ELECTROCATALYTIC REACTIONS: AN INTERESTING PROBLEM OF NUMERICAL CALCULUS

Gladys Elisa GUINEO COBS
Facultad de Química, Universidad de la República, Uruguay
gladysgc@bilbo.edu.uy; gegctrini@mixmail.com

Víctor Eduardo MARTÍNEZ LUACES
Facultad de Química, Universidad de la República, Uruguay
victor@bilbo.edu.uy; victor@eiffel.fing.edu.uy

ABSTRACT

Electro – chemistry provides interesting problems for applied mathematicians. An example of this is the adsorption of Carbon Dioxide over Platinum surfaces (Mendez, E., Martins, M.E. & Zinola, CF, 1999). In fact, this problem was studied in other papers, were several methods of linear algebra, ordinary Differential Equations, Statistics and Numerical Calculus were used (Martínez Luaces, V., Zinola, F. & Méndez, E., 2001).

Now, in this paper, we try to show part of the richness of the problem (Martínez Luaces, V., 2001, b), in order to use it in Numerical Calculus courses for Chemical Engineering and other chemical careers.

Important concepts as numerical derivatives, and typical processes as fitting curves and determining coefficients numerically (Mathsoft Incorporated, 1999), can be illustrated in the context of this scientific and technological problem, closely related with other disciplines of these careers.

This kind of problems provides a good opportunity for interdisciplinary work, but not only in their solution. In fact, they can be taught in the same way, by a group of teachers of several disciplines. Also, it is possible to propose project – works to the students, taking parts of the problem or making small changes in order to motivate them with a real – life mathematical and chemical challenge.

We discuss results of these and other situations, experimented in the chemistry Faculty at Montevideo, Uruguay by the Mathematical Education research group ((Martínez Luaces, V., 2001, b) and (Martínez Luaces, V., 1998, a)). Taking into account all these experiences, we propose some conclusions and recommendations for this kind of mathematical service courses for chemical students.

KEYWORDS: Differential Equations, Qualitative behavior, Runge - Kutta, Electro catalytic Reactions.

1. Introduction

Electrochemistry is an interesting branch of Chemistry, which provides motivating mathematical problems of Differential Equations, Linear Algebra, Statistics and Numerical Calculus.

In this paper we will try to show part of the potential richness of one of this problems. More precisely, we will study the adsorption of Carbon Dioxide over surfaces of Platinum.

This is a very important problem to solve, due to chemical and economical reasons. In fact, adsorption, absorption and electro-deposition reduce active surface of Platinum electrodes, and this fact produces a consequently waste of money (Zinola, F., Méndez, E. & Martínez Luaces, V.,1997)

Form the Mathematical Education view point, these problems provide for Mathematics teachers a wide possibility of interaction with other subjects, in order to present real problems to their students. This kind of problems led to a better motivation, for students of Chemical Engineering, Food Technology Engineering, and other chemical careers, as it will be shown later.

2. The chemical problem and the numerical approach.

Electrodes for chemical laboratories and/or chemical industries are made of Platinum Iridium, etc.. All these metals are very expensive, in fact, they are even more expensive than gold. For this reason, it is very important to use these electrodes in the most efficient way.

Electro-chemical and electro-catalytical reactions reduce active surface of these electrodes. For example, the adsorption of Carbon Dioxide over Platinum surfaces is one of these problems studied by researchers (Méndez, E., Martins M.E., Zinola, CF., 1999)

If all reactions are electro-chemical, this problem led us to a system of Ordinary Differential Equations (O.D.E.), as follows:

$$\begin{cases} \dfrac{dA_1}{dt} = -(k+r).A_1 \\ \dfrac{dA_2}{dt} = k.A_1 - s.A_2 + u.A_3 \\ \dfrac{dA_3}{dt} = r.A_1 + s.A_2 - u.A_3 \end{cases}$$

In this system, the variable $\boldsymbol{t}$ is time, A_1, A_2, A_3 are surface-concentrations of carbon dioxide adsorbates and k, r, s, u are kinetic constants. It is important to remark that for physical and chemical reasons, all this variables and constants are always positive numbers (Zinola, F., Méndez, E. & Martínez Luaces, V.,1997).

This kind of ODE System always has a null eigenvalue and this is a consequence of the stechiometry of these reactions. This fact makes impossible to explain two inflection points (Martínez Luaces, V., 2001, a) in the experimental curves of surface-concentration vs. time (Martínez Luaces, V. & Guineo Cobs, G., to appear). So, this is not an electro-chemical process and it is necessary to postulate an electro-catalytical mechanism in order to explain it (Martínez Luaces, V., 2001, a). The O.D.E. system is the same in both cases, but in the electro-catalytical one k, r, s and u are exponential functions depending of variable time.

Then, from this problem we obtain an ODE system with constant coefficients in the electro-chemical case and another one with variable coefficients in the electro-catalytical case.

From the Mathematical Education view point, it is possible to propose a project-work in Numerical Calculus courses, based on this problem.

3. The project - work for Numerical Calculus courses

The O.D.E. system:

$$\begin{cases} \dfrac{dA_1}{dt} = -(k+r).A_1 \\ \dfrac{dA_2}{dt} = k.A_1 - s.A_2 + u.A_3 \\ \dfrac{dA_3}{dt} = r.A_1 + s.A_2 - u.A_3 \end{cases}$$

can be proposed to students of chemical careers (after modeling the chemical problem) and let them try to solve it with different kinetic constants values, using for example Runge-Kutta methods (Dahlquist, G., Bjorck, A. & Anderson, N., 1974). If coefficients remain constant (electro-chemical case), students can solve the ODE system with different non-negative values for *k, r, s* and *u.* In this case, they will realize that they cannot obtain the necessary number of inflection points. In fact, experimental curves show at least four inflection points(see graphic 1)

In the other case (the electro-catalytical one), they work with variable coefficients. More precisely, they are exponential functions like: $k(t) = k_1.e^{k_2.t}$, $r(t) = r_1.e^{r_2.t}$, $s(t) = s_1.e^{s_2.t}$ and $u(t) = u_1.e^{u_2.t}$. That means that they have now, eight values to change in the O.D.E. system.

A typical student of Chemistry, would easily realize that k_2, r_2, s_2 and u_2 must be small numbers. If he put not so small values in the exponents, curves will go up (or down) very fast, in contradiction with experimental results. For the same reason, it is not possible to assign big numbers for k_1 and the other coefficients.

Is important to remark that k_1, r_1, s_1, and u_1, are positive numbers (for chemical reasons the kinetic functions $k(\boldsymbol{t})$, $r(\boldsymbol{t})$, $s(\boldsymbol{t})$ and $u(\boldsymbol{t})$ cannot be negative, for all values of variable t), but the exponent coefficients k_2, r_2, s_2 and u_2, can be positive, negative or zero.

An exponent coefficient zero, reduces strongly the possibility of obtaining inflection points, so it is not recommendable. So, next step will be essay with positive and/or negative small numbers for the exponent coefficients.

If all the exponent coefficients are positive, then, the corresponding curve of A_1 surface concentration shows a negative concavity for small values of variable ***t***. This fact is in contradiction with experimental curves.

Graphic 2 is an example of curves that can be obtained with positive exponent coefficients.

Let's consider again the A_1 surface-concentration curve. This curve depends only on the first differential equation of the O.D.E. system, as can be easily observed. Then, only $k(\boldsymbol{t})$ and $r(\boldsymbol{t})$ determine its behavior. In particular, if k_2 and r_2 are both negative numbers, there are not inflection points in this curve (see for example, graphic 3) and if both are positive, there is an unique inflection point, as in graphic 2. Both cases do not correspond with reality, so students must try with one positive exponential coefficient and the other one must be negative.

Graphic 4 shows the numerical solutions with $k_2>0$ and $r_2<0$, and graphic 5 does the same for $k_2<0$ and $r_2>0$ (in both cases s_2 and u_2 are positive). In a first approximation, both cases (graphic 4 and graphic 5) can be acceptable.

Next step will be study the behavior of curves corresponding to A_2 and A_3 surface-concentrations. The most reasonable option would be solving numerically the O.D.E. system with all the sign possibilities, that is, four cases with $k_2>0$ and $r_2<0$ and other four cases with $k_2<0$ and $r_2>0$. These cases are shown in graphics 6 to 11 (remember that graphics 4 and 5 correspond to a pair of these combinations).

With teachers´ help, students observe that from all these graphics, there is only one case, really accurate with experimental data. This combination has $k_2<0$, $r_2>0$, $s_2<0$ and $u_2>0$, so the remaining work consists only in choosing the best numerical values for these constants and also, the best numerical values for the other coefficients, that is: k_1, r_1, s_1 and u_1 (all of them must be positive, as was mentioned before).

Graphic 12 shows the best results obtained trying with different values, taking into account the signs recommended for the exponential constants (k_2, r_2, s_2 and u_2) and for the multiplicative coefficients (k_1, r_1, s_1 and u_1). Then, the best kinetic functions will be:

$$k(t) = 0.091 \cdot e^{-0.27 \cdot t}$$

$$r(t) = 0.0031 \cdot e^{0.08 \cdot t}$$

$$s(t) = 0.31 \cdot e^{-0.07 \cdot t}$$

$$u(t) = 0.7 \cdot e^{0.007 \cdot t}$$

These final values of exponential and multiplicative constants provide a satisfactory numerical solution for the chemical problem, but for this paper, the most important thing is the process, not the results. In fact, this process can be done by students or by groups of students, with help of Numerical Calculus teachers.

This kind of oriented project-work was put into practice in several courses between 1996 and 1999, with very successful results. In fact, it is important to note that this problem (even in the electro-catalytical case) can be solved analytically (Martínez Luaces, V., 2001, a) and in several cases, coefficients and kinetic constants can be obtained using numerical derivatives, combined with statistical methods (Martínez Luaces, V., Zinola, F. & Méndez, E., 2001). For these reasons , both problems (electro-chemical and electro-catalytical) were used to propose small project-works to the students in second year courses, that is: Numerical Calculus, Statistics and Differential Equations. As we will see later, students react positively to this style of teaching based on real scientific and technological problems related with other disciplines of their careers.

4. Results.

In a previous paper (Martínez Luaces, V. & Casella, S., 1996) an expert group of teachers, researchers and university authorities were consulted about Mathematics service courses. Almost all of them mentioned the importance of real-life problems in order to motivate students of non-mathematical careers.

In concordance with experts opinion, students of chemical careers reacted positively to mathematical problems related with other subjects, as it was shown in another paper (Martínez Luaces, V., 1998, a). In fact, their answers to several questions about applications, relations with other disciplines and real-life problems, presented an interesting connection with their answers about mathematical courses motivation.

Recently, some techniques of Multivariate Statistical Analysis were used in order to compare the results obtained by teachers of the Mathematical Department at Chemistry Faculty, in Montevideo (Gómez, A. & Martínez Luaces, V., to appear).

In this case, the instrument was a list of 25 questions about teachers, programs, assessment, etc. This questionnaire was prepared specially by experts in Education of two different faculties (Chemistry Faculty and Engineering Faculty, University of the Republic of Uruguay), that worked together in this project.

The answers of the students remain anonymous and the information was processed automatically by a scanner without any participation of teachers.

The results of this study showed again that students have a good reaction to an applied approach in Mathematics. Obviously, this kind of approach makes an important change in motivation and then in the attitude of students towards Mathematics. Also, it is possible to identify a small group of very important variables: knowledge of the teacher, a good learning environment, order and management of the class and the already mentioned motivation and applied approach. These variables are not independent but their correlation is not easy to understand. For example, there are teachers with good knowledge, who are also able to give an applied approach of what they teach, but unbelievably they are not capable of motivating the students. As a consequence, the final and global result of their evaluation is not good enough. It is possible to show a large group of examples and counterexamples useful to understand the correlation between the variables listed above.

It is important to remark that in the questionnaire, two of the questions proposed asked specifically about applications to other disciplines and connections with real-life problems. A Cluster Analysis of these two questions showed a group of five teachers of the department, separate from the others, as the better ones. Four of this five teachers are professors of second year courses, that is, courses where this kind of problems were presented, discussed and used as a source of project-work for the students (Gómez, A. & Martínez Luaces, V., to appear).

5. Conclusions

Real-life problems and situations related with other subjects, are very useful for Mathematics teachers in order to motivate their students in service courses.

In case of Mathematics courses for Chemical Engineering, Food Technology Engineering, and other chemical careers, these problems can be obtained form Physical-chemistry and Electro-chemistry. These two disciplines are already known for their richness in O.D.E. and P.D.E. problems, but also they provide interesting exercises and problems for Linear Algebra, Statistics and Numerical Calculus courses, as it was showed in this paper.

Searching, developing and solving these problems need an interdisciplinary group, that in the best situation can be integrated by mathematicians and chemists. Implementation of these problems in the classroom also needs the collaboration of teachers of several disciplines.

This interdisciplinary group can work in the design of activities to be carried out in the classroom, but it would be better if this collaborative work extends to teaching and assessment of the project-works proposed to the students.

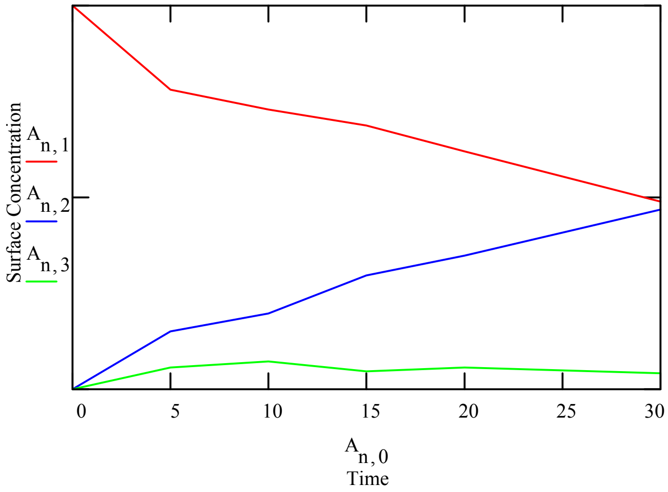
Several experiences in this direction were developed in Uruguay with excellent results (see for example (Martínez Luaces, V.,1998, b) and (Martínez Luaces, V., 2001, b)).

As it was said in an important paper of ICMI (ICMI, 1986), this collaborative teaching represents "the ideal situation" for mathematical service courses.

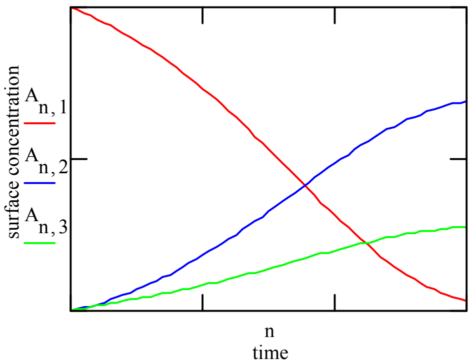
REFERENCES

- Dahlquist, G. Bjorck, A., Anderson, N., 1974, *Numerical Methods*. New Jersey: Prentice – Hall.
- Gómez, A., Martínez Luaces, V., to appear, "Evaluación docente utilizando Análisis Multivariado", *Acta Latinoamericana de Matemática Educativa.* México: CLAME (Ed.).
- ICMI 1986, "Mathematics as a service subject", *L´Enseignement Mathématique* **32**, 159-172.
- Martínez Luaces, V., Casella, S., 1996, "La educación matemática en las diferentes ramas de la Ingeniería en el Uruguay hoy", in *Memorias del II Taller sobre la enseñanza de la Matemática para Ingeniería y Arquitectura*, La Habana, Cuba: ISPJAE (Ed.).
- Martínez Luaces, V., 1998, a, "Matemática como asignatura de servicio: algunas conclusiones basadas en una evaluación docente", *Números. Revista de didáctica de matemáticas*. ***36***. 65 – 67.
- Martínez Luaces, V., 1998, b, "Considerations about Teachers for Mathematics as a Service Subject at the University" in *Pre-proceedings of the ICMI Study Conference*, Singapore: Nanyang Technological University, pp. 196-199.
- Martínez Luaces, V., 2001, a, "Reacciones electroquímicas y electrocatalíticas: un problema de Matemática Aplicada" *Actas COMAT 1999* (CD). Matanzas: UMCC. ISBN 959 - 160097 - 6.
- Martínez Luaces, V., 2001, b, "Enseñanza de matemáticas en carreras químicas desde un enfoque aplicado y motivador".*Números. Revista de didáctica de las matemáticas.**45***, 43-52.
- Martínez Luaces, V., Guineo Cobs, G., to appear "Un problema de Electroquímica y su Modelación Matemática" *Anuario Latinoamericano de Educación Química.*
- Martínez Luaces, V., Zinola, F., Méndez, E., 2001, "Problemas matemático-computacionales en el estudio de mecanismos de reacciones químicas". *Actas COMAT 95-97-99 (CD).* Matanzas: UMCC. ISBN 959 - 160097 - 6.
- Mathsoft Incorporated 1999, *MathCad 8 Student Versión,* Cambridge, MA, USA: Mathsoft Incorporated (Ed.).
- Méndez, E., Martins M.E., Zinola, CF., 1999, "New effects in the Electrochemistry of Carbon Dioxide on platinum by the application of potential perturbations". *Journal Electroanalitic. Chemistry.* ***41.*** 477.
- Zinola, F., Méndez, E., Martínez Luaces, V., 1997, "Modificación de estados adsorbidos de Anhídrido Carbónico reducido por labilización electorquímica en superficies facetadas de platino" in *Proc. Congreso Argentino de Fisicoquímica*, Tucumán, Argentina: UNT.

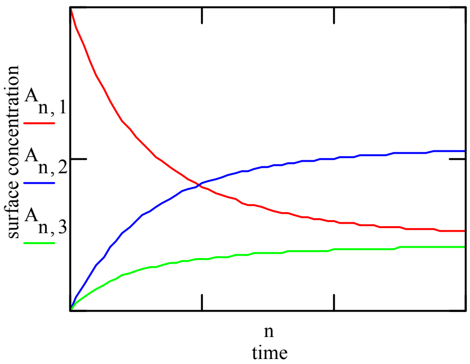
Graphic1:



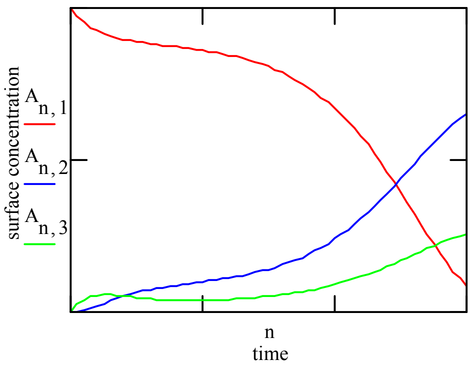
Graphic 2: $k_2>0$, $r_2>0$, $s_2>0$, $u_2>0$



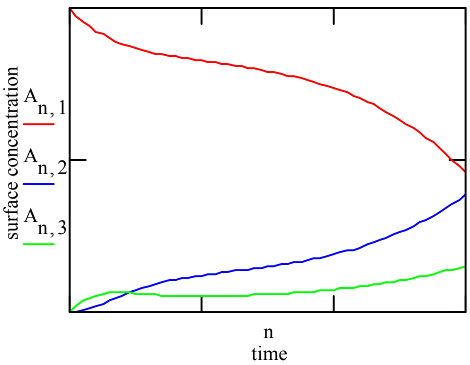
Graphic 3: $k_2<0$, $r_2<0$, $s_2>0$, $u_2>0$



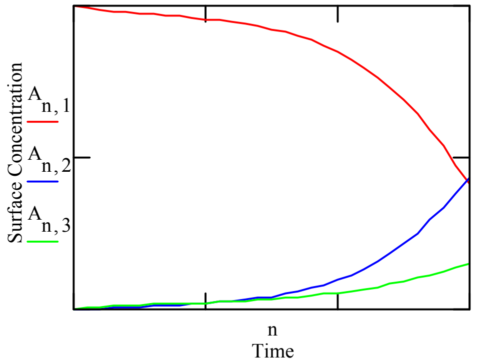
Graphic 4: $k_2>0$, $r_2<0$, $s_2>0$, $u_2>0$



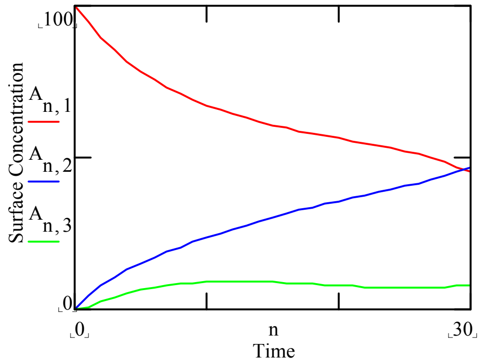
Graphic 5: $k_2<0$, $r_2>0$, $s_2>0$, $u_2>0$



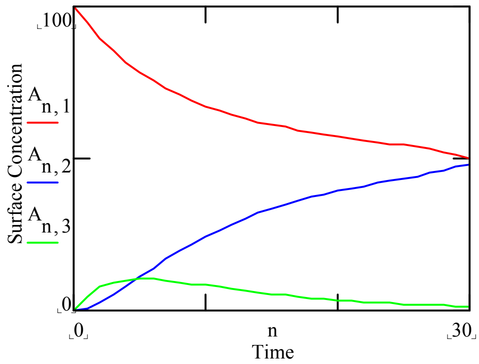
Graphic 6: $k_2>0$, $r_2<0$, $s_2<0$, $u_2<0$



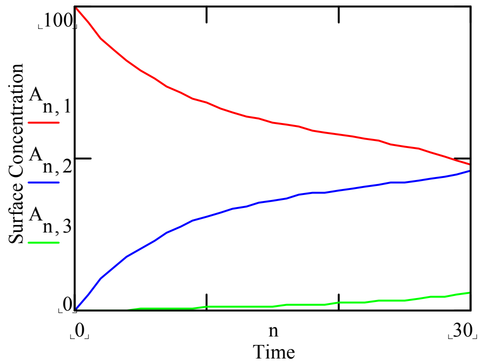
Graphic 7: $k_2<0$, $r_2>0$, $s_2<0$, $u_2<0$



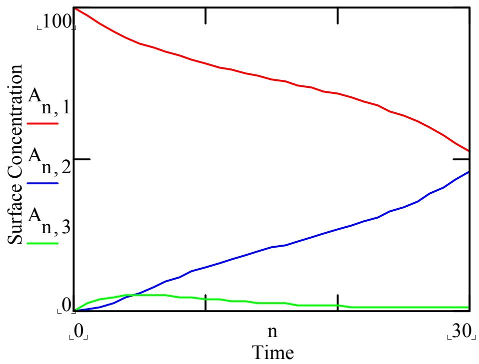
Graphic 8: $k_2>0$, $r_2<0$, $s_2>0$, $u_2<0$



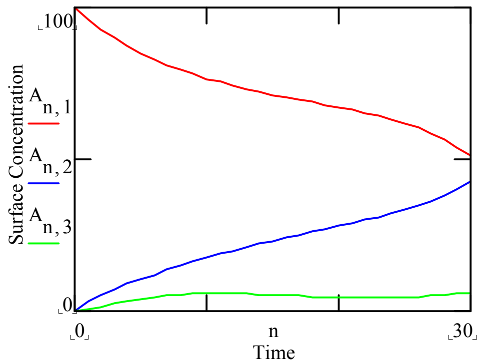
Graphic 9: $k_2<0$, $r_2>0$, $s_2>0$, $u_2<0$



Graphic 10: $k_2>0$, $r_2<0$, $u_2<0$, $s_2>0$



Graphic 11: $k_2<0$, $r_2>0$, $u_2<0$, $s_2>0$



Graphic 12

$k(t) := 0.091 \cdot e^{-0.27 \cdot t}$ $r(t) := 0.0031 \cdot e^{0.08 \cdot t}$

$s(t) := 0.31 \cdot e^{-0.07 \cdot t}$ $u(t) := 0.7 \cdot e^{0.007 \cdot t}$