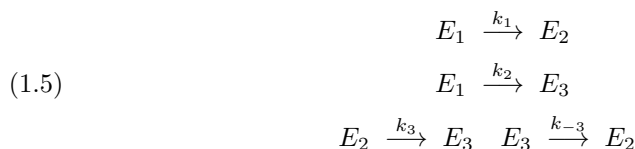
If  $k_1$  and  $k_{-1}$  are the kinetic constants, this mechanism includes two first order reactions, the direct one:



and the opposed one:



In the adsorption of Carbon Dioxide ( $CO_2$ ) over Platinum ( $Pt$ ) surfaces, three different adsorbates were observed. If  $E_1$ ,  $E_2$  and  $E_3$  represent these adsorbates, then the mechanism that showed the best fit with the experimental curves was the following:



where  $k_1, k_2, k_3$  and  $k_{-3}$  are the kinetic constants.

If  $[E_1]$ ,  $[E_2]$ ,  $[E_3]$  represent the adsorbates surface concentrations, then the corresponding mathematical model is the following:

$$(1.6) \quad \begin{cases} \frac{d[E_1]}{dt} = -(k_1 + k_2)[E_1] \\ \frac{d[E_2]}{dt} = k_1[E_1] - k_3[E_2] + k_{-3}[E_3] \\ \frac{d[E_3]}{dt} = k_2[E_1] + k_3[E_2] - k_{-3}[E_3] \end{cases}$$

In the mutarotation of Glucose example, the O.D.E. associated system matrix [2] is:

$$(1.7) \quad A_1 = \begin{pmatrix} -k_1 & k_{-1} \\ k_1 & -k_{-1} \end{pmatrix}$$

and in the adsorption of Carbon Dioxide ( $CO_2$ ) over Platinum ( $Pt$ ) surfaces, the O.D.E. associated system matrix is:

$$(1.8) \quad A_2 = \begin{pmatrix} -k_1 - k_2 & 0 & 0 \\ k_1 & -k_3 & k_{-3} \\ k_2 & k_3 & -k_{-3} \end{pmatrix}$$

In both cases (i.e., for matrices  $A_1$  and  $A_2$ ), the matrices eigenvalues are easy to compute. The eigenvalues corresponding to  $A_1$  are  $\lambda_1 = 0$  and  $\lambda_2 = -(k_1 + k_{-1}) < 0$  and for  $A_2$  are:  $\lambda_1 = 0$ ,  $\lambda_2 = -k_1 - k_2 < 0$  and  $\lambda_3 = -k_3 - k_{-3} < 0$  (see [2] for this result).

Taking into account these results, it seems that there is a null eigenvalue and all the others are negative. If this conjecture was true, then the O.D.E. system solutions would be stable but not asymptotically.

In this paper the precedent conjecture will be proved for mechanisms involving  $n$  chemical compounds, all of them only linked by reversible first order reactions. As a

final remark, the consequences of these results in the propagation of measurements errors for this kind of mechanisms will be analysed.

## 2. ANALYSIS OF MECHANISMS INVOLVING TWO, THREE OR FOUR SUBSTANCES

In this section we will consider chemical mechanisms involving two, three or four substances that will be notated as  $E_1, E_2, E_3$  and  $E_4$ . These species will be linked by all the possible reversible chemical reactions. For instance, if only two reactants  $E_1$  and  $E_2$  are involved, the corresponding mechanism consists in only one reversible reaction. The situation can be schematized as:



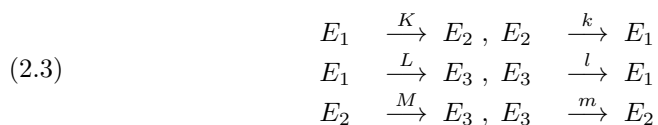
being  $K$  the kinetic constant for the direct reaction and  $k$  the corresponding one for the opposed one. It is easy to note that this mechanism is the same as (1.2), with a different notation.

In this case the characteristic equation is:

$$(2.2) \quad p(\lambda) = \det(A - \lambda I) = \det \begin{pmatrix} -K - \lambda & k \\ K & -k - \lambda \end{pmatrix} = \lambda^2 + (K + k)\lambda = 0$$

and the eigenvalues are  $\lambda_1 = 0$  and  $\lambda_2 = -(K + k) < 0$ .

If three species  $E_1, E_2$  and  $E_3$  are linked by all the possible reactions between them, the chemical mechanism will be:



where capital letters were used for the direct reactions kinetic constants and lower-case letters for the corresponding opposed reactions. The mathematical model for this mechanism is:

$$(2.4) \quad \frac{d}{dt} \begin{pmatrix} [E_1] \\ [E_2] \\ [E_3] \end{pmatrix} = \begin{pmatrix} -K - L & k & l \\ K & -k - M & m \\ L & M & -l - m \end{pmatrix} \begin{pmatrix} [E_1] \\ [E_2] \\ [E_3] \end{pmatrix}$$

In this equation, all the associated matrix columns add to zero, so its determinant is zero and  $\lambda = 0$  is one of the eigenvalues. Moreover, the characteristic equation is:

$$(2.5) \quad p(\lambda) = \det(A - \lambda I) = \det \begin{pmatrix} -K - L - \lambda & k & l \\ K & -k - M - \lambda & m \\ L & M & -l - m - \lambda \end{pmatrix} = 0$$

Algebraic manipulations lead to a third order polynomial equation of this form:

$$(2.6) \quad p(\lambda) = -\lambda^3 - a\lambda^2 - b\lambda = 0 \quad \implies \quad p(\lambda) = (-\lambda)(\lambda^2 + a\lambda + b) = 0$$

where

$$(2.7) \quad \begin{array}{l} a = K + L + M + k + l + m \\ b = KM + Kl + Km + LM + Lk + Lm + Ml + kl + km \end{array}$$

It is important to note that  $K, L, M, k, m$  and  $l$  are positive numbers since they are kinetic constants, so  $a > 0$  and  $b > 0$ . Solving equation (2.6) the following

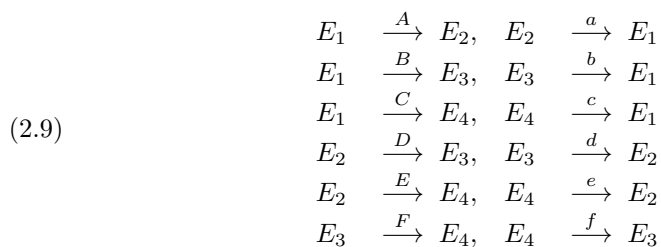
eigenvalues are obtained:

$$(2.8) \quad \lambda_1 = 0, \quad \lambda_2 = \frac{-a + \sqrt{a^2 - 4b}}{2}, \quad \lambda_3 = \frac{-a - \sqrt{a^2 - 4b}}{2}$$

The eigenvalues  $\lambda_2$  and  $\lambda_3$  depend on  $\Delta = a^2 - 4b$ , which at least in theory can be positive, negative or zero. For instance, if all the kinetic constants were the same number ( $K$ ), then  $a = K + L + M + k + l + m = 6K$  and  $b = KM + Kl + Km + LM + Lk + Lm + Ml + kl + km = 9K^2$ , so  $\Delta = a^2 - 4b = 36K^2 - 36K^2 = 0$ . From the stability view point, the sign of  $\Delta = a^2 - 4b$  is irrelevant, since in all cases  $\text{Re}(\lambda_2) < 0$  and  $\text{Re}(\lambda_3) < 0$  because  $a > 0$  and  $b > 0$  then, the O.D.E. system has a null eigenvalue and the other two have a negative real part. As a consequence, all the solutions are stable, but not asymptotically.

The last result admits an interesting generalization for the eigenvalues of the associated matrix: if all the reactions involved in the mechanism are first order unimolecular reactions reversible or not then, for every eigenvalue  $\lambda$  it can be proved that  $\text{Re}(\lambda) \leq 0$  and  $\text{Re}(\lambda) = 0$  if and only if  $\lambda = 0$ . This result is a consequence of the general form of the associated matrix obtained through an inverse modelling approach [3] [4] and the Gershgorin circle theorem (see [5] for more details).

Finally, if four chemical species  $E_1, E_2, E_3$  and  $E_4$  are linked by all the possible unimolecular reactions between them, the chemical mechanism will be:



and the O.D.E. system is:

$$(2.10) \quad \frac{d}{dt} \begin{pmatrix} [E_1] \\ [E_2] \\ [E_3] \\ [E_4] \end{pmatrix} = \begin{pmatrix} -A - B - C & a & b & c \\ A & -a - D - E & d & e \\ B & D & -b - d - F & f \\ C & E & F & -c - e - f \end{pmatrix} \begin{pmatrix} [E_1] \\ [E_2] \\ [E_3] \\ [E_4] \end{pmatrix}$$

Algebraic manipulations lead to a fourth order characteristic equation of this form:

$$(2.11) \quad p(\lambda) = \lambda^4 + \alpha\lambda^3 + \beta\lambda^2 + \gamma\lambda = 0 \quad \implies \quad p(\lambda) = \lambda \cdot (\lambda^3 + \alpha\lambda^2 + \beta\lambda + \gamma) = 0$$

Once again the determinant is zero and the coefficient  $\alpha$  is the sum of the kinetic constants, i.e.,  $\alpha = A + B + C + D + E + F + a + b + c + d + e + f$ . Nevertheless, for this analysis the most important coefficient is  $\gamma$ , which is a large sum of products like  $abc$ ,  $bcD$ ,  $fAE$  and  $CEF$ , among others (the whole sum consists in 64 products of three kinetic constants). If the reactions are reversible like in (2.9), all these constants are positive and so,  $\gamma > 0$  and then, the null eigenvalue is always a simple root of the characteristic equation.

Summarizing, if two, three or four substances are involved and all the reactions of the mechanism are reversible,  $\lambda = 0$  is a simple eigenvalue, and the other ones have negative real part.

## 3. A GENERAL RESULT

In the previous cases, the characteristic equations were:

$$(3.1) \quad p(\lambda) = \lambda^2 + (K + k)\lambda = 0$$

$$(3.2) \quad p(\lambda) = -\lambda^3 - a\lambda^2 - b\lambda = 0$$

$$(3.3) \quad p(\lambda) = \lambda^4 + \alpha\lambda^3 + \beta\lambda^2 + \gamma\lambda = 0$$

Note that the equations (3.1), (3.2) and (3.3) are just simplified versions of equations (2.2), (2.6) and (2.11), respectively. All of them are of the form:

$$(3.4) \quad p(\lambda) = (-1)^n \lambda^n + c_{n-1} \lambda^{n-1} + \dots + c_2 \lambda^2 + c_1 \lambda = 0$$

where  $c_1 = K + k > 0$  in equation (3.1),  $c_1 = -KM - \dots - km < 0$  in equation (3.2) and  $c_1 = abc + \dots + CEF > 0$  in equation (3.3).

Then, the sign of  $c_1$  is positive if an even number of substances react and negative if the chemical species are an odd number. It can be noted also that there are  $\binom{6}{2} = 15$  possible combinations of two kinetic constants and 9 of them are present in the coefficient  $c_1$  of equation (3.2), while in equation (3.3), 64 of the  $\binom{12}{3} = 220$  possible combinations of three kinetic constants are involved in the same coefficient.

In general, if  $n$  substances react, the absolute value of the coefficient  $|c_1|$  is a positive number, since it is a sum of products of  $n - 1$  positive kinetic constants. Being in all cases  $c_1 \neq 0$ , it can be concluded that  $\lambda = 0$  is a simple eigenvalue, while the other eigenvalues can be multiple (double, triple, etc.). On one hand, from the O.D.E. solutions point of view, the non-zero eigenvalues give linear combinations of functions like:

$$(3.5) \quad \exp(\lambda t), t \exp(\lambda t), t^2 \exp(\lambda t), \dots, t^p \exp(\lambda t)$$

depending on the algebraic and the corresponding geometric multiplicity of the eigenvalue  $\lambda$ .

Taking into account that  $\text{Re}(\lambda) < 0$ , all the functions given in (3.5) tend to zero as  $t \rightarrow +\infty$ . On the other hand, for the null eigenvalue, the corresponding exponential function  $\exp(\lambda t)$  is a constant, so the O.D.E. system solutions will be stable but not asymptotically.

## 4. CONCLUSIONS

In the precedent section it was proved that if  $n$  species react following a reversible first order reactions mechanism then the O.D.E. solutions show a weak stability (i.e., they are stable but not asymptotically).

In Chemical Kinetics experiments there are always small errors in measurements in the initial concentrations. Those errors will remain bounded, but they do not tend to vanish as the reaction proceeds.

It is important to know, whether or not, the paper results can be extended to other chemical mechanisms. It can be noted that the general result about the weak stability of the O.D.E. solutions strongly depends on the previous statement about the coefficient  $c_1$ . This argument cannot be generalized to other kind of reactions. For example, if the mechanism involves both reversible and irreversible reactions, there exist counter-examples once again, obtained through an inverse modelling approach where  $c_1 = 0$  and the null eigenvalue may be double, triple, etc. In these

cases, a weak stability result can be obtained at least for mechanisms involving two or three reactants [5], if they are linked through unimolecular first order reactions.

**Acknowledgment.** The author wishes to thank Marjorie Chaves for the useful discussions relating to this paper.

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