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KINETIC ANALYSIS FOR LIQUID-PHASE REACTIONS FROM PROGRAMMED TEMPERATURE DATA. II. SEQUENTIAL DISCRIMINATION OF POTENTIAL KINETIC MODELS *

M.I. ORTIZ URIBE [1], A. ROMERO SALVADOR [2] and A. IRABIEN GULIAS [1]

[1] *Departamento de Química Técnica, Facultad de Ciencias, Universidad del País Vasco, Apdo. 644, Bilbao (Spain)*

[2] *Departamento de Fisico-Química de los Procesos Industriales, Facultad de Ciencias Químicas, Universidad Complutense, Madrid (Spain)*

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ABSTRACT

The sequential discrimination of potential kinetic models for non-isothermal, linear programmed temperature data, has been introduced.

The influence of the initial concentration, C_0, and the heating rate, β, in the kinetic curves has been used for the sequential discrimination of the kinetic model and parameters.

A kinetic analysis at constant temperature and/or constant conversion enable us to separate the influence of the concentration and/or the temperature in the kinetic analysis from thermoanalytical curves.

This method seems to be useful and optimal for reaction analysis in the liquid phase.

Non-isothermal experiments allow a systematic approach to the kinetic behaviour of a wide range of variables, temperature and/or initial concentration, leading to a maximum knowledge of the reaction through a minimum experimental effort.

INTRODUCTION

In a kinetic investigation, it is not known a priori which is the rate-controlling step and, therefore, the form of the rate equation or the model. Also unknown, of course, are the values of the rate coefficients, k, or in other words, of the parameters of the model.

A kinetic investigation, therefore, consists mainly of two parts: model discrimination and parameter estimation. This can only be based on experimental results [1].

Exhaustive research has been carried out for the discrimination of kinetic models from isothermal kinetic data, and application of the differential method of kinetic analysis [2–6] or the integral method of kinetic analysis

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* For part I, see Thermochim. Acta, 94 (1985) 323.

[7–17]. In these works several degrees of sophistication have been considered for the objective function.

Sequential methods for optimal design of experiments have been introduced in kinetic analysis under isothermal conditions.

In the design of experiments, much is just common sense. However, when the cases are complex, a rigorous, systematic approach may be required to achieve maximum efficiency. Until recently, most designs were of the factorial type. During the last few years, however, sequential methods have been

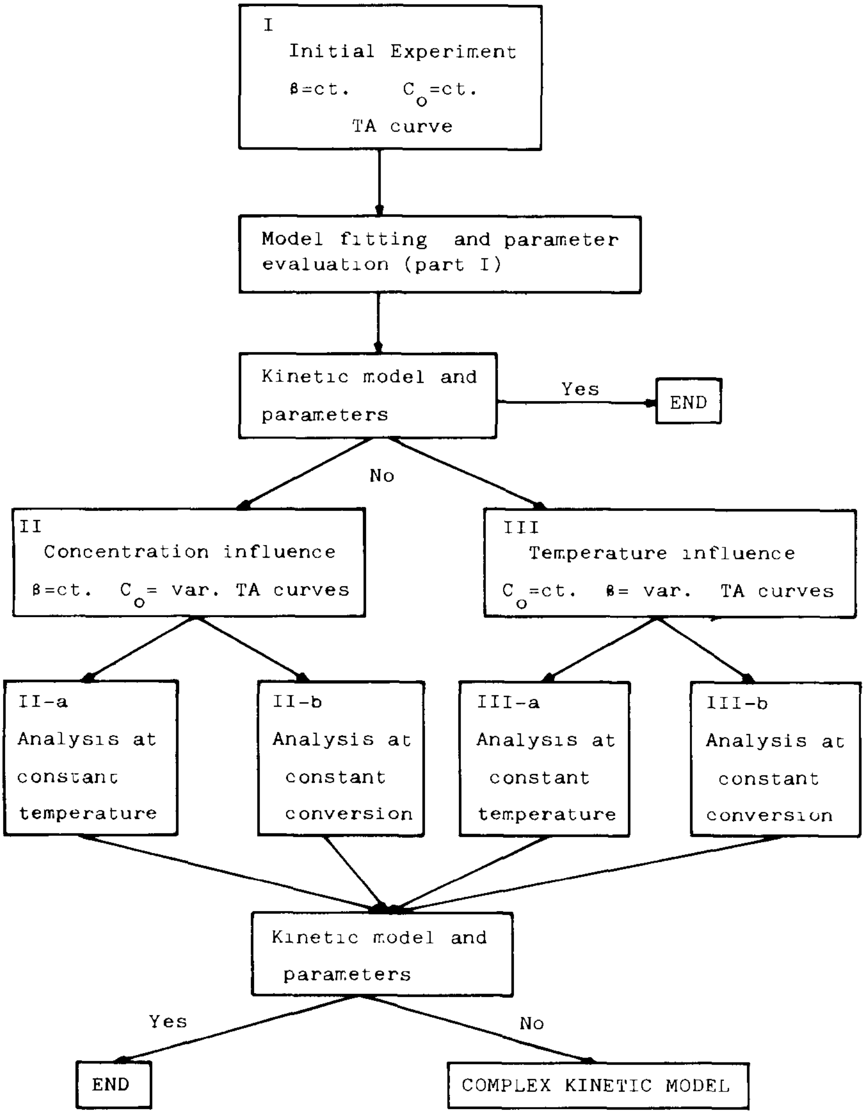

Fig. 1. Scheme of the sequential discrimination.

proposed that design an experiment taking advantage of the information and insight obtained in the previous experiments.

Two types of sequential methods have been proposed: optimal discrimination and optimal estimation.

Under isothermal conditions, Box and Hill [18] and others [19,20] have used the divergence between two rival models for an optimal discrimination. Kittrell [20] and Box and Lucas [21] have given procedures for optimal parameter estimation.

Non-isothermal experiments can be useful in carrying out optimal kinetic analysis for many reactions in the liquid phase.

In the first part a thermoanalytical method has been explained in order to fit a kinetic model and to obtain the kinetic parameters from a non-isothermal (linear temperature rise) kinetic curve.

In the simulation, the discrimination between rival models has been shown, but only a difference between correlation coefficients, which can be small, decides the selected kinetic model, so that in this work a sequential method for the design of experiments under a linear temperature programme is explained, because often the data are too scanty or are not sufficiently precise, but, even more often, the design is poor, so that the variables are not varied over a sufficient range; there is no fitting technique that can compensate for a poor experimental design.

We propose an optimal determination of a kinetic model and the kinetic parameters, in the sense that from a minimum of experimentation a maximum of information is obtained in reactions in the liquid phase with a potential kinetic law and a non-isothermal sequential method with three different steps, as it is shown in Fig. 1.

Step I has been explained in part I of this work and steps II and III will be explained in this paper.

The sequential method can avoid the experimental effort required in the conventional investigation of reaction kinetics.

KINETIC DISCRIMINATION UNDER NON-ISOTHERMAL CONDITIONS

As it has been shown in part I of this communication, the kinetic equation which expresses the relationship between the conversion, x, and the non-dimensional temperature, y, for a given reaction taking place in the liquid phase, under a linear temperature rise is

$$\mathrm{f}(x) = \frac{AT_0}{\beta C_0^{1-n}} \int_1^y \exp\left(\frac{-Ar}{y}\right) \mathrm{d}y \tag{1}$$

where, $AT_0/\beta C_0^{1-n}$ is a non-dimensional modulus and Ar is the Arrhenius number.

The kinetic data are obtained from an experiment carried out under programmed temperature at a given heating rate, β.

In part I, a theoretical method has been developed to carry out the kinetic evaluation for a given reaction by using only one non-isothermal curve.

However, in cases where the reaction-specific characteristics make it difficult to discriminate the kinetic model and to calculate the parameters, it is necessary to carry out more experimentation in order to discern the difference between the possible kinetic models.

In this paper such a sequential method of experimentation is proposed to discriminate the model and to obtain the kinetic parameters.

This method depends on the consideration that the temperature–conversion curves obtained under programmed temperature depend on the experimental variables C_0 and β. From a non-isothermal experimentation considering, either of the two variables, it is possible to obtain a series of curves that will allow us to analyse the kinetic model more exactly.

In this way, if the kinetic analysis of the initial curve is not enough to distinguish between the various kinetic models or if the calculated differences have no significance, it is possible to continue the kinetic analysis with a sequential experiment considering the initial concentration or the heating rate as variables.

Theoretical basis of the non-isothermal kinetic analysis. Initial concentration as variable

When the y value range and the β values have been taken using different values of the initial concentration, the following procedure to discriminate the kinetic model is proposed.

As a relationship exists between the $f(C)$ function and the initial concentration depending on the reaction order, n, for potential kinetic models, an observation of the kinetic y vs. x curves with different initial concentrations enable us to discriminate the $n = 1$ possibility from the others. If the kinetic x vs. y curves are superimposed, it may be concluded that the kinetic model is of first order, because in this case $f(C) = f(x)$, so that the non-dimensional modulus $AT_0/\beta C_0^{1-n}$ does not depend on the initial concentration.

When the kinetic order is other than one, a special analysis of the kinetic x vs. y curves at different values of the initial concentration must be performed.

The non-isothermal curves may be analysed in two different ways: considering the results at constant conversion or those at constant temperature.

Analysis at constant temperature

As it is shown in Fig. 2, from the experimental results of x vs. y at a given value of C_0, it is possible to obtain for each value of y a series of conversions values.

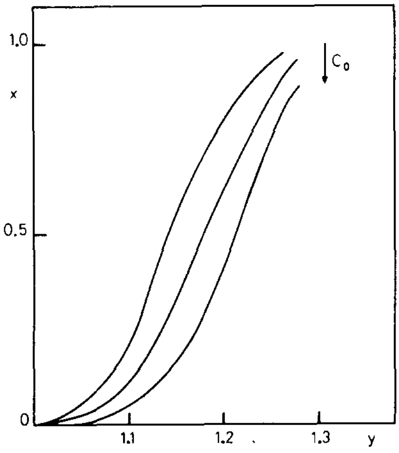

Fig. 2. Results at different initial concentrations.

The kinetic equation (1) may be expressed as follows

$$C_0^{1-n} = \frac{AT_0}{\beta} \int_1^y \exp\left(\frac{-Ar}{y} \right) f(x) \mathrm{d}y \tag{2}$$

by linearization

$$(1 - n) \ln C_0 = \ln k + \ln f(x) \tag{3}$$

where $k = AT_0/\beta \int_1^y \exp(-Ar/y) \mathrm{d}y$.

From the different fittings between ln f(x) and ln C_0 for each value of n, it will be possible to discriminate the experimental order.

A figure showing the relationship between the correlation coefficients and the fitted orders may be drawn (Fig. 3) and the n value that corresponds to the maximum correlation coefficient will determine the experimental order.

With the slope, kinetic parameters may be evaluated as follows.

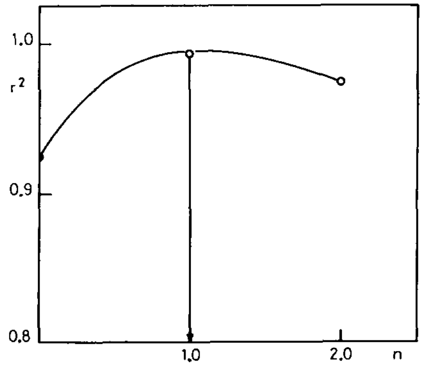

Fig. 3. Correlation coefficients for different reaction orders.

For a given value of y, an Ar number is selected and subsequently the $\int_1^y \exp(-Ar/y)\mathrm{d}y$ value may be calculated. By fitting these values against the slope by linear regression methods a series of r^2 vs. Ar values will be obtained.

From the Ar number which corresponds to the maximum r^2 value, the activation energy may be calculated exactly and from the slope of this fitting the pre-exponential factor, A, is obtained.

Analysis at constant conversion

The procedure is similar to the previous one.

The term, $AT_0/\beta f(x)$ in the equation

$$C_0^{1-n} = \frac{AT_0}{\beta f(x)} \int_1^y \exp\left(\frac{-Ar}{y}\right)\mathrm{d}y \tag{4}$$

is kept constant for each value of the conversion.

With the calculated y values it will be necessary to try different Arrhenius numbers in order to calculate the integral, I, values.

By linearization of the previous equation

$$(1-n)\ln C_0 = \ln k' + \ln I \tag{5}$$

where, $k' = AT_0/\beta f(x)$

By fitting the results to this expression using standard linear regression techniques, an r^2 vs. Ar fitting will be obtained. Simultaneously, the kinetic order, n, will be estimated.

The pre-exponential factor, A, will be calculated from the preceding slopes, $k' = AT_0/\beta f(x)$, for the $f(x)$ function which corresponds to the correct n value.

Theoretical basis of the non-isothermal kinetic analysis considering the heating rate as variable

Although by using the described method it is possible to carry out a discrimination of the kinetic model for the initial concentration influence of the reactant in the temperature–conversion results, it is not possible in some cases to obtain satisfactory results by this method, since a change in the initial concentration may change the kinetic mechanism in reactions taking place in the liquid phase and, subsequently, the kinetic model may be changed depending on the initial concentration.

In these cases the next method enables us to carry out the sequential discrimination of the kinetic models [22].

Analysis at constant temperature

The discrimination of the kinetic model takes into account the same theoretical basis as the previous method, studying the influence of the β

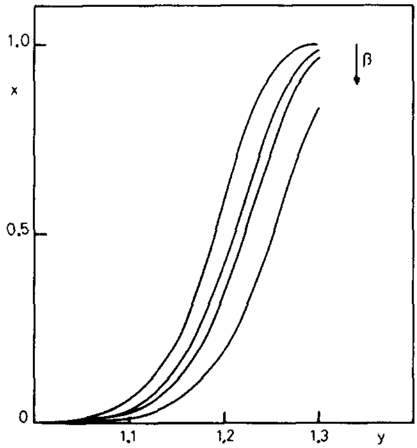

Fig. 4. Results at different heating rates.

parameter, instead of that of the C_0 parameter. The experimental curves will have the shape shown in Fig. 4.

For a given value of y, the corresponding x vs. β data can be obtained with the equation

$$\ln f(x) = \ln\frac{1}{\beta} + \ln k \tag{6}$$

where $k = AT_0/C_0^{1-n}\int_1^y \exp(\frac{Ar}{y})\mathrm{d}y$ is kept constant for each y value. Also, for a given n value, the curves shown in Fig. 5, may be drawn, as it has been shown in ref. 22.

From the fittings between the correlation coefficients and the kinetic

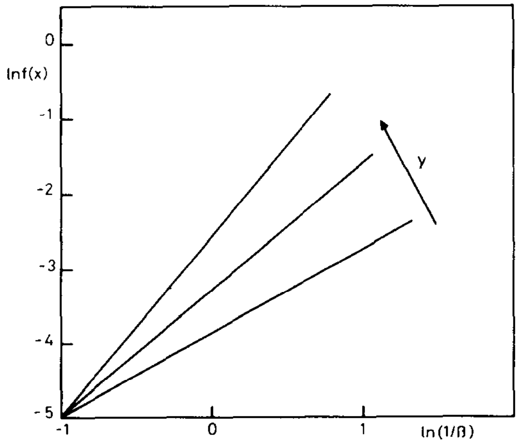

Fig. 5. Study at constant temperature.

order, the best value for the experimental results will be determined. The kinetic parameters A and E are calculated following the method described previously.

Analysis at constant conversion

This method is similar to that described above. The equation to be used is

$$\ln \beta = \ln k' + \ln I \tag{7}$$

where, $k' = AT_0/\mathrm{f}(x)C_0^{1-n}$ and $I = \int_1^y \exp(\frac{-Ar}{y})\mathrm{d}y$, by considering the β vs. y values for the chosen conversions.

In this way, it is possible in any case to discriminate the kinetic model for a reaction taking place in the liquid phase, when the experimental results are fitted well by a potential expression. An experimental procedure as well as analytical methods are proposed in order to obtain the maximum information with the minimum experimentation.

TESTING OF THE METHOD

The proposed methods have been tested using the acid-catalyzed trioxane depolymerization as an example. The activation energy, $E = 74.17$ kJ mol^{-1}, and the pre-exponential factor, $A = 5.56 \times 10^9$ min^{-1}, have been taken from the literature [23–25]. .

Taking $n = 1$, the kinetic curves have been simulated for different values of the initial concentration, C_0, and of the heating rate, β, and the proposed methods have been tested.

Initial concentration as variable

Considering $\beta = 1$°C min^{-1} the y vs. x curves have been simulated using different values of C_0. In every case the same curve has been obtained as it is shown in Fig. 6.

From these results it has been shown that the f(x) function does not depend on the initial concentration, C_0, and for this reason it may be assured that the reaction is first order with respect to trioxane.

Heating rate as variable

The y vs. x curves are simulated for $\beta = 0.5$, 0.8, 1 and 2°C min^{-1} as it is shown in Fig. 4.

Analysis at constant temperature

The first analysis is the kinetic model determination. On this basis, and using the y vs. x curves for different values of the parameter, the f(x) values

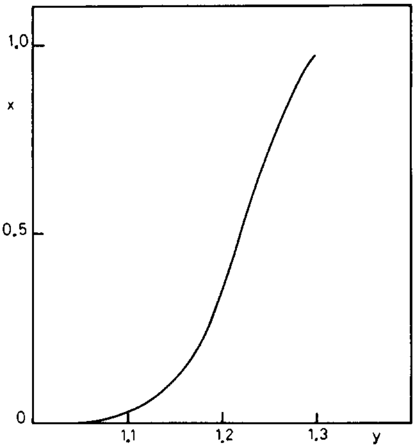

Fig. 6. Initial concentration as variable for $n = 1$.

TABLE 1

Results at constant temperature

	$n = 1$	$n = 2$	$n = 0$
$y = 1.18$	0.999	0.996	0.996
$y = 1.22$	0.999	0.977	0.974
$y = 1.26$	0.999	0.88	0.87
$y = 1.30$	0.999	0.803	0.668

which correspond to the chosen y value are calculated. In this analysis the reaction order, n, is taken as parameter. y values of 1.18, 1.22, 1.26 and 1.30 are taken in order to make the analysis cover a significant range of conversion. The results of the least-squares fittings between $f(x)$ and $1/\beta$ (from linearization of eqn. 1) are shown in Table 1.

Although the results show us that the best fit is obtained for $n = 1$, it is necessary to notice that from the data obtained when y is equal to 1.18, it is not possible to discriminate the different orders, due to the small values of the corresponding conversions for every heating rate.

The activation energy and pre-exponential factor are calculated. The values obtained are in good agreement with those taken from the literature.

Analysis at constant conversion

Since, by using the proposed method it is necessary to try different Arrhenius numbers, the equation

$$\beta = \frac{AT_0}{C_0^{1-n} f(x)} \int_1^y \exp(-Ar/y) dy \tag{8}$$

TABLE 2

Results at constant conversion

x	0.1	0.3	0.5	0.7	0.8
Ar	30.2	28.3	32.3	30.4	31.1
r^2	0.995	0.998	0.999	0.997	0.999

is solved by a series development, as shown in ref. 22, and by linearization as follows

$$\ln \frac{Ar/ET_0^2}{f(x)} - \frac{Ar}{y} = \ln \frac{\beta}{y^2} \tag{9}$$

x values of 0.1, 0.3, 0.5, 0.7 and 0.8 are taken. Linear regression of $\ln \beta/y^2$ against $1/y$ leads to the Arrhenius number, as it is shown in Table 2.

The resulting Arrhenius number is 30.5, which is in good agreement with the real one.

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