EXPERIMENTAL AND THEORETICAL ANALYSIS OF A CRITICAL CHEMICAL REACTION: DECOMPOSITION OF HYDROGEN PEROXIDE (H_2O_2)

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ABSTRACT: *The decomposition of hydrogen peroxide was studied using a reaction calorimeter.The solution of Iron (III) Nitrate was used as a homogeneous catalyst. The reaction rate was quantified from the course of the heat flux due to reaction measured during the experiments. To this end, the reaction rate was modeled as: a) a first order reaction, and b) an "mth" order reaction. The studies showed that the obtained results based on the assumption of a first order reaction were not good as expected, while the model based on "mth" order kinetics provided much better results and the experimental data could be well described.*

1. INTRODUCTION

The main role of hydrogen peroxide in the actual industry and the versatility that this compound presents to be used as an intermediate in many processes and also the use of hydrogen peroxide in the remediation of soils and wastewater treatment is one of the motivations for this work.

The catalyzed decomposition of the hydrogen peroxide is a subject of study to many researchers around the world. There have been several researches on the decomposition catalyzed by iron compounds. Chou and Huang [1] studied this decomposition catalyzed by iron oxide in a fluidized bed reactor. Lin and Gurol [2] studied the effects of goethite as a catalyst to the same reaction. De Laat and Gallard [3] investigated the kinetics of the homogeneous decomposition by ferric ion. All the studies cited the importance of this reaction especially to the wastewater treatment. Several models that describe the kinetics of reaction were previously presented.

This work intends to analyze the kinetics of the homogeneously catalyzed decomposition of hydrogen peroxide with ions of iron (III) using data from the heat released during the reaction, obtained by the use of reaction calorimetry. The possibility of using the heat flux data to obtain kinetic parameters lies in the energy balance that connects kinetics with the energy content of the substances.

2. THEORY

2.1. Decomposition of hydrogen peroxide

Hydrogen peroxide decomposes into water and oxygen through a disproportionation reaction:

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2 \tag{1}$$

The homogeneous decomposition catalyzed by metal ions in a low oxidation state occurs via typical free radicals reactions. The most used ions are ferrous and cuprous. The mechanism of decomposition with ferrous ion is known as the Haber – Weiss Cycle [4]:

HOOH + Fe2+ → Fe3+ + OH- + ·OH
HOOH + Fe3+ → Fe2+ + H+ + ·OOH (2)
·OOH → O2 + ·H

$$2\ H_2O_2 \xrightarrow{Fe^{2+}/Fe^{3+}} O_2 + 2\ H_2O$$

The solution with hydrogen peroxide and ferrous ions is known as Fenton's reagent and is used for the initiation of polymerizations, hydroxylation of aromatic derivatives and oxidative couplings, among others [4].

The decomposition of hydrogen peroxide is a very exothermic reaction as already presented. The heat released is sufficient to vaporize the water in the solution what makes the concentration of peroxide rise until a point at which the decomposition becomes autocatalytic, or in other words, self-sustainable [4]. This high amount of heat released makes the processes, in which hydrogen peroxide is used as an auxiliary, more difficult regarding safety aspects.

2.2. Kinetics of the decomposition of hydrogen peroxide

In the case of the decomposition of hydrogen peroxide, the reaction is regarded as irreversible, since one of the products is gaseous oxygen and it can not react back because it leaves the aqueous phase of the reaction. Taking equation (1) that represents such decomposition, the reaction rate would be formulated as:

$$r = kC_{H_2O_2} \tag{3}$$

Since in equation (3), the power of the hydrogen peroxide concentration is equal to one, this equation for the reaction rate describes a kinetic of first order for this decomposition.

Assuming that the reaction is not elementary and that it is not first order with respect to the concentration of hydrogen peroxide, the rate equation for this decomposition would be:

$$r = kC_{H_2O_2}^{m} \tag{4}$$

Equation (4) is a more general and describes an "mth" order reaction. It resumes to equation (3) when "m" is equal to unity.

In the case of a pseudo-first order, some attempts to clarify the influences of pH and the concentration of catalyst that are grouped in the kinetic constant were made. A model for a pseudo-first order kinetics with such parameters in an explicit way was presented in [5] as:

$$r = k\frac{C_{cat,init}}{C_{H^+} + 0.01}C_{H_2O_2} \tag{5}$$

2.3. Mass and energy balances

In this work, a reaction calorimeter containing a homogeneous reaction mixture was employed. To describe the development of heat fluxes due to reaction in the reaction calorimeter, a mathematical model was used as described below.

For the continuous stirred tank reactor (CSTR), it is assumed an ideal mixing condition. This means that the composition in any point of the reactor is equal and so the properties of the mixture inside the reactor are the same as in the outflow.

With the characteristics above, the mass balance with a "mth" order kinetics is:

$$V_r \frac{d(C_{H_2O_2})}{dt} + C_{H_2O_2}\frac{d(V_r)}{dt} = \dot{V}_{in} C_{H_2O_2,in} - \dot{V}_{out} C_{H_2O_2} - kC^m_{H_2O_2} V_r \tag{6}$$

Assuming that Vr is constant ($\dot{V}_{in} = \dot{V}_{out}$ and ρ=constant) and rearranging the equation above, a new variable appears. It is the division of the volumetric inflow, $\dot{V}$, by the volume of the reactor, Vr, and this is equivalent to 1/τ, where τ represents the residence time for the reactor. This residence time can be taken as the average time that the mass going into the reactor stays inside and for the assumption that Vr is constant, τ is also a constant.

$$\frac{dC_{H_2O_2}}{dt} = \frac{C_{H_2O_2,in} - C_{H_2O_2}}{\tau} - kC^m_{H_2O_2} \tag{7}$$

Initial conditions at t = 0: CH2O2 = CH2O2, init, Vr = Vr,init, $\dot{V}_{in} = \dot{V}_{out}$

The variation of the concentration with time happens only during the time that the steady state is not reached or when problems force the reactor out of the steady state. Otherwise, the steady state is followed and the differential term with respect to time is equal to zero. For a first order kinetics (m=1), the solution for this case can be done analytically. But with an "mth" order kinetics, the solution can only be done numerically.

For the energy balance, the same assumptions used to develop the mass balance hold. Also, it is assumed that there is no change in kinetics and potential energies, and that all heat fluxes and the shaft work are zero except for the heat fluxes respective to the reaction and to the cooling.

$$\frac{d(\rho V_r H)}{dt} = \dot{V}_{in}\rho H_{in} - \dot{V}_{out}\rho H_{out} + \dot{Q}_{reaction} - \dot{Q}_{cooling} \tag{8}$$

Furthermore, the enthalpy is a function of the composition, temperature and pressure, but primarily temperature [6]. So, it can be written as the product of the temperature of the system, Tr, and the average heat capacity at constant pressure of the system, Cp.

$$H = C_p T_r \tag{9}$$

It is possible to define also some equations for the heat flux. The most important heat fluxes here are the heat flux of the reaction, $\dot{Q}$reaction, and the heat flux of cooling, $\dot{Q}$cooling. They are defined as:

$$\dot{Q}_{reaction} = \Delta H_{reaction} r V_r \tag{10}$$

$$\dot{Q}_{cooling} = UA(T_r - T_j) \tag{11}$$

where: Tr is the temperature in the reactor; Tj is the temperature in the cooling system (jacket); A is the area of heat transfer; U is the overall coefficient for heat transfer of the system.

Substituting equations (9), (10) and (11), equation (8) is rearranged as the energy balance for the CSTR following a "mth" order kinetics:

$$\frac{dT_r}{dt} = \frac{(T_{r,in} - T_r)}{\tau} + \frac{\Delta H_{reaction} kC^m_{H_2O_2}}{\rho C_p} - \frac{UA(T_r - T_j)}{\rho C_p V_r} \tag{12}$$

Initial conditions at t = 0: CH2O2 = CH2O2, init, Vr = Vr,init, Tr = Tr,init, Tj = Tj,init.

2.4. Free parameters estimation

In this study, Matlab is the program used to solve numerically mass and energy balances and for the optimization of the kinetic parameters of reaction. The error function to be optimized is given by equation (13):

$$OF = \sqrt{\frac{1}{M-2}\sum_{i=1}^{M}(\dot{Q}_{\exp_i} - \dot{Q}_{reaction\ i})^2} \tag{13}$$

The concentration profile inside the reactor is used to calculate the reaction rate, r, using the same kinetics used to solve the mass balance. The reaction rate is then used to calculate the heat flux of reaction, $\dot{Q}$reaction, according to equation (10) giving the theoretical heat calculated. The heat calculated is fitted to the experimental data, $\dot{Q}$exp. The error must be as close to zero as possible so that the best values for the free parameters are obtained.

3. EXPERIMENTAL SECTION

3.1. Equipment

To quantify heat effects related to the course of the reactions, a commercially available reaction calorimeter was used (RC1, Mettler-Toledo). The double-jacketed reactor (AP01) allowed for the analysis of volumes between 0.5 and 2 L. The stirrer speed could be varied between 30 and 850 rpm. Both the jacket temperature, Tj, and the temperature of the reactor contents, Tr, could be measured precisely. This allowed for the calculation of the heat flux through the reactor wall. In this study, the isothermal mode was applied to perform experiments, i.e., Tr was kept constant.

3.2. Procedures

The conditions for the six experiments performed are summarized in table (1). The influences of hydrogen peroxide and catalyst concentration and of the initial temperature of the reactor on the reaction rate and the heat flow behavior were evaluated.

The hydrogen peroxide solution used was a 30% mass from Merck. The original solution was weighted and afterwards diluted to give the concentrations in table 1. The pH of the solution was adjusted with the addition of nitric acid, from Fluka (65 vol.%). The solution of Iron(III) Nitrate was made with the Iron(III)-nitrate nonahydrate from Merck (more than 98% pure).An experiment run was started with the solution of hydrogen peroxide in the reactor. The solution of ferric nitrate was added slowly in a semi-batch mode through the dosing pump and the addition was controlled by the computer in terms of mass. The dosing period was fixed at 30 minutes (1800 seconds) for all experiments.

Table 1. Parameters for reaction calorimetry experiments

Exp.	Conc. H_2O_2 (mol/L) $C_{H2O2,\ in}$	Vol. (L)	pH	Catalyst Dosing rate (g/min)	Amount of Catalyst dosed	T_r (°C)	Stirrer Speed (rpm)
1	2	1	0.84	3	90g at 0.5M	20	200
2	2	1	0.84	1.5	45g at 0.5M	20	200
3	1	1	0.84	3	90g at 0.5M	20	200

4	2	1	0.84	3	90g at 0.5M	15	200
5	2	1	0.84	1.5	45g at 0.5M	15	200
6	1	1	0.84	3	90g at 0.5M	15	200

4. RESULTS AND DISCUSSION

4.1. Estimation of kinetic parameters – assumption of first order kinetics (m=1)

The extraction of the reaction rate constant, k, out of the heat data from experiments was done by an algorithm written in Matlab comparing the results from the experiment with the calorimeter and the calculated heat that should be evolved, with equations previously presented. The first approach to estimate the kinetic parameters was done with the assumption that the kinetics of the hydrogen peroxide decomposition was first order regarding the concentration of hydrogen peroxide.

With a first order reaction, the only free parameter to be estimated in the model is k, since the order of reaction, m, is set to 1. To the extraction of a value for k, equation (5) [5], was used. This equation was used because of the explicit influence of pH and catalyst concentration to the kinetics of the reaction.

The values of the optimized reaction rate constant, k, and the values of the objective function, OF [equation (13)], for all experiments are presented in table 2. The closer this value is to zero, the better the optimization. This table also gives the value of kwirges previously reported by Wirges [5] for comparison.

Table 2. Values of k for the experiments performed assuming first order kinetics

Exp.	T [°C]	OF	k x 10^4 [s-1]	k_{wirges} [5] x10^4 [s-1]
1	20	3.75886	39	3.624
2		1.86852	43	
3		0.911788	47	
4	15	3.11636	15	1.715
5		0.45964	7.49	
6		0.814421	6.65	

Since the reaction rate constant is a function only of temperature, its value should not present great variation. It is possible to see that the values that present the biggest difference are the ones for experiments 1 and 4. These were also the experiments that present the worst optimization results. The values for the amount of catalyst added and for the concentration of hydrogen peroxide were the highest values used during the experiments. The best result was obtained in experiment 5.

Taking the other two experiments for each temperature, the difference between the values obtained was not significant. In fact, the difference between k from experiment 3 to 2 was 9.3%. The k for experiment 5 was 12.6% higher than k from experiment 6. However, comparing the values of k to the calculated values, kwirges, the differences were significant.

The mean value for k from experiments 2 and 3 was 0.0045. This value was almost 12.5 times higher than the value of kwirges. For experiments 5 and 6, the mean value was 0.000707 and it was 4 times higher than kwirges. Experiments 1 and 4 were not taken into consideration, because the values obtained for k were very different from the other two correspondent experiments.

4.2. Estimation of kinetic parameters – assumption of mth order kinetics

The experimental data was analyzed with an “mth” order kinetics since the results obtained with a first order kinetics could not describe the experimental data.

The results for the optimization for all experiments are presented in Figure 1. It can be seen that the calculated and measured heat flows were in very good agreement for the “mth” order reaction for all experiments.

The parameters obtained from the optimization are summarized in Table 3. The table also presents the error for the optimization, OF, equation (13).

Table 3. Values of k and m for the experiments performed assuming "mth" order kinetics.

Exp.	T [°C]	OF	m	k x 10^4	k_{wirges} x 10^4
1	20	0.3298	0.761	5.61	3.624
2		0.1878	0.714	4.46	
3		0.1796	0.945	8.18	
4	15	0.1406	0.666	2.84	1.715
5		0.0839	0.640	1.18	
6		0.0817	0.767	2.12	

It can be seen from Figure 1 and Table 3 that the values of k present a clear variance even with a better optimization result.

The values of k for the experiments 1 to 3 were bigger than the others, since for these experiments the temperature was higher. The maximal difference between the values has a factor of 2. The difference between the values of k and kwirges was not as big as the one found when assuming first order reaction. The maximal difference was seen for experiment 3 with k value around 2 times higher than kwirges.

For experiments 4 to 6, the values of k were lower since the temperature was decreased in comparison to experiments 1 to 3. The maximal difference between the values of k has a factor of 3. Also the difference between the values of k and kwirges was not as big as for the first order kinetics. The biggest difference was found in experiment 4 with k value around 1.5 times higher than kwirges.

The values obtained for m presented a variation going from 0.64 to 0.945. The highest value was obtained for experiment 3. This is the value closest to one, what would mean a first order kinetics. As seen in the previous results, experiment 3 is indeed the one that is closest to the behavior of a first order kinetics.

All other experiments presented a noticeable deviation from the first order kinetics. The values for m for these experiments were not very different.

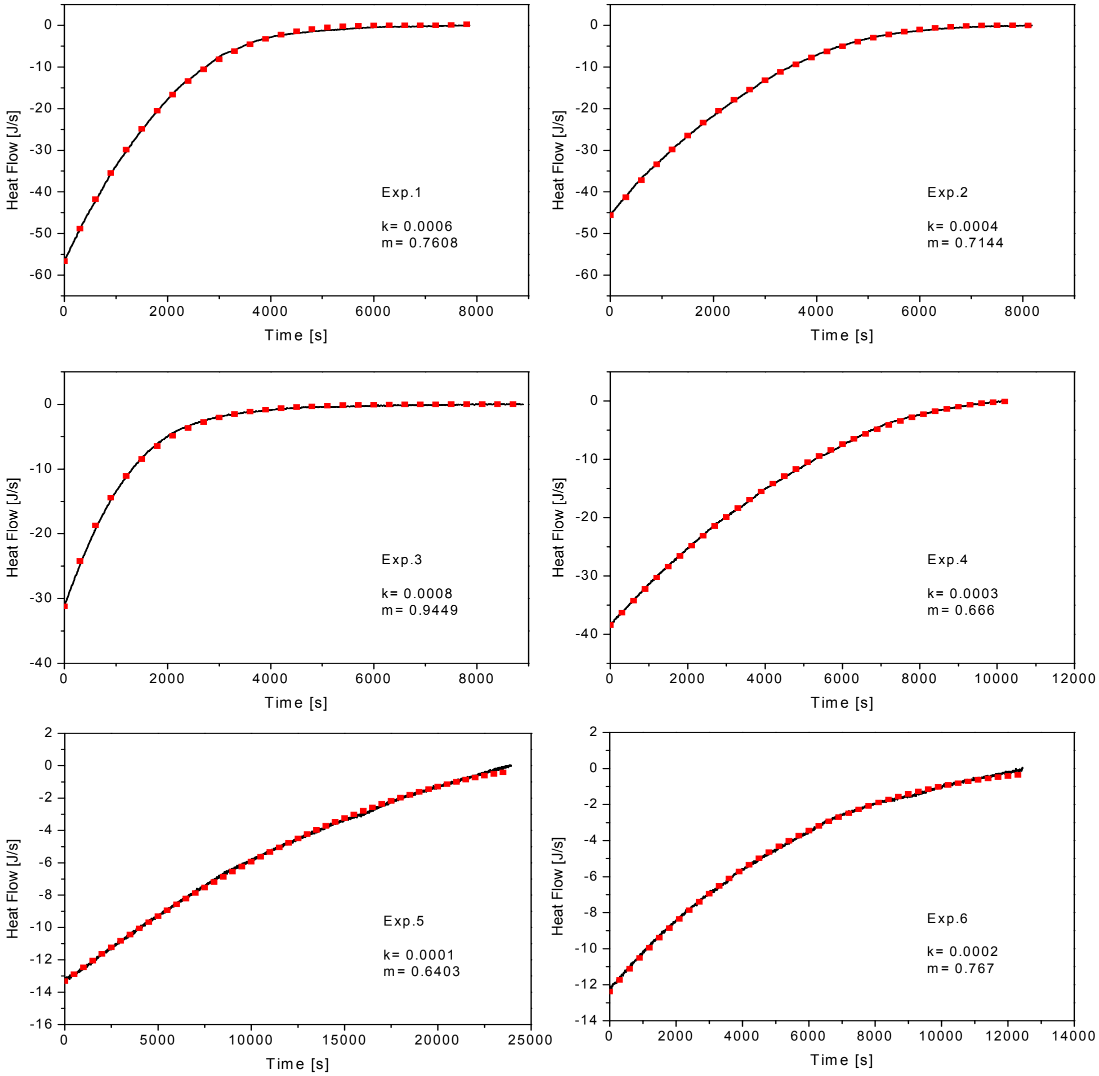

Figure 1. Optimizations for the extraction of k according to mth order kinetics – measured data: solid line; caculation: squares

5. SUMMARY AND CONCLUSIONS

The main objective of this study is the estimation of the kinetics for the decomposition of hydrogen peroxide catalyzed by ferric iron using heat flux data measured with a reaction calorimeter. This approach to kinetics study was based on the coupling of the reaction rate with mass and energy balances.

The heat data obtained from the reaction calorimetry were fitted to a mathematical model based on mass and energy balances for a batch reactor coupled by the reaction rate equation. This reaction rate was modeled as: a) a first order reaction, and b) an “mth” order reaction.

Matlab was used to solve the model equations and to compare predictions to experimental data in order to estimate the reaction rate constant, k, and the order of the reaction, m.

The application of reaction calorimetry to obtain kinetic data from reactions was found to be a very good approach. It can give a good understanding about the kinetics of the reaction based on simple experiments, without the need of constant sampling and subsequent concentration analysis.

The optimization results based on the assumption of a first order reaction were not good as expected. All rate models for the decomposition of hydrogen peroxide found in the literature were based in a first or pseudo-first order reaction with respect to the concentration of hydrogen peroxide. In this study, this behavior was not confirmed. In most articles previously published, the concentrations were not as high as the ones used in this study. Most of the works in the literature focused on the use of hydrogen peroxide for the remediation of wastewater and the concentrations were very low (in the order of 10-3 mol/L). In the present work, the conditions were different, the mechanism of reaction might have changed and the model based on a first order kinetics could not describe the experimental data properly.

The model based on "mth" order kinetics provided significantly better results and the experimental data could be well described. All orders estimated for the experiments were below 1, but there were significant differences between the individual experiments.

With a "mth" order kinetics, the values obtained for k were not constant for the same temperature. Differences of a factor of 2 for 20°C and of 3 for 15°C between the values obtained were found. Nevertheless, the average value for k at each temperature was very close to the calculated value based on Arrhenius equation with the parameters previously reported by Wirges [5].

The extraction of kinetic parameters from measured heat flux data was successful and proved that the use of such approach is possible.

NGHIÊN CỨU PHẢN ỨNG HÓA HỌC TỚI HẠN: PHẢN ỨNG PHÂN HỦY HYDRÔ PERÔXÍT (H_2O_2)

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TÓM TẮT: *Phản ứng phân hủy hydro preroxit đã được nghiên cứu bằng thiết bị đo hiệu ứng nhiệt của phản ứng (calorimeter). Xúc tác được dùng trong nghiên cứu này là dung dịch Nitrate sắt (3). Vận tốc phản ứng đã được xác định từ dòng hiệu ứng nhiệt của phản ứng đo được bằng thực nghiệm. Để xác định hằng số phản ứng, vận tốc phản ứng được mô phỏng theo hai trường hợp: a) phản ứng bậc 1 và b) phản ứng bậc m. Các nghiên cứu cho thấy rằng, kết quả thu được khi giả thiết phản ứng bậc một không tốt, trong khi đó mô hình vận tốc phản ứng dựa trên phản ứng bậc m cho kết quả tốt hơn rất nhiều và nó có thể mô phỏng chính xác kết quả thực nghiệm.*

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