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THE DECOMPOSITION OF HYDROGEN PEROXIDE
A non-linear dynamic model

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Abstract

All thermal systems are subject to problems of thermal regulation. These can be understood through the use of thermochemical systems, in particular for those in the liquid phase. A dynamic linear model was earlier applied to obtain both the reaction enthalpy and the rate constant at constant temperature for the catalytic decomposition of hydrogen peroxide. This first model did not yield a good fitting between the calculated and experimental data. The hypothesis that the rate constant was independent of temperature was too strong.

In the present study, a more elaborate, non-linear model was developed, which takes into account the rate constant variations as a function of temperature (Arrhenius law). This model allowed the activation energy to be determined. The calculated data then successfully fitted the experimental data. The literature indicates that the first-order rate law is not valid for a certain range of concentrations; the present model verified this.

The results of dynamic modelling confirm and increase the precision of results obtained in different ways. The developed model is validated through these comparisons.

Keywords: dynamic modelling, hydrogen peroxide, kinetic, thermodynamic

Introduction

A consideration of system dynamics is essential in almost all fields of study. Static studies generate interesting results, but these are insufficient in considerations of industrial or even semi-industrial environments. Dynamic and phenomenological modelling is based on an analysis of the dynamic responses of a system and on the simplified thermal balance [1].

The linear models already in existence allow the enthalpy of a reaction to be determined and the rate constant to be estimated [2].

The non-linear model presented here, based on the first-order reaction of the catalytic decomposition of hydrogen peroxide, was used to determine the activation energy and estimate the pre-exponential factor (Arrhenius law).

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Experimental approach

Dynamic modelling was first applied to the study of 'instantaneous' reactions of the acid-base type, which are not subject to rate laws [3]. The models generated are simple (linear) yet efficient, and the reaction enthalpies are determined with a good level of precision (within a 2% deviation from the values obtained by traditional calorimetric methods). Such studies can be improved by considering reactions in the liquid phase which obey a kinetic law.

The chemical reaction

The decomposition of hydrogen peroxide is an exothermic reaction occurring in the liquid phase, which obeys a first-order rate law under certain experimental conditions; it has been used to determine the kinetic data on the basis of an adiabatic method [4] which has been extensively studied [5–7].

Reactions in the liquid phase have the advantage of simplifying problems involving thermal exchange. Additionally, complex reactions such as those encountered in the food industry can often be replaced by an equivalent simplified reaction which obeys first-order kinetic laws. It is for this reason that the decomposition of hydrogen peroxide, catalysed in an acidic environment by a homogeneous catalyst, comprises an interesting test:

$$H_2O_2 \xrightarrow[HNO_3]{Fe(NO_3)_3} H_2O + 0.5O_2$$

One of the characteristic features of this reaction is that the rate law it follows depends on the concentration ratio $[H_2O_2]/[Fe^{3+}]$. Indeed, when $[H_2O_2]/[Fe^{3+}]$ is high, first-order kinetic decomposition is observed for hydrogen peroxide with respect to its concentration [8].

Barb *et al.* [5] observed that if this ratio is low, then kinetics of 3/2 are observed with respect to $[H_2O_2]$; when $[H_2O_2]/[Fe^{3+}]>100$, another kinetic dependence is observed.

For the purposes of this study, conditions were set such that a first-order decomposition with respect to peroxide was obtained [2, 3, 5].

Experiments

The reaction was carried out with hydrogen peroxide stabilized at 30%, catalysed by iron(III) nitrate nonahydrate in nitric acid solution [7] (Merck products).

Several experiments were performed at different concentrations of $[H_2O_2]$, the catalyst concentration being maintained constant.

In the work with different ratios of $[H_2O_2]/[Fe^{3+}]$, we modified only $[H_2O_2]$. The different $[H_2O_2]$ were obtained by dilution of a stock solution which was titrated with $KMnO_4$ prior to the experiments, a concentration of 9.2 mol l^{-1} being found. $[Fe^{3+}]$ was of the order of $1.4 \cdot 10^{-2}$ mol l^{-1}, the pH was set to 1.5 and the total volume was 20 cm^3 in all experiments.

The reaction took place in a 50 cm^3 glass balloon flask topped and equipped with a thermocouple linked to a computerized data collection system. The temperature of the reaction medium was recorded every second, as was the ambient temperature [8]. The medium was stirred continuously so as to ensure a homogeneous temperature, which allowed a simplified thermal balance to be obtained. The system therefore freely exchanged energy with the surrounding environment.

In the present study, this reaction was studied by the method described below in order to compare the results generated by the non-linear model with those to be found in the literature. It was hoped that this comparison would validate the experimental approach proposed here.

Dynamic modelling

The experimental approach can be summarized as modelling – identification – determination of the values sought, which is possible thanks to an understanding of the physical properties of the system and to its dynamic study.

If it is assumed that the reactor – reagent system can be represented by a single temperature, then the thermal balance is as follows:

$$MC_p\frac{dT}{dt}=-K(T-T_a)+\frac{dQ}{dt} \tag{1}$$

As the reaction is exothermic, the heat given off per unit time is

$$\frac{dQ}{dt}=-\Delta H_r V+\frac{d[H_2O_2]}{dt} \tag{2}$$

where T – system temperature (°C), T_a – ambient temperature (°C), MC_p – water equivalent thermal mass of the system (J K^{-1}), K – system/surrounding environment exchange coefficient (J K^{-1} s^{-1}), Q – quantity of heat emitted by the reaction (J), ΔH_r – reaction enthalpy (J mol^{-1}), $[H_2O_2]$ – hydrogen peroxide concentration at time t (mol l^{-1}) and V – volume of reaction mixture (l).

The decomposition of hydrogen peroxide under the experimental conditions described above obeys a first-order kinetic law [5]:

$$\frac{d[H_2O_2]}{dt}=-K_o e^{-E_a/RT}[H_2O_2] \tag{3}$$

where E_a is the activation energy of the reaction and K_o is the pre-exponential factor, which depends on the catalyst concentration [5]:

$$K_o=K'_o\frac{[Fe^{3+}]}{[H^+]+K_F} \tag{3a}$$

where K_F is the $Fe(NO_3)_3$ hydrolysis constant: $K_F=5\cdot10^{-3}$ mol l^{-1}.

By taking into account the dependence of the rate constant on temperature, we attain a non-linear system made up of two variables, temperature and concentration, for which only the former variable is measured.

Equation (1) is therefore written as

$$\frac{dT}{dt} = -\alpha(T - T_a) + \frac{\Delta HV}{MC_p} K_o e^{-E_a/RT} [H_2O_2] \qquad (4)$$

and

$$\frac{d[H_2O_2]}{dt} = -K_o e^{-E_a/RT} [H_2O_2] \qquad (3)$$

where $\alpha = K/MC_p$ is calculated by logarithmic linearization of the relaxation phase of the experimental curve [1, 3], and MC_p is obtained by modelling the relaxation plots of different masses of water [1, 8].

It should be recalled that the only information we have concerns the temperature of the reaction medium at each time t and the initial concentration $[H_2O_2]_o$.

The differential equation systems (4) and (5) are solved numerically by the Euler method [10]. That numerical method is sufficient for this work, but in a more precise and systematic future parametric identification we shall use a more precise method such as the Runge-Kutta 4th order. For the present work, the methods give the same results. The parameters ΔH, K_o and E_a are estimated by minimizing the square error between the solution $T(t)$ of the model and the experimental curve [11].

Linear modelling

To determine these parameters, we must first estimate the initialization values for the parametric identification program. To this end, we need consider only the rate constant k^* to be independent of temperature (the model is then linear) [2], and use the data recorded during the experiments. In this case, Eq. (3) becomes

$$\frac{d[H_2O_2]}{dt} = k^*[H_2O_2] \qquad (3b)$$

where

$$k^* = K_o e^{-E_a/RT} \text{ (Arrhenius law)}$$

At time $t=0$, $T(0) = T_a$ and $dT/dt = a$, where a, the slope at the origin, is measured graphically.

Under these conditions, the reaction enthalpy according to Eq. (4) is

$$\Delta H = \frac{aMC_p}{k^* V [H_2O_2]_o} \qquad (5)$$

The rate constant k^* is calculated by taking T_{max}, the maximum temperature measured at time t_{max}:

$$\frac{dT_{\max}}{dt}=0=-\alpha(T_{\max}-T_a)+\frac{\Delta H_r V k^*[H_2O_2]_{t_{\max}}}{MC_p}$$

By integrating Eq. (2), we obtain

$$[H_2O_2]_{t_{\max}}=[H_2O_2]_o e^{(-k^* t_{\max})}$$

It therefore follows that

$$k^*=-\frac{1}{t_{\max}}\left[\ln\frac{\alpha(T_{\max}-T_a}{a}\right] \tag{6}$$

and the value of ΔH can therefore be calculated (Eq. (5)).

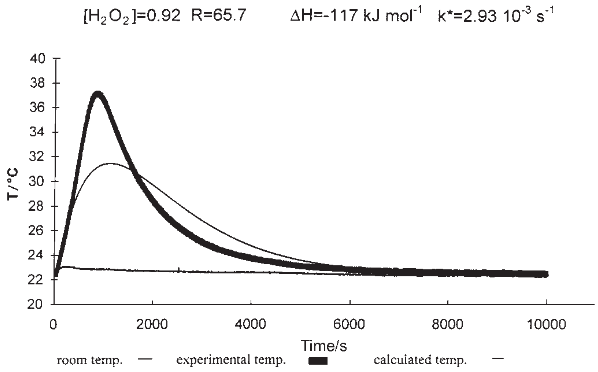

Fig. 1 Comparison between experimental and linear modelling simulations

The results obtained with the linear model give a first evaluation of the reaction enthalpy: the values of ΔH are relatively coherent and the mean is equal to 120 kJ mol^{-1}. An example is shown in Fig. 1. We were not able to obtain the enthalpy of decomposition of hydrogen peroxide from the literature, but as we have already shown for other thermochemical reactions that the enthalpy is well determined by the linear model [1, 8], we can assume that the initial value can be used to begin testing. This preliminary work also gives the parameters MC_p and α. It is important to note that, even if the shapes of the calculated and experimental data plots are somewhat similar, the hypothesis concerning the rate constant is too strong and it can be seen that this model is not appropriate (Fig. 1).

Non-linear modelling

It remains now to identify the three parameters ΔH, K_o and E_a. The way is to minimize an objective function based on the least square criterion, which takes into account the difference between the experimental curve and the solution $T(t)$ of the above equation system. The hypothesis relating to k^* is then abandoned and the rate constant is considered to be a function of temperature.

In order to simplify the identification, we vary the values K_o and ΔH, and calculate the activation energy E_a by using the following equation:

$$E_a = -RT_o \ln\left(\frac{MC_p a}{\Delta HVK_o[H_2O_2]_o}\right) \tag{7}$$

which is obtained by rewriting Eq. (4) for the following conditions:

$$T_o = T_a; \quad \left[\frac{dT}{dt}\right]_o = \frac{dT}{dt}(0) = a \text{ (slope at the origin)}$$

Several attempts are made for $1 \cdot 10^{14} < K_o < 1 \cdot 10^{19}$ according to the value given in the literature ($K_o = 1 \cdot 10^{16}$ s^{-1}). The value given by the linear model is used in Eq. (7), but that value must be varied (manual method).

The curves shown in Figs 2–7 reflect the optimization attained for the more representative experimental data and reveal the difference between the experimental results and those generated by the model following parametric identification.

The numerical results which correspond to these plots but also to other experiments are presented in Table 1. The standard deviations in Table 1 permit the simulation of experiments (least square criterion).

The following diagram represents the simulation obtained with the non-linear model.

Results and discussion

Table 1 lists the corresponding numerical results. For all the experiments, the best results were obtained with $K_o = 10^{16}$ s^{-1}.

It is known that the ratio $[H_2O_2]/[Fe^{3+}]$ determines the kinetic law of the reaction; according to the literature, this must be lower than 100 for a first-order rate. As a

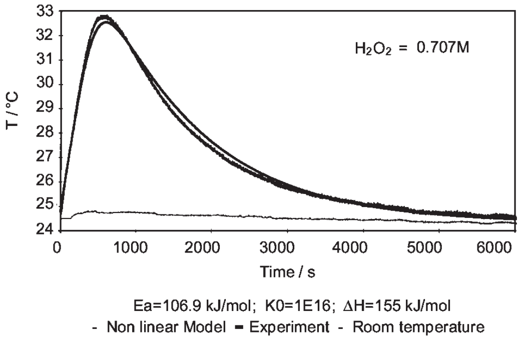

Fig. 2 Comparison between experimental and model graphs $[H_2O_2]/[Fe^{3+}]=50.5$

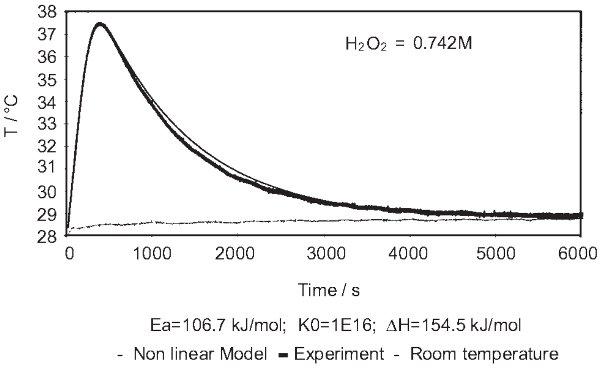

Fig. 3 Comparison between experimental and model graphs $[H_2O_2]/[Fe^{3+}]=53$

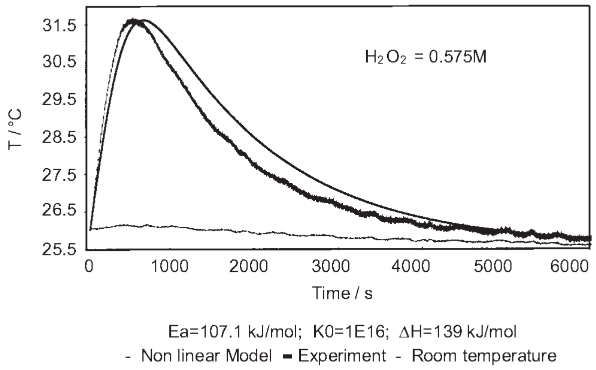

Fig. 4 Comparison between experimental and model graphs $[H_2O_2]/[Fe^{3+}]=41.1$

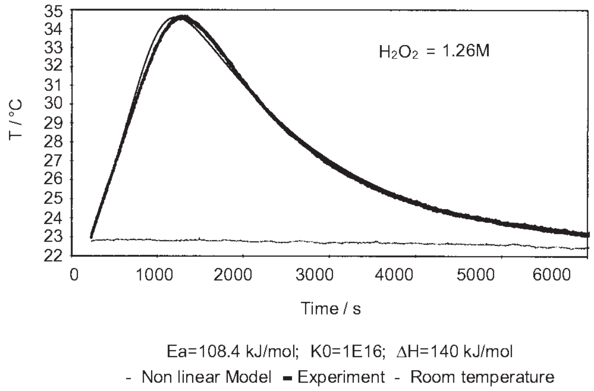

Fig. 5 Comparison between experimental and model graphs $[H_2O_2]/[Fe^{3+}]=90$

result, we carried out the experiments at a range of concentrations such that the ratio was between 100 and 36.5.

Additionally, experiments involving a ratio in excess of 100 were also processed in order to verify the first assertion.

The response generated by the model following optimization for the different $[H_2O_2]$ is, as a general rule, in accordance with the experimental temperature curve.

For low concentrations corresponding to $[H_2O_2]/[Fe^{3+}]<50$, however, the simulation curve is less satisfactory (Fig. 4 and the standard deviations in Table 1). It seems that under these conditions the first-order model no longer fits, whereas for concentration ratios >50, the curves coincide almost exactly (Figs 2, 3 and 5 and the standard deviations in Table 1).

When the ratio is near or equal to 100 (Fig. 6), the model is no longer valid.

Experiments at $[H_2O_2]>1.4$ mol l^{-1} were carried out (Fig. 7 and Table 1). The results of these experiments reveal that, as expected, first-order kinetics are no longer followed when $[H_2O_2]/[Fe^{3+}]>100$.

Table 1 Numerical results obtained by modelling

$[H_2O_2]_o$/ mol l^{-1}	$[H_2O_2]_o$/ $[Fe^{3+}]$	$10^4\alpha$/ s^{-1}	a/ K s^{-1}	MC_p/ J K^{-1}	$-\Delta H$/ kJ mol^{-1}	E_a/ kJ mol^{-1}	Standard deviation
0.511	36.5	8.0	0.0106	191.1	145.0	107.3	0.46
0.575	41.1	6.9	0.0163	190.6	139.2	107.1	0.70
0.613	43.8	7.0	0.0180	190.8	145.0	106.9	0.40
0.707	50.5	7.5	0.0203	191.0	155.0	106.9	0.17
0.742	53.0	9.2	0.0367	191.2	154.5	106.7	0.18
0.876	62.5	7.8	0.0190	190.8	152.0	105.8	0.21
0.920	65.7	8.3	0.0332	189.8	151.9	106.7	0.20
1.120	80.0	7.5	0.0116	191.0	142.5	108.6	0.11
1.195	85.0	7.4	0.0100	191.0	146.0	108.7	0.10
1.260	90.0	6.4	0.0133	191.0	140.0	108.4	0.16
1.314	94.0	8.0	0.0181	190.9	155.0	107.8	0.24
1.400	100.0	5.7	0.0951	190.9	149.3	105.2	1.20
1.703	120.0	7.9	0.0200	191.0	142.0	108.3	1.90
2.300	164.0	9.4	0.176	189.9	148.8	106.5	2.10

Table 2 compares the kinetic parameters found in the present study with those observed by other authors. Table 2 demonstrates the vast range of values given for the pre-exponential factor. It is well known that, in the study of kinetics, this parameter is very difficult to evaluate in view of its definition over a temperature range between 0 and ∞ [12]. The experimental conditions, of course, are quite different and a 'reparameterization' of the Arrhenius law is desirable. The value of K_o is high as compared with those of E_a and ΔH. As a result, the model is only weakly sensitive to variations

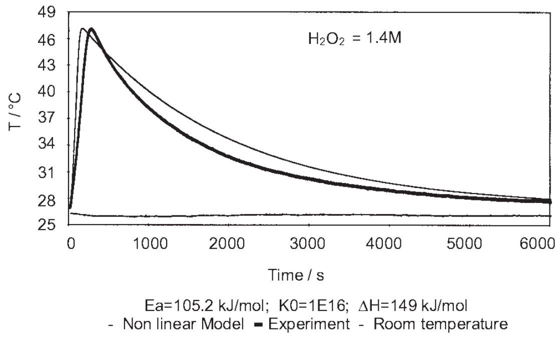

Fig. 6 Comparison between experimental and model graphs $[H_2O_2]/[Fe^{3+}]=100$

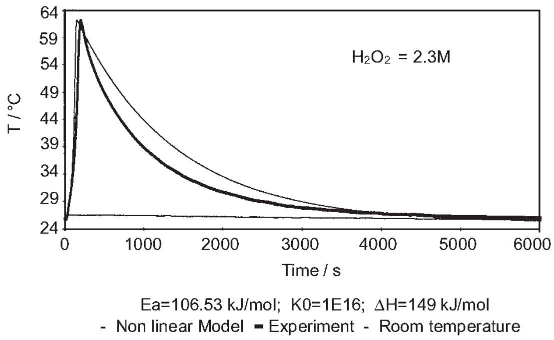

Fig. 7 Comparison between experimental and model graphs $[H_2O_2]/[Fe^{3+}]=164$

in this parameter. Indeed, a considerable variation in K_o (approximately 10^2) is necessary to cause a clear modification in the response of the model. On the basis of the literature values, the best results obtained in the present study were for $K_o=1.0 \cdot 10^{16}$ s^{-1}. A future paper will present a more precise and systematic parametric identification, using Gauss-Newton type methods to obtain ΔH, K_o and E_a independently. The kinetic order will also be determined.

It was on the basis of this value that we proceeded to determine ΔH, in order to obtain the best possible simulation of the experimental curve.

It should be noted that the values of ΔH obtained for the non-linear model did not differ considerably from those calculated by using the linear model. We recall that these latter values were our initialization parameters.

Only one value was found in the literature for the reaction enthalpy of the decomposition of H_2O_2: about 100 kJ mol^{-1} [13]. However, good agreement is observed between the values obtained, the mean of which is 148 kJ mol^{-1}. Other reactions were studied by using this modelling method and the enthalpy values conformed to those in the literature [8]; this validates the value found during this work.

The mean activation energy, as determined by the model, differs by only 2% from those obtained by other authors using more classical methods (Table 2).

Table 2 Comparison with results obtained from the literature

Authors	Analytical method	K'_o/s^{-1}	E_a/kJ mol^{-1}
Barb *et al*. [5]	Titration by $KMnO_4$	$3.6\cdot10^{14}$	100.5
Bohnson and Robertson [6]	Isothermal	$1.2\cdot10^{15}$	103.4
Hugo and Schaper [4]	Adiabatic measurement	$1.9\cdot10^{15}$	105.0
Köppner [9]	Differential thermal analysis	$3.8\cdot10^{16}$	108.0
Mean		$1.0\cdot10^{16}$	104.3
Present study	Dynamic modelling (non-isothermal conditions)	$2.6\cdot10^{16}$	106.4*

E_a is obtained by taking the mean of the activation energies given in Table 1

The results of the present study suggest that dynamic and phenomenological modelling is a simple and general method which generates results in agreement with those obtained by using other methods. This method has the advantage of simultaneously providing the kinetic parameter E_a and the reaction enthalpy.

Conclusions

The modelling process proposed in the present study needs a simplified thermal balance coupled to a proposed kinetic law, and the identification of the parameters introduced in the equations by minimizing the deviation between the numerical solutions and the experimental data (least square criterion).

It is important that if the kinetic law chosen is not the true law of the reaction, and parameter identification is never possible, then the model is validated.

The modelling is used not only to determine thermokinetic values, but also to certify the order of a reaction.

In this study, for concentration ratios $[H_2O_2]/[Fe^{3+}]$ between 50 and 100, this is a first-order reaction. Outside this concentration range, the kinetics is different and in a future study we shall seek the relevant law.

We can confirm that this represents a simple and rapid means of obtaining important thermodynamic and kinetic information on thermochemical reactions in the liquid phase.

Additionally, it is evident that the model generated is both simple and easy to use from a computerization point of view. In food and industrial processes, it is often useful to consider the complex chemical reactions involved as the automaticians' 'black box', and to replace them by equivalent global and simplified reactions. This approach is not in contradiction with the more classical chemistry studies. In fact, it represents an interesting complementary means of obtaining simple and convenient models which subsequently allow a real-time control of the processes. The results obtained here validate this approach remarkably well.

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