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Mathematical modeling of Ru(VI)-catalyzed oxidation of alcohols by hexacyanoferrate(III)

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The title kinetics reaction has been modeled with a system of ordinary differential equations, for the concentrations of the compounds. In these equations, the velocity constants are unknown. In this work, the four constants had been evaluated by minimizing a mean squares expression comparing the experimental measures of the concentration of hexacyanoferrate(III) with the solution of the system of ordinary differential equations. This problem has not a unique solution and there is an infinite set of constants which minimize the expression. Several sets of possible constants have been analyzed. One of them has been obtained estimating two of the constants with the stationary state approach. For the model to be well posed the constants must fulfill a condition. Information about the order of magnitude of the constants has been reached.

KEY WORDS: numerical methods, optimization, ordinary differential equations, kinetics, alcohols, oxidation

1. Introduction

The study of the kinetics of alcohol oxidation by a number of oxidants using transition metal ions as catalysts has become increasingly important due to the necessity of finding economical and environmentally friendly conditions for carrying out this important transformation [1,2]. Recently, oxo-complexes of ruthenium(IV) [3], ruthenium(VI) [4], and Ru(VII) [5] have been used as homogeneous catalysts. The catalyzed oxidation of primary and secondary alcohols by the hexacyanoferrate(III) ion, in aqueous alkaline media, proceeds in such a way that the catalyst oxidizes the substrate through the formation of a Ru(VI)-substrate

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complex, which dissociates in a slow step to give the corresponding aldehyde or ketone and the reduced form of catalyst, Ru(IV) [6,7]. The role of the co-oxidant, involves catalyst regeneration in a subsequent step. A number of authors have proposed a fast step for the catalyst regeneration because a zero order is found with respect to time for hexacyanoferrate(III). However, we have previously found that the order with respect to concentration varies from zero to one on decreasing the initial concentration of hexacyanoferrate(III) [8]. This result could indicate that the catalyst regeneration step has a comparable rate to that of decomposition of the Ru(VI)-substrate complex. In previous work only two of the four velocity constants involved in the mechanism were approximated [9]. The aim of the work described here was a calculation of the four constants involved in the kinetics of reaction. So, it has been modeled with a system of ordinary differential equations for the concentrations of the compounds. The system is well posed when a condition among the constants if fulfilled. In these equations the velocity constants are unknown. They had been evaluated by minimizing a mean squares expression comparing the experimental measures of the concentration of hexacyanoferrate(III) with the solution of the system of ordinary differential equations. An infinite number of constants adjusts suitably the data to the theoretical model. Some information about the order of magnitude of the constants can be said.

2. Mathematical model

In figure 1 the mechanism proposed by Mucientes et al. for the oxidation of 2-propanol by hexacyanoferrate(III) can be seen. In this mechanism only the slow steps of the reaction will be considered. The reactants with excess of concentration will be treated as constant, in our case the concentration of 2-propanol. So, the compounds in the model are RuO_4^{2-}, (C^-2), $Fe(CN)_6^{3-}$ and $RuO_3(OH)^{3-}$, and its evolution in time is modeled by the following coupled system of ordinary differential equations:

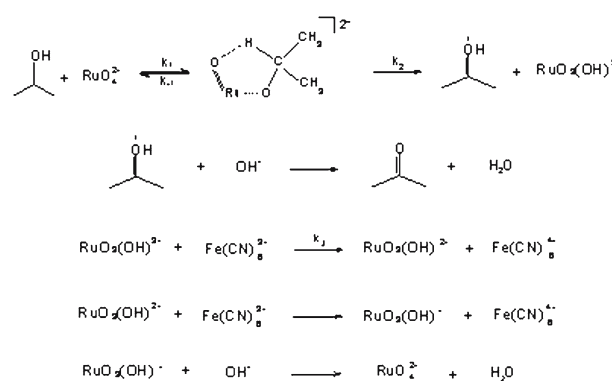

Figure 1. Mechanism of oxidation of 2-propanol catalized by RuO_4^{2-}.

$$d[RuO_4^{2-}]/dt = k_{-1}[C^{2-}] + k_3[RuO_3(OH)^{3-}][Fe(CN)_6^{3-}] - [Alcohol][RuO_4^{2-}]k_1, \quad (1)$$

$$d[C^{2-}]/dt = k_1[Alcohol][RuO_4^{2-}] - k_2[C^{2-} - k_{-1}[C^{2-}], \quad (2)$$

$$d[Fe(CN)_6^{3-}]/dt = -2k_3[RuO_3(OH)^{3-}][Fe(CN)_6^{3-}]. \quad (3)$$

For $RuO_3(OH)^{3-}$ the balance of mass for ruthenium will be used:

$$Ru_{total} = [RuO_4^{2-}]+[RuO_3(OH)^{3-}]+[RuO_3(OH)^{2-}] +[RuO_3(OH)^{-}]+[C^{2-}]. \quad (4)$$

As $RuO_3(OH)^{2-}$ and $RuO_3(OH)^{-}$ are very reactives and its concentration is very low at any time, equation (4) can be written as:

$$Ru_{total}=[RuO_4^{2-}]+[RuO_3(OH)^{3-}]+[C^{2-}] \quad (5)$$

and the concentration of $[RuO_3(OH)^{3-}]$ by:

$$[RuO_3(OH)^{3-}]=Ru_{total}-[RuO_4^{2-}]-[C^{2-}]. \quad (6)$$

Introducing this expression into equations (1) and (3), and denotating: $x_1=[RuO_4^{2-}]$, $x_2=[C^{2-}]$, and $x_3=[Fe(CN)_6^{3-}]$, the following system is obtained:

$$\begin{aligned} x_1' &= k_{-1}x_2+k_3(Ru_{total}-x_1-x_2)x_3-[Alcohol]x_1k_1, \\ x_2' &= k_1[Alcohol]x_1-(k_2+k_{-1})x_2, \\ x_3' &= -2k_3(Ru_{total}-x_1-x_2)x_3, \end{aligned} \quad (7)$$

which describes the evolution in time of the reactants described by the mechanism in figure 1.

3. Mathematical study of the differential equations

In order to study theoretically the solutions of the system of first order differential equations (7), we calculate first the fixed points (constant solutions) and next its stability properties. Equating to zero the derivatives in the system (7), the fixed points are the solutions of the following system of algebraic equations:

$$\begin{aligned} 0 &= k_{-1}x_2+k_3(Ru_{total}-x_1-x_2)x_3-[Alcohol]x_1k_1, \\ 0 &= k_1[Alcohol]x_1-(k_2+k_{-1})x_2, \\ 0 &= -2k_3(Ru_{total}-x_1-x_2)x_3. \end{aligned} \quad (8)$$

The solution of this system is unique: $x_1= 0$, $x_2= 0$, and $x_3= 0$. Therefore, there is only a fixed point ($\vec{x} = \vec{0}$).

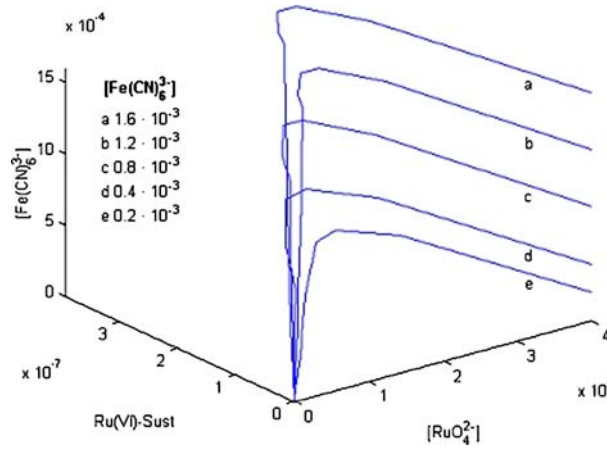

Figure 2. Evolution of the three concentrations $[RuO_4^{2-}]$M, [Ru(VI)-Sust]M, and $[Fe(CN)_6^{3-}]$M.

In order to study the stability[1] of this solution, we denote the system $\vec{x}'=\vec{F}(\vec{x})$, where $\vec{x}=(x_1, x_2, x_3)^t$ and

$$\vec{F}(\vec{x}) = \begin{pmatrix} k_{-1}x_2+k_3(\mathrm{Ru}_{\mathrm{total}}-x_1-x_2)x_3-[\mathrm{Alcohol}]x_1k_1 \\ k_1[\mathrm{Alcohol}]x_1-(k_2+k_{-1})x_2 \\ -2k_3(\mathrm{Ru}_{\mathrm{total}}-x_1-x_2)x_3 \end{pmatrix}. \tag{9}$$

We derive the jacobian matrix of $\vec{\mathrm{F}}$ at the fixed point $\vec{0}$.

$$J = \mathrm{DF}(\vec{0}) = \begin{pmatrix} -Ak_1 & k_{-1} & k_3R \\ Ak_1 & -(k_2+k_1) & 0 \\ 0 & 0 & -2k_3R \end{pmatrix}, \tag{10}$$

where $A = [\mathrm{Alcohol}]$ and $R = \mathrm{Ru}_{\mathrm{total}}$. In this case $A = 0.5\,\mathrm{M}$ and $R = 4 \times 10^{-6}\,\mathrm{M}$.

We calculate with MATLAB the eigenvalues of this matrix

$$\lambda_1 = -2k_2R, \tag{11}$$

$$\lambda_{2,3} = -\frac{1}{2}\left(Ak_1 + k_1 + k_2 \pm \sqrt{(Ak_1 - k_1 - k_2)^2 + 4Ak_1k_{-1}}\right) \tag{12}$$

the three eigenvalues are negative when $k_{-1} < k_1+k_2$. In this case the fixed point is stable and all the solutions near by tend to zero as time goes. This is the real behavior of the concentrations, therefore, the model is well posed for values of the constants such that $k_{-1} < k_1 + k_2$. This fact can be appreciated in figure 2, where several numerical solutions[2] of the system (7) have been represented for

[1]It informs about the evolution of solutions near the fixed point.
[2]Calculations done with the MATLAB subroutine for stiff systems ode15s [10,11].

$k_1 = 96$, $k_2 = 203$, $k_3 = 3.93 \times 10^4$, and $k_{-1} = 167$. As expected, the concentrations of the three compounds RuO_4^{2-}, $Ru(VI) - Sust(C^{-2})$, and $Fe(CN)_6^{3-}$, disappear with time.

4. Calculation of the velocity constants

In this part an estimation of the constants k_1, k_2, k_3, and k_{-1} of the mechanism proposed in figure 1 is done by adjusting to the experimental data in ref. [8]. The experimental measures of absorvance, A, are related to the hexacyanoferrate(III) concentration, X, through the Lambert–Beer law: $A = X \times \epsilon$. Therefore, we look for the values of k_1, k_2, k_3, and k_{-1} which minimize the function

$$F(k_1, k_2, k_3, k_{-1}) = \sum_{i=1}^{n} (X(t_i) - x_3(t_i, k_1, k_2, k_3, k_{-1}))^2, \tag{13}$$

where t_i refers to the different consecutive times in the reaction. There is not an explicit expression for x_3, but the numerical solution of the system of ordinary differential equations (7).

The optimization iterative method Levenberg–Mardquardt has been used in order to find the minima of the function F. The method has been implemented by the subroutine of MATLAB lsqcurvefit [12–15]. There are infinite solutions to this problem. Depending on the initial values of (k_1, k_2, k_3, k_{-1}), the method drives to different minima of order 10^{-9}. For instance, for $k_1 = k_2$ and $k_3 = 4.3 \times 10^4$, we find a curve of minima of the function F which can be seen in the representation of F in figure 3. In this figure, the curve of minima $k_{-1}(k_1)$ is shown in figure 4. This curve can be approximated by interpolation with a polynomial of degree four:

$$k_{-1} = -1.09 \times 10^{-6} k_1^4 + 5.35 \times 10^{-4} k_1^3 - 5.97 \times 10^{-2} k_1^2 + 2.37 k_1 + 17.95. \tag{14}$$

This approximation together with the curve can be appreciated in figure 5. A plot joining $k_{-1}(k_1)$ and $k_1 + k_2 = 2k_1$ is shown in figure 6. In this figure the condition of well posedness ($k_{-1} < k_1 + k_2$) is satisfied for values of k_1 less than 153.

As a summary, the following values of the constants produce errors in the adjusting of order 10^{-9}:

$$\begin{aligned} &k_1 \in [50, 153], \qquad k_2 = k_1, \qquad k_3 = 4.3 \times 10^4, \\ &k_{-1} = -1.09 \times 10^{-6} k_1^4 + 5.35 \times 10^{-4} k_1^3 - 5.97 \times 10^{-2} k_1^2 + 2.37 k_1 + 17.95. \end{aligned} \tag{15}$$

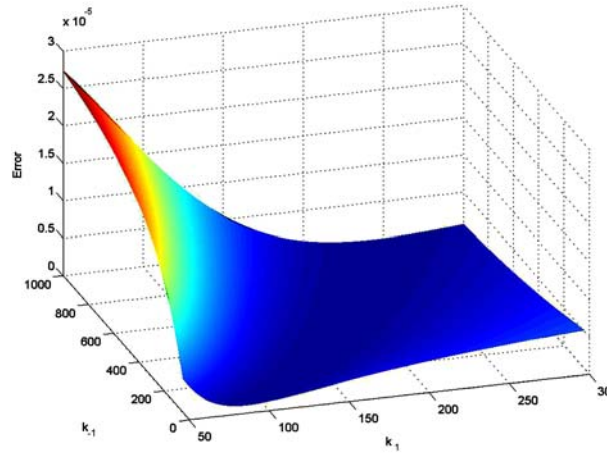

Figure 3. Error function F as a function of k_1 and k_{-1} in the case $k_2 = k_1$ and $k_3 = 4.3 \times 10^4$.

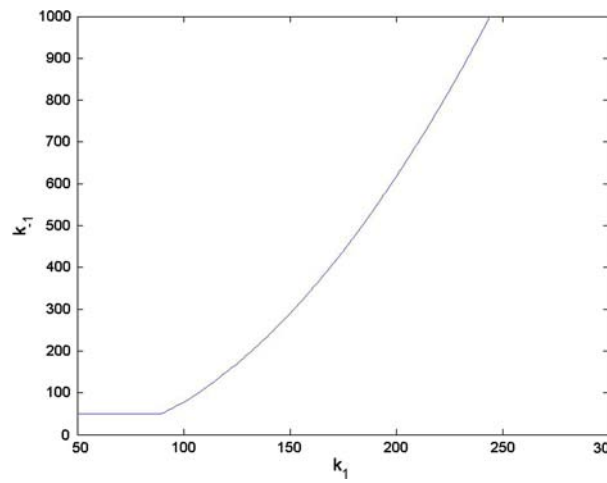

Figure 4. Curve of minima of F, $k_{-1}(k_1)$ in the case $k_2 = k_1$ and $k_3 = 4.3 \times 10^4$.

In figure 7, the approximation together with the experimental data can be seen for $k_1 = k_2 = 150$, $k_3 = 4.3 \times 10^4$, and $k_{-1} = 284$, in this picture the goodness of the adjusting is appreciated. The error is $F = 8.8 \times 10^{-9}$. In the case of a low concentration of hexacyanoferrate(III) the adjusting is worse due to the fact that the variation of absorvance for the total time of reaction is small. Any value of the constants related by the expressions (15) produces an identical approximation.

These values (15) are only an example, assuming $k_1 = 2k_1$ a different set of values would be obtained, but also in good agreement with the experimental data and errors of order 10^{-9}. Therefore, there is an infinite number of possible

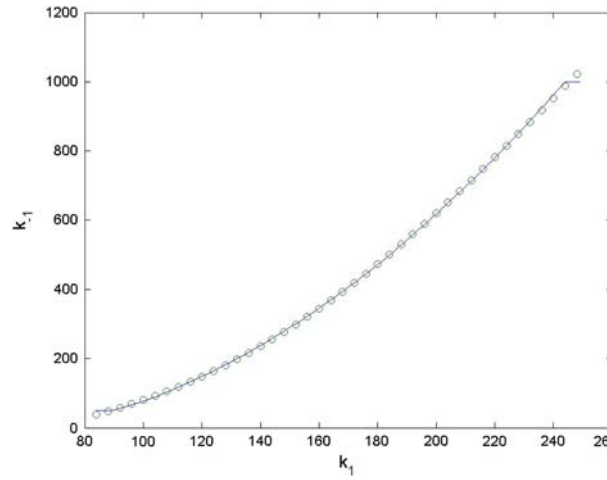

Figure 5. Curve of minima of F, $k_{-1}(k_1)$ (full line) together with the approximation by a polynomial of degree four (circles) in the case $k_2 = k_1$ and $k_3 = 4.3 \times 10^4$.

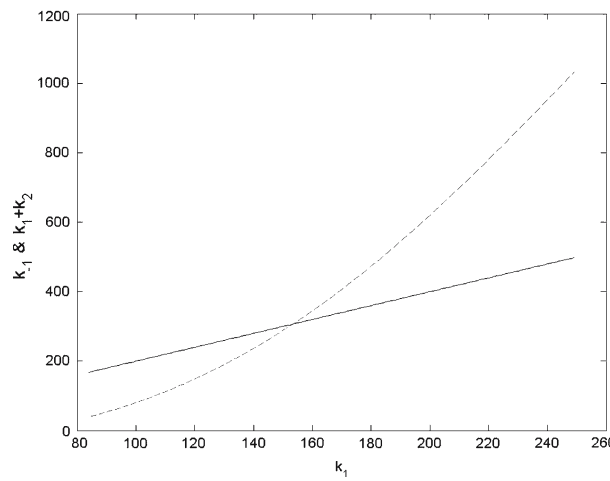

Figure 6. Curve of minima of F, $k_{-1}(k_1)$ (dashed line) together with $k_1 + k_2 = 2k_1$ (full line) in the case $k_2 = k_1$ and $k_3 = 4.3 \times 10^4$.

values of the constants for which the adjusting is good enough. What we can say certainly is the order of the different constants, so k_1, k_2, and k_{-1} are $O(10^2)$, while k_3 is $O(10^4)$.

4.1. Calculation by the stationary state approach

In ref. [8] Mucientes et al. estimate k_2 and k_3 using the stationary state approximation. These values are $k_2 = 256\,\mathrm{min}^{-1}$ and $k_3 = 3.85 \times 10^4\,\mathrm{l\,mol}^{-1}\,\mathrm{min}^{-1}$.

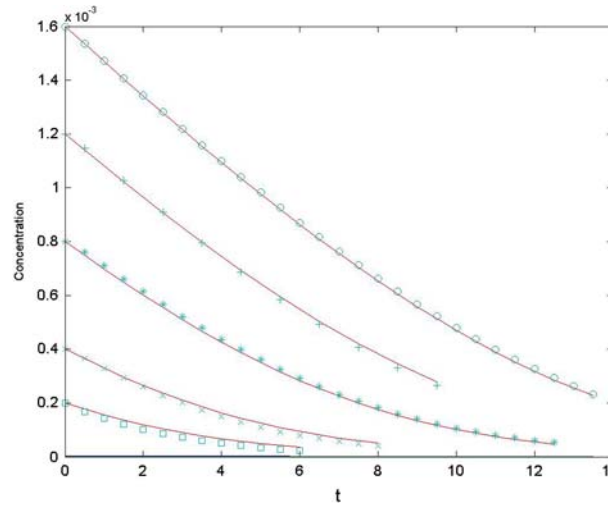

Figure 7. Theoretical and experimental concentration of hexacyaneferrate(III) for the case $k_1 = k_2 = 150$, $k_3 = 4.3 \times 10^4$, and $k_{-1} = 284$.

Keeping these values as fixed, the minimization problem is in two variables. Therefore, we look for the values of k_1 and k_{-1} which minimize the function

$$F(k_1, k_{-1}) = \sum_{i=1}^{n} (X(t_i) - x_3(t_i, k_1, k_{-1}))^2, \tag{16}$$

as in expression (13), t_i refers to the different consecutive times in the reaction and x_3 is the numerical solution of the system of ordinary differential equations (7).

A plot of this function of two variables can be observed in figure 8. Again there are not unique values of k_1 and k_{-1} which minimize the expression (16), but there is a curve of values $k_{-1}(k_1)$. This curve can be seen in figure 9. This curve can be approximated by interpolation with a straight line:

$$k_{-1} = 4.96k_1 - 257.82. \tag{17}$$

This approximation together with the curve can be appreciated in figure 10. A plot joining $k_{-1}(k_1)$ and $k_1 + k_2 = k_1 + 256$ is shown in figure 11. In this figure, the condition of well posedness ($k_{-1} < k_1 + k_2$) is satisfied for values of k_1 less than 130.

As a summary, the following values of the constants produce errors in the adjusting of order 10^{-8}:

$$k_1 \in [50, 130], \qquad k_2 = 256, \qquad k_3 = 3.85 \times 10^4, \qquad k_{-1} = 4.96k_1 - 257.82. \tag{18}$$

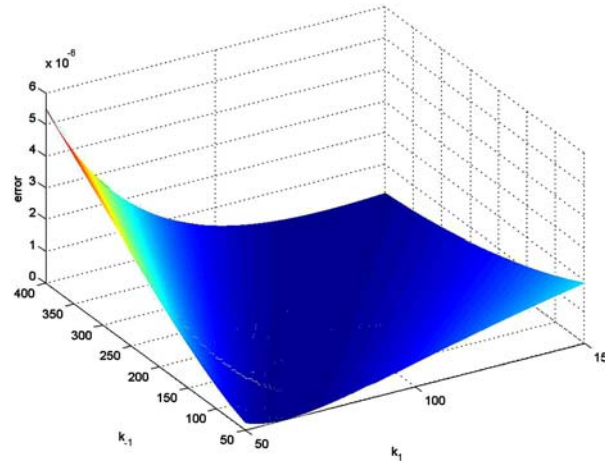

Figure 8. Error function F as a function of k_1 and k_{-1} in the case $k_2 = 256$ and $k_3 = 3.85 \times 10^4$.

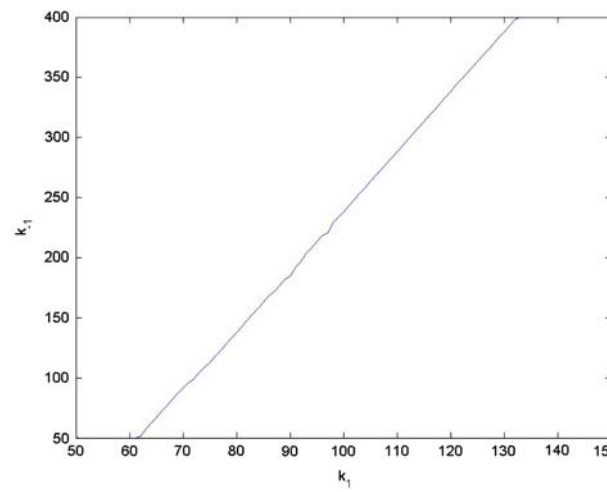

Figure 9. Curve of minima of F, $k_{-1}(k_1)$ in the case $k_2 = 256$ and $k_3 = 3.85 \times 10^4$.

In figure 12, the approximation together with the experimental data can be seen for $k_1 = 100$, $k_2 = 256$, $k_3 = 3.85 \times 10^4$ and $k_{-1} = 238$, in this picture the goodness of the adjusting is appreciated. The error is $F = 1.7 \times 10^{-8}$. In the case of a low concentration of hexacyanoferrate(III) the adjusting is worse due to the fact that the variation of absorvance for the total time of reaction is small. Any value of the constants related by the expressions (18) produces an identical approximation.

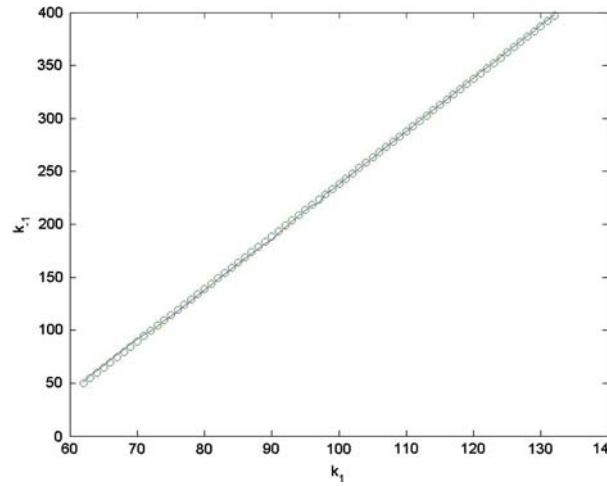

Figure 10. Curve of minima of F, $k_{-1}(k_1)$ (full line) together with the approximation by a straight line (circles) in the case $k_2 = 256$ and $k_3 = 3.85 \times 10^4$.

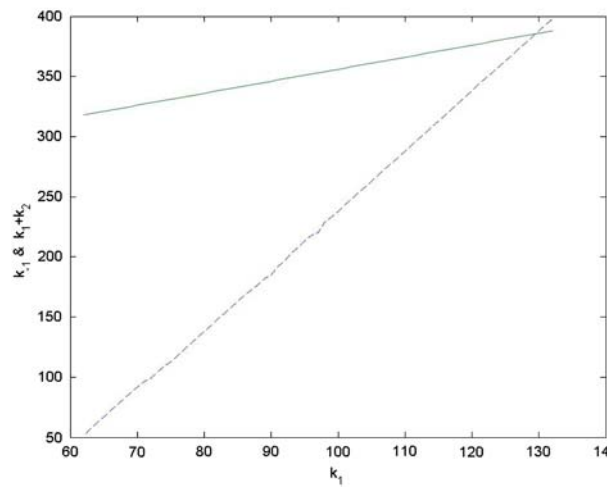

Figure 11. Curve of minima of F, $k_{-1}(k_1)$ (dashed line) together with $k_1 + k_2 = k_1 + 256$ (full line) in the case $k_2 = 256$ and $k_3 = 3.85 \times 10^4$.

4.2. Statistics

As the adjusting is nonlinear and there is not an explicit expression for the theoretical concentration, which is the numerical solution of a system of ordinary differential equations, the statistics is a mathematical research question. In

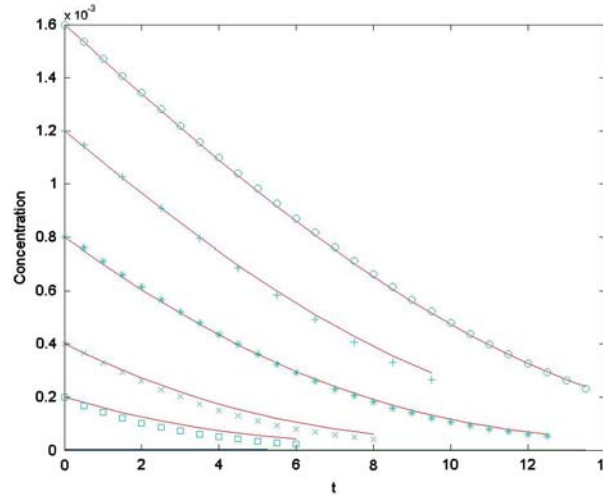

Figure 12. Theoretical and experimental concentration of hexacyaneferrate(III) for the case $k_1 = 100,\ k_2 = 256,\ k_3 = 3.85 \times 10^4$, and $k_{-1} = 238$.

ref [16, 17] a statistical parameter is proposed in order to know the goodness of the approximation

$$F_k = \frac{\sum_{i=n-k+1}^{n} (X(t_i) - x_3(t_i, k_1, k_2, k_3, k_{-1}))^2}{\sum_{i=1}^{k} (X(t_i) - x_3(t_i, k_1, k_2, k_3, k_{-1}))^2}, \tag{19}$$

where k is the round toward the nearest lower integer of $(n+3)/4$ and the subindex 'i' refers to the sequence of residuals $R_i = (X(t_i) - x_3(t_i, k_1, k_2, k_3, k_{-1}))^2$ ordered starting from the largest one: $R_1 > R_2 > \cdots > R_n$. In this case $n = 95$ and $k = 24$. With this test, the nulle hypothesis of homogeneous absolute errors ordered randomly will be rejected when F_k is too large. In table 1 the values obtained with this test are shown. For instance, in the case $k_1 = 96,\ k_2 = 203,\ k_3 = 3.93 \times 10^4,\ k_{-1} = 167$, and $F_k = 0.0132$. The values of F_k are order less than one, therefore the absolute errors are homogeneous.

Table 1
F_k parameter to show the goodness of the approximation.

k_1	k_2	k_3	k_4	F_k
150	150	4.3×10^4	284	0.0403
100	256	3.85×10^4	238	0.0137
96	203	3.93×10^4	167	0.0132

5. Conclusions

An achievement of the article is to describe a general computational methodology to evaluate a number of constants in a kinetical model of which only a numerical evaluation can be done. A mean squares problem to adjust experimental data to the numerical model depending on four kinetical constants has been solved. There is an infinite combination of these constants which produces a good approximation. Several examples of this combinations have been obtained. One of them starting from the stationary state approach. For the model to be well posed the constants must fulfill the condition $k_{-1} < k_1 + k_2$. The order of the different constants can be certainly estimated, so k_1, k_2, and k_{-1} are $O(10^2)$, while k_3 is $O(10^4)$.

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