INTERNATIONAL SYMPOSIUM ON

Chemistry of Solutions

VILLA DE LEYVA (BOYACÁ) SEPTIEMBRE 18 – 22 DE 2011

En este número de la Revista Colombiana de Química se publican, después de haber sido sometidos a evaluación por pares, algunos de los trabajos presentados en dicho Simposio

Rev. Colomb. Quím., 2012, **41**(1): 111-122

THERMOKINETIC STUDY OF THE ZERO, FIRST AND SECOND ORDER REACTIONS IN A PSEUDO-ADIABATIC CALORIMETER: Numerical approach and experimental data

ESTUDIO TERMOCINÉTICO DE LAS REACCIONES DE ORDEN CERO, UNO Y DOS EN UN CALORÍMETRO PSEUDO-ADIABÁTICO: Aproximación numérica y datos experimentales

ESTUDO TERMOCINÉTICO DAS REAÇÕES DE ORDEM ZERO, UM E DOIS NUM CALORÍMETRO PSEUDOADIABÁTICO: aproximação numérica e dados experimentais

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Recibido: 11/11/11 – Aceptado: 20/03/12

ABSTRACT

The signal produced by a pseudo-adiabatic calorimeter is simulated by numerical solution of the differential equations that model the chemical kinetics [1], the thermal properties of the calorimetric cell [2], and the response of the thermistor used as a thermometric sensor [3].

$$\frac{d[A]}{dt} = -k_i[A]^n \qquad [1]$$

$$\left(K_{cal} + C_{ps}\right)\frac{dT}{dt} = -\left(\frac{d[A]}{dt}\Delta H_r V\right) - K_t(T - T_{amb}) + w_p + i^2R_0 \qquad [2]$$

$$C_{pt}\left(\frac{dT_t}{dt}\right) = i^2\left(R_0 e^{\left[B\left(\frac{1}{T_t} - \frac{1}{T_{ref}}\right)\right]}\right) - K_t^*(T_t - T) \approx i^2R_0 - K_t^*(T_t - T) \qquad [3]$$

These equations show that the calorimetric signal is related with concentration in a complex way. Therefore, a comparison between the signals of the three basic kinetics reactions (zero, first and second order) was made, as a first step to obtain a standard procedure to follow chemical kinetics using a calorimeter. In order to help understanding this relationship, the initial rate method was applied

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to the simulated data to assess the relationship between the order and the kinetic constants calculated with those used for the simulations. As it was expected, the initial rate method for the calorimetric data, do not give a slope directly related with the order of the reaction, as it would be produced, for example, in data from a spectrophotometer. However, a linear relationship was found between what we call the "calorimetric order" and the kinetic order. Finally, the developed procedure was applied to the study of the H_2O_2 decomposition catalyzed with Fe^{3+} in homogeneous phase and with activated carbon in heterogeneous phase, finding the order and the kinetics constants of the global processes, which were in close agreement with those in the literature.

Key words: Thermokinetics, pseudo-adiabatic calorimeter, zero, first and second order kinetics, simulations, H_2O_2 decomposition.

RESUMEN

La señal producida por un calorímetro pseudo-adiabático se simuló mediante la solución numérica de las ecuaciones diferenciales que modelan la cinética química [1], las propiedades térmicas de la celda calorimétrica [2] y la respuesta del termistor que se usó como sensor termométrico [3].

$$\frac{d[A]}{dt} = -k_i[A]^n \qquad [1]$$

$$\left(K_{cal} + C_{ps}\right)\frac{dT}{dt} = -\left(\frac{d[A]}{dt}\Delta H_r V\right) - K_t(T - T_{amb}) + w_p + i^2R_0 \qquad [2]$$

$$C_{pt}\left(\frac{dT_t}{dt}\right) = i^2\left(R_0 e^{\left[B\left(\frac{1}{T_t} - \frac{1}{T_{ref}}\right)\right]}\right) - K_t^*(T_t - T) \approx i^2R_0 - K_t^*(T_t - T) \qquad [3]$$

Los resultados obtenidos de las simulaciones se usaron para hacer una comparación entre las señales de las tres cinéticas básicas (orden cero, uno y dos). Esto sirvió para establecer un protocolo de estudio de la cinética de una reacción a partir de medidas calorimétricas, lo cual resulta fundamental, ya que, como se ve en las ecuaciones anteriores, la relación entre el orden de reacción y la señal calorimétrica no es sencilla. Para esclarecer este punto, se realizó el estudio de las señales calorimétricas simuladas, empleando el método de las velocidades iniciales, y se compararon los resultados así obtenidos (orden de reacción y constante cinética) con los valores usados para las simulaciones. Como era de esperarse, los "órdenes de reacción calorimétricos" no coincidieron con los órdenes cinéticos usados en las simulaciones, como sí sucede, por ejemplo, en el caso de datos espectrofotométricos. Sin embargo, se pudo establecer una relación lineal entre el "orden calorimétrico" y el orden cinético que permite obtener el orden de reacción de un proceso que se estudia con un calorímetro. Finalmente, el procedimiento desarrollado se aplicó a los resultados calorimétricos experimentales de la descomposición del H_2O_2 catalizada en fase homogénea con Fe^{3+} y en fase heterogénea con carbón activado, encontrando los órdenes de reacción y las constantes cinéticas respectivas de cada proceso global, los cuales presentaron buena coincidencia con los valores reportados en la literatura.

Palabras clave: termocinética, calorímetro pseudo-adiabático, cinéticas de orden cero, uno y dos, simulaciones, descomposición de H_2O_2.

RESUMO

O sinal produzido por um calorímetro pseudoadiabático foi simulado mediante a solução numérica das equações diferenciais que modelam a cinética química [1], as propriedades térmicas da célula calorimétrica [2] e da resposta do termistor que foi usado como sensor termométrico [3].

$$\frac{d[A]}{dt} = -k_i[A]^n \qquad [1]$$

$$\left(K_{cal} + C_{ps}\right)\frac{dT}{dt} = -\left(\frac{d[A]}{dt}\Delta H_r V\right) - K_t(T - T_{amb}) + w_p + i^2 R_0 \qquad [2]$$

$$C_{pt}\left(\frac{dT_t}{dt}\right) = i^2\left(R_0 e^{\left[B\left(\frac{1}{T_t} - \frac{1}{T_{ref}}\right)\right]}\right) - K_t^*(T_t - T) \;\approx\; i^2 R_0 - K_t^*(T_t - T) \qquad [3]$$

Os resultados obtidos das simulações foram usados para realizar uma comparação entre os sinais das três cinéticas básicas (ordem zero, um e dois). Isso serviu para estabelecer um protocolo de estudo da cinética de uma reação a partir de medidas calorimétricas, o qual resulta fundamental, já que como se vê nas equações anteriores, a relação entre a ordem de reação e o sinal calorimétrico não é simples. Para esclarecer este ponto, foi realizado o estudo dos sinais calorimétricos simulados usando o método das velocidades iniciais e compararam-se os resultados assim obtidos (ordem de reação e constante cinética) com os valores usados para as simulações. Como era de esperar, as ordens de reação "calorimétricas" não coincidiram com as ordens cinéticas usadas nas simulações, como sucede no caso de dados espectrofotométricos. No entanto, foi possível estabelecer uma relação linear entre a ordem "calorimétrica" e a ordem cinética que permite obter a ordem de reação de um processo que se estuda com um calorímetro. Finalmente, o procedimento desenvolvido foi aplicado aos resultados calorimétricos experimentais da decomposição de H_2O_2 catalisada em fase homogênea com Fe^{3+} e em fase heterogênea com carvão ativado, encontrando as ordens de reação e as constantes cinéticas respectivas de cada processo global, os quais apresentaram boa coincidência com os valores reportados na literatura.

Palavras-chave: termocinética, calorímetro pseudoadiabático, cinéticas de ordem zero, um e dois, simulações, decomposição de H_2O_2.

INTRODUCTION

Solution calorimetry is used to obtain thermodynamic information about chemical processes (1, 2, 3). It is clear, that the kinetic information is inside the calorimetric data, but it is not so easy (or at least not so common), to obtain that information (4, 5). This paper presents an approach to obtain kinetic information from the calorimetric data. In a previous work (6), a home-made pseudo-adiabatic calorimeter was characterized, and the parameters values obtained from that study were used, in this paper, to produce simulated signals of the three basic kinetics processes: zero, first and second order. The simulated data were treated using the well know kinetic method of initial rates to achieve the order and the kinetic constants of the processes (7). In this way, we were able to compare the exact values of the kinetics constants used for simulations, with those obtained after the application of the initial rate method. After the comparison, it was possible to construct a linear relationship between the kinetic order of the reaction and what we call the "calorimetric order" of the reaction found by the initial rate method apply directly to the calorimetric data. This procedure was used with calorimetric experimental data obtained during the decomposition of the H_2O_2 catalyzed with Fe^{3+} in homogeneous phase and with activated carbon in heterogeneous phase. A satisfactory agreement was found between the values obtained using the procedure developed in this work and values in the literature (8, 9, 10). Additionally, the study of the neutralization of the NaOH with HCl, used as a patron, is presented to examine the whole process and establish a limit to the protocol, especially when the kinetics are extremely fast, as it is the case for the neutralization reaction (11).

MATERIALS AND METHODS

The calorimeter

A Dewar flask was used as a calorimetric cell, and it was submerged in a water thermostat. The whole system was inside an air thermostat. The solutions used for the experiments where inside the air thermostat contained in vessels, as it is showed in Figure 1. Additional details of the calorimeter can be seen in reference (6).

Reagents and calorimetric experiments

All reagents used were of analytical grade. NaOH was Mol Labs; H_2O_2 30 % was Panreac; activated carbon was J.T. Baker, HCl 36 % and $Fe(NO_3)_3.9H_2O$ were Merck. Adequate dilutions were used to obtain the required concentrations. Two solutions were mixed to start the reaction using the dispositive show in the center of Figure 1, numeral b.

Simulations

The simulations were made by solving, numerically, a system of three coupled differential equations. The first one comes from the general chemical reaction:

$$A \rightarrow \blacksquare$$

This can be expressed as:

$$\frac{d[A]}{dt} = -k_i[A]^n \qquad [1]$$

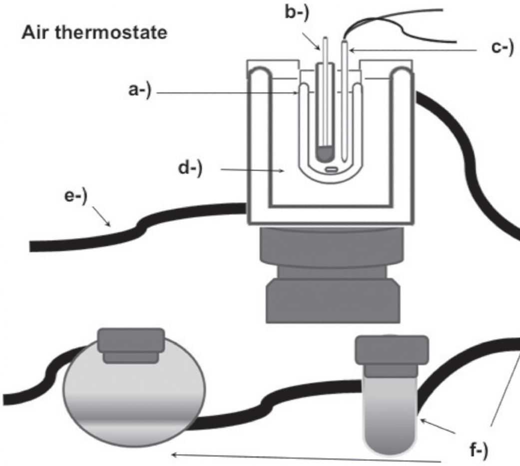

Figure 1. The calorimeter: a-) Dewar flask, b-) addition dispositive, c-) thermistor, d-) water at constant temperature (298.15 ± 0.05 K), e-) rubber tubes for circulation of water at constant temperature (298.15 ± 0.05 K) and, f-) vessels for the storage of reagents previous to the start of the reaction.

Where $[A]$ is the concentration of the reagent A, t is time, and k_i is the kinetic constant with $i = 0$, 1 or 2, depending of the kinetic order n of the reaction. The second equation represents the calorimetric cell behavior:

$$\left(K_{cal} + C_{ps}\right)\frac{dT}{dt} = -\left(\frac{d[A]}{dt}\Delta H_r V\right) - K_t(T - T_{amb}) + w_p + i^2R_0 \qquad [2]$$

Where K_{cal} is the heat capacity of the calorimetric cell, C_{ps} is the heat capacity of the solvent, T is temperature, ΔH_r is the enthalpy of the reaction, V is the volume of the reaction mixture, K_t is the overall heat transfer constant of the calorimetric cell, T_{amb} is the constant temperature of the thermostat, w_p is a term added to take account of the unspecific sources or sinks of heat (12), i is the current that flow through the thermistor and R_0 is the resistance of the thermistor at 298,15 K. The third equation represents the behavior of the thermistor used as a sensor:

$$C_{pt}\left(\frac{dT_t}{dt}\right) = i^2\left(R_0 e^{\left[B\left(\frac{1}{T_t} - \frac{1}{T_{ref}}\right)\right]}\right) - K_t^*(T_t - T) \qquad [3]$$

This can be approximated as:

$$C_{pt}\left(\frac{dT_t}{dt}\right) = i^2R_0 - K_t^*(T_t - T)$$

If the temperature of the thermistor T_t is “close” to the reference temperature T_{ref} of the thermistor, in this case 298,15 K, (“close” means no more than 3 K degrees of difference between them); C_{pt} and K_t^* are, respectively, the heat capacity and the overall heat transfer constant of the thermistor and B is a characteristic constant of the thermistor. Table 1 presents the numerical values of the parameters used for simulations. These values were found by a simplex optimization process where a calibration reaction, the neutralization of NaOH with HCl, was simulated, and the results were adjusted changing the parameters of table 1, until the agreement between the experimental data and the simulated ones was trustworthy (6).

RESULTS AND DISCUSION

The simulations show the clear effect of the kinetic order of the reaction over the calorimetric signal when the kinetic rate parameter k and the initial concentration A_0 are constant, Figure 2.

In Figure 3a, the kinetic order of the reaction is generalized to any number possible between 2 and -2. A nice sequence, from 2 to almost 0.5 order, was found and, after that, the differences in order, particularly for the negative ones, it is not clear because the differences are small. Figure 3b try to describe this issue in a most tangible way. Figure 3b is an expansion of Figure 3a.

The initial rate method. The initial rate method was used to determine the kinetic order of the reaction from calorimetric data. Simulated data for 8 kinetics orders between 0.25 and 2 every 0.25 units were tested. At each order, five different initial concentrations were used (0.014, 0.028, 0.0049, 0.057 and 0.071 M). Figure 4a shows an example for the case of first order, and Figure 4b, shows an enlargement of these simulated results. These figures describe the set of data that we used to obtain the kinetic information from the calorimetric measurements.

The initial rate method was applied to the simulated calorimetric data, and then,

Table 1. Values of the parameters used to obtain the simulated calorimetric signals.

Parameter	Symbol	Value
Reaction constant	k_i	1×10^{-1} M^{-1} s^{-1}
Reaction enthalpy	ΔH_r	-8.3×10^{4} J mol^{-1}
Heat capacity of the calorimetric cell	K_{cal}	28 J K^{-1} (a)
Overall heat constant of the calorimetric cell	K_t	6,68 J K^{-1} s^{-1} (a)
Reaction volumen	V	$3,5\times10^{-2}$ L
Non specific factors	w_p	1×10^{-3} J s^{-1} (a)
Current through the termistor	i	5.08×10^{-4} A (a)
Heat capacity of the thermistor	C_{pt}	50 J K^{-1} (a)
Overall heat constant of the thermistor	K_t^*	1 J K^{-1} s^{-1} (a)
Characteristic constant of the thermistor	B	100 K^{-1} (a)

(a) Simplex optimized value.

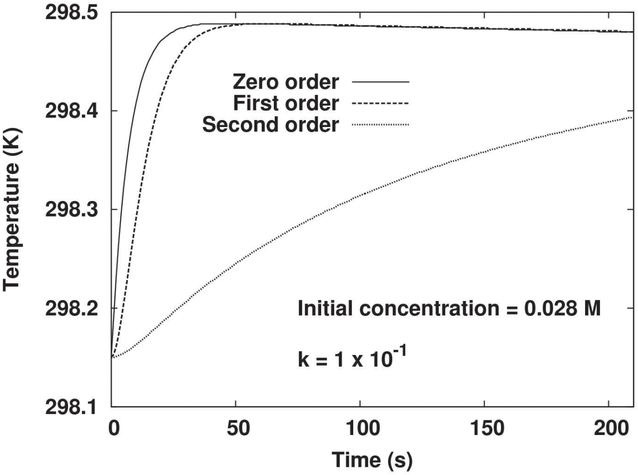

Figure 2. The effect of the kinetic order over the calorimetric signal. The kinetic constant k, and the initial concentration of A were the same in the three cases.

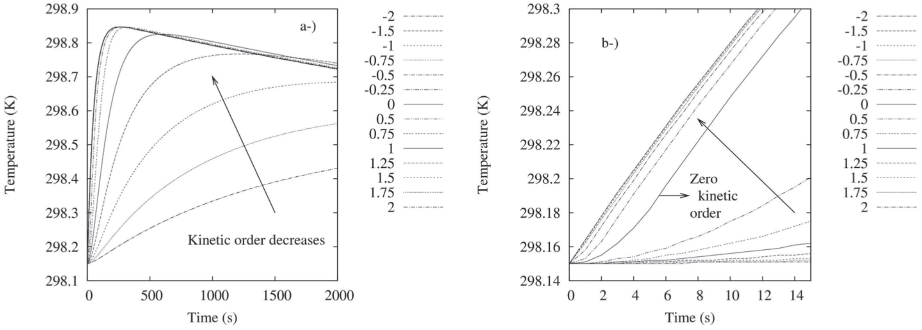

Figure 3. A generalized behavior of the calorimetric signal as a function of the kinetic order of reaction: a-) Calorimetric signal as a function of the kinetic order and, b-) the expansion of the previous figure. The kinetic constant k, and the initial concentration of A were the same in all cases.

we were able to obtain a relationship between the kinetic order of the reaction, and that we call "the calorimetric order", Figure 5.

The ideal relationship would be a straight line with slope equal to one and intercept equal to zero; instead, a straight line with slope different to one and intercept different to zero was obtained. However, this relationship is particularly useful to obtain the kinetic order of the reaction from the calorimetric data, and it can be used to obtain that information from experimental calorimetric results as we will discuss in the next part of this

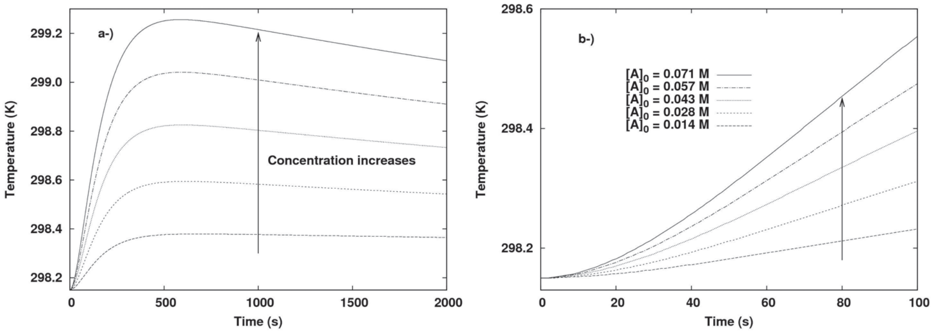

Figure 4. The effect of concentration over the calorimetric signal: a-) first kinetic order as a function of concentration and, b-) the expansion of the previous figure. The kinetic constant was 1x10^{-1} s^{-1}.

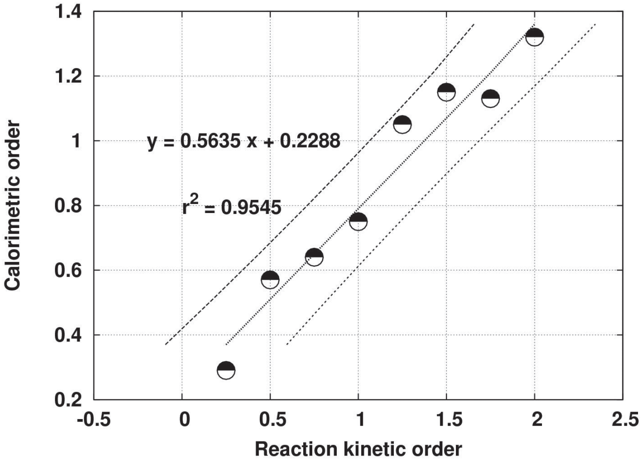

Figure 5. The relationship between the "calorimetric order" and the kinetic order of reaction. The external dashed lines are the confidence interval of the linear regression.

paper. It is important to notice, before to follow with the experimental data, that the "calorimetric order" it is not equal to the "kinetic order" because the signal in calorimetry, the right hand side of the equation [2], has more than one term, and then the slope of the log-log plot of the calorimetric data is not the kinetic order of the reaction.

Experimental results. The decomposition of H_2O_2 in homogeneous phase catalyzed by Fe^{3+} was studied experimentally using the calorimeter described previously. The experimental data was compared with the simulations for different orders finding that the overall process is a clear second order, Figure 6. Observe the slope of the log-log plot, figure 7, and compare it with Figure 5. The interpolation of the "calorimetric order", 1.316, in the calibration curve produces a kinetic order of 1.92 ≈ 2.

This behavior is consistent with a mechanism were the Fe^{3+} is an essential part of the process, see reference (6) and it can be resume in the global reaction:

$$H_2O_2 + Fe^{3+} \rightarrow Products \qquad [4]$$

Equation [4] is a second order reaction.

On the other hand, the same process catalyzed by activated carbon, a heterogeneous process, shows first kinetic order, (data are not showed because they are similar to figures 6 and 7). The experiment was made at constant concentration of H_2O_2 (0.043 ± 0.002 M) and variable quantities of activated carbon (0.2000, 0.4000, 0.6000 and 1.0000 ± 0.0003 g per 35.0 ± 0.1 ml of reaction volume). In this case, the slope of the log-log plot was 0.812 which, after interpolation in the calibration curve, produce a kinetic order of 1.03 ≈ 1 with respect to the activated carbon. This result agrees with previous studies using other techniques (10), which demonstrate the accuracy of the protocol developed to achieve the kinetic order of a reaction from calorimetric data. It must be said that these two processes of catalyzed decomposition of the H_2O_2 are complex; specially the heterogeneous one. The effect of the H_2O_2 over the surface of the activated carbon could be of different types (13, 14); but the meaning of the calorimetric data is how much is the total heat evolution of the process; there is no easy way to obtain information about the individual steps occurring during the decomposition reaction (15). Then, the kinetic information, obtained from calorimetric data is, also, the kinetic information of

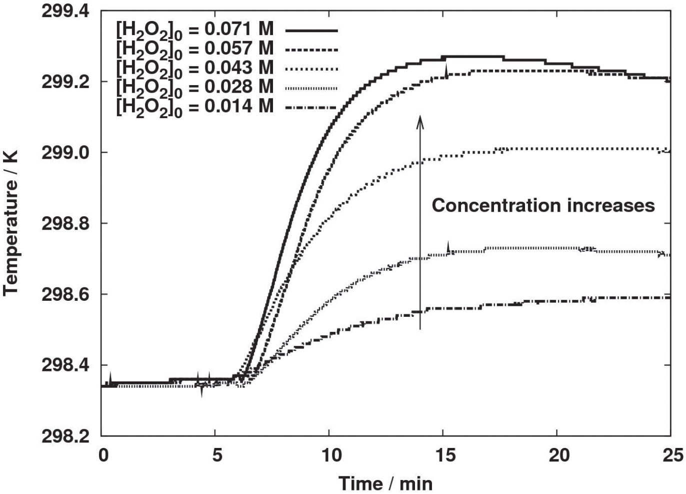

Figure 6. Experimental calorimetric data of the decomposition of H_2O_2 catalyzed with Fe^{3+}. The Fe^{3+} concentration was constant an equal to 0.038 ± 0.002 M. The uncertainty in the concentrations of H_2O_2 is also ± 0.002 M.

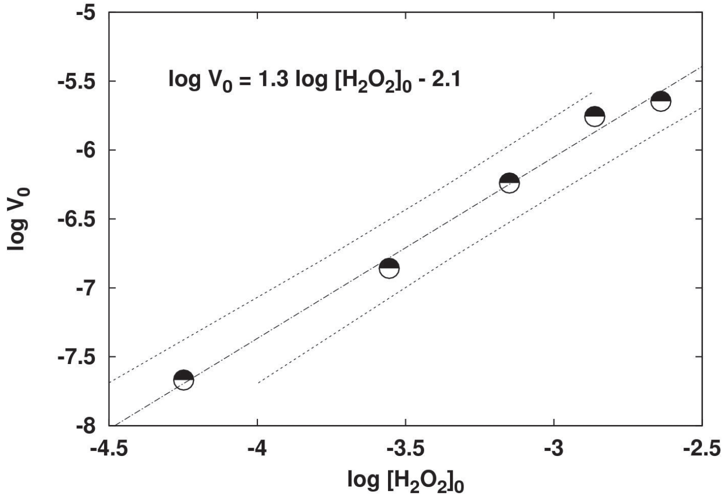

Figure 7. The initial rate method applied to the calorimetric data of figure 6, the decomposition of H_2O_2 catalyzed with Fe^{3+}. The external dashed lines are the confidence interval of the linear regression.

the total process, and the order of reaction is for the global process of decomposition of H_2O_2, including any changes of the surface or any other process involved (16).

Finally, as a way to control the whole process, and because it is a calibration reaction for the calorimeter, too; the neutralization reaction of NaOH with HCl was studied. The results showed a second order for the kinetics which is what it is expected, and a reasonable agreement in the value of the kinetic constant. However, it is necessary to mention that, due to the huge value of the second order constant of the neutralization process, it is not possible to obtain a clear distinction between zero, first or second order reactions, when the calorimeter data are taken at intervals of 1 second, as it was the case in the calorimeter used for this work. In this case, to see the difference in the calorimetric signal as a function of the kinetic order, it is necessary to collect data at time intervals in the range of the inverse of the kinetic constant of the reaction, it means at intervals around of 10^{-10} seconds. This is a warning, because the procedure to obtain the kinetic order of the reaction works only if the kinetic constant of the process under investigation, has a value that generate data in a scale of time longer than the time scale of data acquisition.

CONCLUSIONS

An easy way to relate, what we call, the "calorimetric order", with the kinetic order of the reaction was presented. The relationship was resumed in a linear equation, and it was used to obtain the kinetic order of three experimental processes: The decomposition of the H_2O_2 catalyzed by Fe^{3+} in homogeneous phase, the same process but catalyzed by activated carbon in heterogeneous phase, and the neutralization of NaOH with HCl. The latter reaction is used as a patron in calorimetry, and in this case, it was helpful to control the entire procedure, allowing to establish a limit to the applicability of the protocol developed, particularly with respect to the magnitude of the kinetic constant of the studied reaction.

ACKNOWLEDGMENTS

This work had partial financial support by the División de Investigación - DIB from Universidad Nacional de Colombia under the project HERMES code 3674. JAB thanks to Departamento de Química and Facultad de Ciencias from Universidad Nacional de Colombia for the financial support to present this work at the “International symposium on Chemistry of solutions”.

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