

## KINETIC ANALYSIS FOR LIQUID-PHASE REACTIONS FROM PROGRAMMED TEMPERATURE DATA. I. SIMPLE ANALYSIS OF POTENTIAL KINETIC LAWS

M.I. ORTIZ URIBE, A. ROMERO SALVADOR \* and A. IRABIEN GULIAS

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

*\* Departamento de Físico-Química de los Procesos Industriales, Facultad de Ciencias Químicas, Universidad Complutense, Madrid (Spain)*

(Received 23 April 1985)

### ABSTRACT

A general explanation of the non-isothermal methods for reaction analysis in the liquid phase has been made.

A description of the results, taking a linear temperature evolution in the reaction, is given for potential kinetic laws.

A non-isothermal thermoanalytical method with a linear temperature rise and concentration measurements in the liquid phase are proposed for the determination of the kinetic model and the kinetic parameters.

This procedure was tested against theoretical data for the depolymerization of trioxane and it was found to be satisfactory. The advantages of this method are that it is relatively simple to use and it allows the determination of the influence of both temperature and concentration on the kinetic model from one experiment.

### INTRODUCTION

A chemical reaction converts starting products into final products. Often, intermediates may appear and vanish during the experiment. The progress of the reaction, or its course, is accompanied by a change of an appropriate measuring quantity which may be observed, detected or followed as a function of time by suitable equipment. Frequently, the derivative form of this quantity is proportional to the reaction rate, or represents a value of similar character.

Reaction analysis includes all techniques which are suitable for the detailed characterization of the connecting arrows between reactants and products and the mode of their logical interchange.

From the temperature point of view, two different methods have been followed in the kinetic determination of chemical reactions: isothermal and non-isothermal.

For reactions in the liquid phase, the usual techniques utilize almost all quantities, e.g., identification of products and/or reactants and their quantitative evaluation, dilatometric, polarographic, electrochemical or viscosimetric methods. Much theoretical and experimental work has been carried out in the interpretation of experimental results obtained under isothermal conditions [1,2].

From the heat balance point of view, for a batch experiment the following general expression can be deduced

$$c_p \frac{d(\Delta T)}{dt} + Ua(\Delta T) = r(-\Delta H) \quad (1)$$

where  $\Delta T$  is the difference between the temperature of reaction,  $T_r$ , and the external medium,  $T_e$ .

The isothermal experimentation methods, which are explained in the major part of the books on chemical kinetics, take  $T_r = ct$  and use mass balance equations to obtain kinetic data, taking

$$r = \frac{1}{\nu_i} \frac{dC_i}{dt} \quad (2)$$

Thus, isothermal methods can be classified taking into account the analytical method to determine concentration–time curves.

Non-isothermal methods can first be classified according to heat balance considerations. In this way, an adiabatic method to determine kinetic data and their analysis has been proposed by Root and Schmitz [3], and developed by Hugo and Schaper [4], after taking, in the heat balance,  $UA(\Delta T) \rightarrow 0$  and  $\dot{q} \rightarrow 0$ . The adiabatic method has been particularly suitable for the rapid and simple determination of kinetic data of industrial liquid-phase reactions, but this type of evaluation of kinetic data can lead to substantial errors if the limitations of the method are not considered.

This method obtains kinetic data through temperature measurements under adiabatic conditions, taking

$$T - T_0 = \Delta T_{ad} X \quad (3)$$

and

$$r = r_0 \exp \frac{E(T - T_0)}{RTT_0} f(C) \quad (4)$$

where

$$\Delta T_{ad} = \frac{\Delta H C_0}{\nu_i i \rho C_p}$$

and  $f(C)$  is the kinetic law.

A non-isothermal and non-adiabatic method to analyse the kinetic data of reactions in the liquid phase has been proposed by Matsuda and Goto, for

simple [5] and complex [6] reactions, developing a differential thermal analysis technique (DTA), in which neither the sample nor the reference materials are heated, and the temperatures remain as isothermal as possible, taking

$$r = C_0 \frac{dx}{dt} \quad (5)$$

and, after interpreting the heat balance

$$x = \frac{C_p \Delta T + Ua \int_0^t \Delta T dt}{Ua \int_0^\infty \Delta T dt} \quad (6)$$

so that, under non-isothermal and non-adiabatic conditions, it is possible to obtain conversion-time curves through the difference in temperatures between sample and reaction medium.

Differential thermal analysis (DTA) has been used as analytical method to study reaction kinetics by measuring differences between sample and reference materials for a constant heating rate; i.e., a linear temperature programme is followed in the kinetic determination.

Borchardt and Daniels [7] derived DTA equations with respect to  $n$ th-order irreversible, simple reactions on the assumption that the temperatures in the sample and the reference materials are kept uniform.

Kissinger [8] derived unsteady-state equations for temperature distributions in both sample and reference materials and determined the kinetics and the reaction order of simple decomposition reactions.

Koch [9–12] has proposed different methods for evaluating kinetic parameters, in which DTA experimental curves were simulated by use of numerical interpretation of the basic DTA equations.

According to this method, different chemical reactions have been investigated. Elementary processes, like aromatic diazonium salt hydration [13]; complex processes, like ozonization reactions [14]; and intermediates, such as photoreactions [15], have been studied by DTA techniques.

In this work we propose a new programmed temperature method to obtain and analyse kinetic data, which can be understood as a thermoanalytical method (TA), for liquid-phase reactions, because it is necessary to carry out concentration measurements under non-isothermal conditions so that a linear temperature programme will be performed during the reaction.

The well-known thermogravimetric method for solid-decomposition reactions is introduced in the study of liquid-phase reactions, taking into account that concentration measurements are needed for the determination of conversion-temperature curves. Experimental methods seem to be similar to the isothermal determination, only a heating system is necessary which can control the temperature programme during the reaction.

This thermoanalytical method permits kinetic data of liquid-phase reactions to be obtained for the purpose of the evaluation of chemical reactions.

On account of the technique being non-isothermal, the effect of temperature on the reaction rate is well determined, while that of concentration cannot be evaluated with the same accuracy. Thus, in a future work, a sequential kinetic model discrimination will be explained, for the cases in which a detailed investigation of reaction kinetics is necessary.

#### EXPERIMENTAL METHOD

A kinetic experiment consists of the determination of the composition of a reaction mixture in a reactive system, at a constant heating rate. Thermoanalytical curves can be obtained by analysis of the samples taken from a reactor placed in a heating system, with a linear temperature programme.

#### ANALYTICAL METHOD

##### *Theoretical basis and development of the method*

The kinetic equation of a chemical reaction under isothermal conditions can be expressed by

$$r = \frac{1}{\nu_i} \frac{dC_i}{dt} = F(k, C) \quad (7)$$

where  $C$  is the concentration.

From this equation the relationship between concentration and time is obtained for each temperature

$$C = IF(k_T, t) \quad (8)$$

where, IF is the isothermal function.

For experiments taking place under non-isothermal linear temperature evolution, and for a separable-variables kinetic expression, the equation can be expressed as

$$\frac{-dC}{g(C)} = A \exp(-E/RT) dt \quad (9)$$

and on integrating we obtain

$$\int_0^C \frac{dC}{g(C)} = \int_0^T A \exp(-E/RT) dt \quad (10)$$

where the relationship between concentration and time under non-isothermal conditions can be expressed by

$$C = NIF(T, t) \quad (11)$$

where NIF is the non-isothermal function.

In experiments where a linear temperature programme has been carried out, the relationship between temperature and time can be expressed by:  $T = T_0 + \beta t$ , where  $\beta$  is the heating rate.

If  $\beta$  is introduced into eqn. (10), the following expression is obtained

$$\int_{C_0}^C \frac{dC}{g(C)} = \int_{T_0}^T A \exp(-E/RT) \frac{1}{\beta} dT \quad (12)$$

If a potential kinetic model is supposed,  $g(C) = C^n$  and the different magnitudes are expressed in a non-dimensional way

$$f(x) = \frac{AT_0}{\beta C_0^{1-n}} \int_1^y \exp\left(\frac{-Ar}{y}\right) dy \quad (13)$$

where  $x$  is the conversion,  $y$  the adimensional temperature,  $T/T_0$ ,  $Ar = E/RT_0$ , the Arrhenius number, and  $f(x)$  is the integrated function of the conversion which depends on the potential order.

For a given reaction, when the heating rate,  $\beta$ , is kept constant, the relation between the integral term and the function of the conversion  $f(x)$ , where the correct Arrhenius number is used, will be expressed by a straight line with an origin ordinate equal to zero and a slope equal to  $AT_0/\beta C_0^{1-n}$ ; from this value, the pre-exponential factor,  $A$ , can be obtained.

Since in most chemical reactions taking place in the liquid phase, the Arrhenius number lies between 5 and 50, and the temperatures of reaction range from ambient to the products' boiling points (288–373 K), the corresponding values of  $y$  will range from 1 to 1.3. The values mentioned will be taken as the Arrhenius and  $y$  parameter variation limits, respectively.

From a kinetic experiment with a constant heating rate (288–373 K),  $x$  vs.  $y$  data are obtained; they will depend on the initial concentration and temperature dependence of the kinetic model.

Since the integral  $\int_1^y \exp(-Ar/y) dy = I$  depends on the  $y$  values and the Arrhenius number, it is possible to represent this relation with  $Ar$  as parameter, as it is shown in Fig. 1.

On the other hand, the relationship between the  $f(x)$  function and the conversion,  $x$ , depends on the kinetic model, and if the reaction order is used as the parameter, the curves shown in Fig. 2 will be obtained.

The discrimination procedure of the kinetic model will include the following steps.

(a) From the  $y$  vs.  $x$  data for a given value of  $Ar$ , the  $I$ -integral values will be calculated by using Fig. 1 (another method of specific integration can be used).

(b) For each value of  $n$ , the  $f(x)$  values will be obtained by using Fig. 2.

(c) The  $I$  values from step (a) will be correlated with the  $f(x)$  values from step (b) for each value of  $n$  by using linear regression methods. A series of correlation coefficients vs.  $n$  will be formed, with a maximum for a particular value of  $n$ .

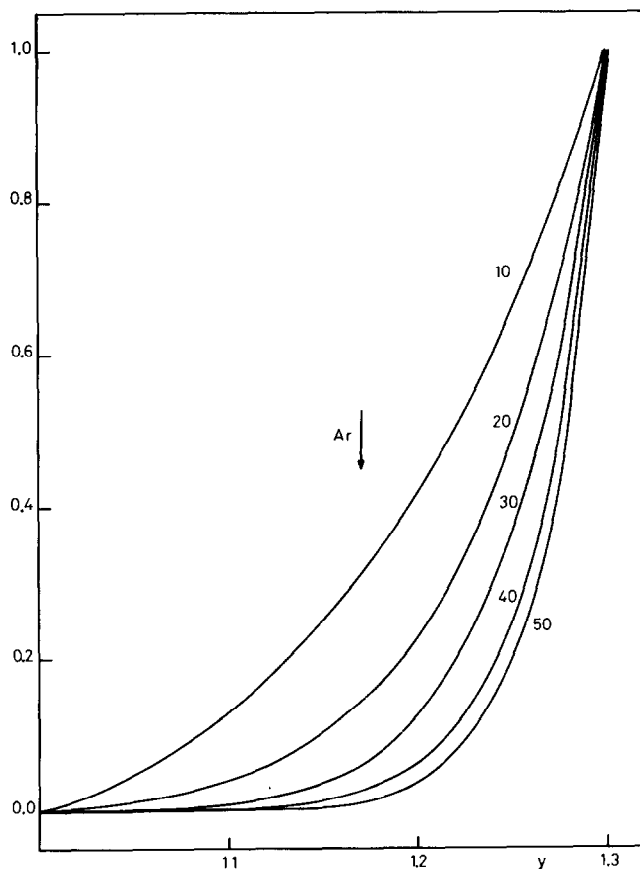


Fig. 1. Graphical relation between  $\int_1^y \exp(-Ar/y)dy$  and  $y$  with the Arrhenius number as parameter.

This procedure may be repeated for different Arrhenius numbers, and so various series of  $r^2$  vs.  $n$  will be obtained. The maximum  $r^2$  value, between the Arrhenius limits, will show the dependence of the kinetic model on concentration, through the corresponding  $n$  parameter. Finally, from the relation between  $I$  and  $f(x)$  for the chosen  $Ar$  and  $n$  values, the pre-exponential factor,  $A$ , may be calculated.

This method enables us to discriminate between the kinetic models and, at the same time, to obtain the activation energy,  $E$ , and pre-exponential factor,  $A$ , from a kinetic curve.

#### *Testing the method*

The developed method has been tested using simulated data: a chemical reaction with  $n$  equal to 1 has been used. The acid-catalyzed trioxane depolymerization has been employed, where the activation energy and

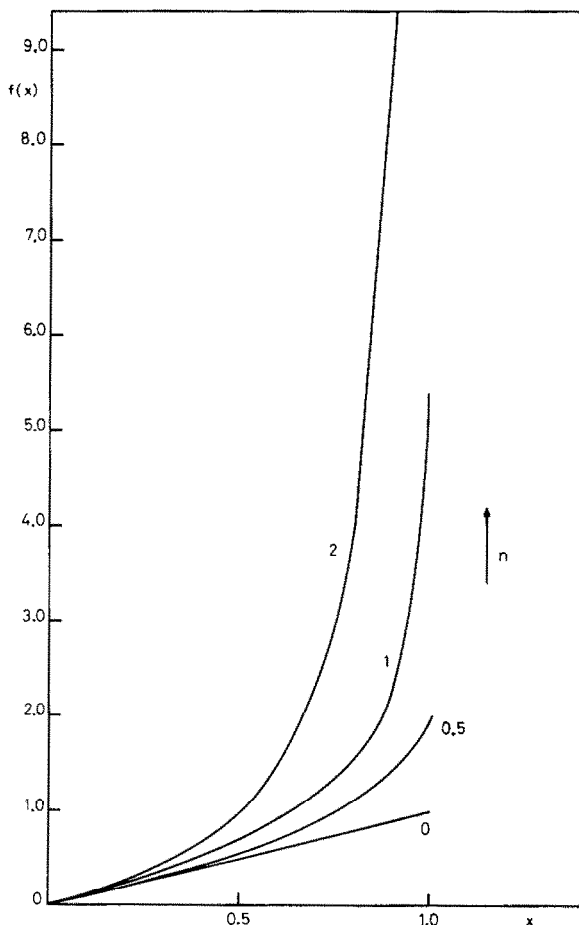


Fig. 2. Graphical relation between  $f(x)$  and  $x$  with the reaction order as parameter.

pre-exponential factor values were taken from the literature [16–18]:  $E = 74.17 \text{ kJ mol}^{-1}$  and  $A = 5.56 \times 10^9 \text{ min}^{-1}$ .

The conversion vs. non-dimensional temperature data are shown in Fig. 3.

With the resulting  $x$  values and using Fig. 2, the corresponding  $f(x)$  values were obtained for cases where  $n = 0$ ,  $n = 1$  and  $n = 2$ .

By using Fig. 1, the  $I$  values can be calculated for the following  $Ar$  values: 10, 20, 30 and 40. The resulting  $I$  integrals for each  $Ar$  value were fitted to the conversion function for each reaction order. The results are shown in Table 1, as correlation coefficients for each  $Ar$ – $n$  pair. From this table it is evident that for the  $Ar$  range used (taken for its physical significance in chemical reactions in the liquid phase), the kinetic model that best describes the studied reaction is that which corresponds to  $n = 1$  as shown in Fig. 4.

For an exact determination of the  $Ar$  parameter, various fittings were carried out, taking  $Ar$  values nearest to the maximum. The results are shown in Table 2.

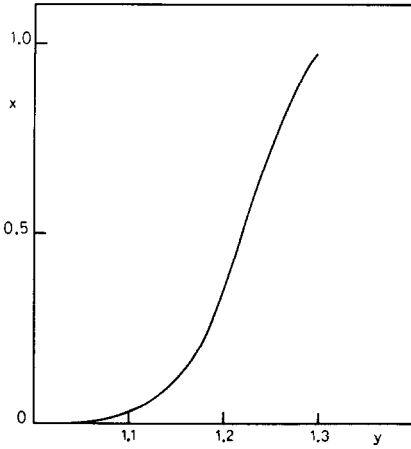


Fig. 3. Simulated conversion versus non-dimensional temperature,  $y$ , for the trioxane depolymerization reaction,  $\beta = 1^\circ\text{C min}^{-1}$ .

TABLE 1

Correlation coefficients for different reaction orders,  $n$ , and Arrhenius numbers,  $Ar$

$n$	$Ar = 10$	20	30	40	50
0	0.977	0.951	0.872		
1	0.865	0.973	0.999	0.986	
2		0.694	0.805	0.89	0.925

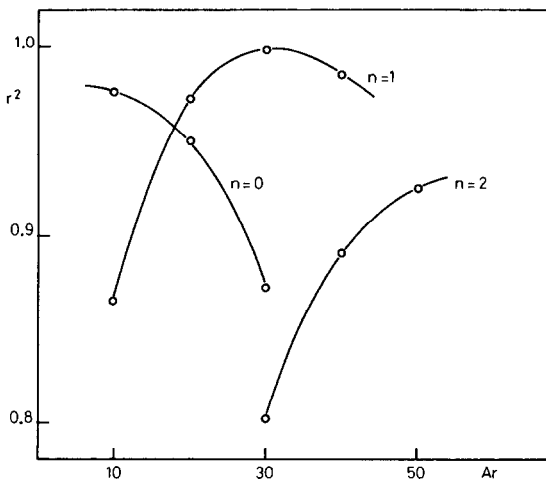


Fig. 4. Correlation coefficients for the Arrhenius number and the reaction order.



TABLE 2

Determination of the best Arrhenius number,  $Ar$ 

$Ar$	25	27	29	30	31	33
$r^2$	0.994	0.998	0.995	0.9997	0.9998	0.996

As it is shown, the best value of the correlation coefficients is obtained for  $Ar = 31$ , which emphasizes the validity of the method for the discrimination of kinetic models for reactions taking place under a temperature programme. It is also demonstrated that the kinetic model and the kinetic parameters can be obtained from only one experimental curve.

This method must be considered among the thermoanalytical methods to determine the kinetic behaviour of a reaction in the liquid phase [19], taking into account that the major part of the discussion on the thermoanalytical methods has been formed through thermal decomposition reactions [20–22].

## REFERENCES

- 1 A.A. Frost and R.G. Pearson, *Kinetics and Mechanism*, 2nd edn., Wiley Interscience, New York, 1961.
- 2 M. Boudart, *Kinetics of Chemical Processes*, Prentice Hall, Englewood Cliffs, NJ, 1968.
- 3 R.B. Root and R.A. Schmitz, *AIChE J.*, 15 (1969) 670.
- 4 P. Hugo and W. Schaper, *Ger. Chem. Eng.*, 3 (1980) 103.
- 5 H. Matsuda and S. Goto, *Can. J. Chem. Eng.*, 62 (1984) 103.
- 6 H. Matsuda and S. Goto, *Can. J. Chem. Eng.*, 62 (1984) 107.
- 7 H.J. Borchardt and F. Daniels, *J. Am. Chem. Soc.*, 79 (1957) 41.
- 8 H.E. Kissinger, *Anal. Chem.*, 29 (1957) 1702.
- 9 E. Koch, *Non-isothermal Reaction Analysis*, Academic Press, New York, 1977.
- 10 E. Koch, *Angew. Chem.*, 82 (1970) 306.
- 11 E. Koch, *Chem. Ind. Tech.*, 44 (1972) 111.
- 12 E. Koch, *Modelling of Chemical Reaction Systems*, Springer Series in Chemical Physics, Vol. 18, Springer Verlag, New York, 1981.
- 13 D. Schulte-Frohlinde and H. Blume, *Z. Phys. Chem., Neue Folge*, 59 (1968) 299.
- 14 S.W. Benson, *Thermochemical Kinetics*, Wiley Interscience, New York, 1968.
- 15 C.S. Foote, *Acc. Chem. Res.*, 1 (1968) 104.
- 16 F.A. Long and M. Paul, *Chem. Rev.*, 57 (1957) 935.
- 17 J.F. Walker and A.F. Chadwick, *Ind. Eng. Chem.*, 39 (1947) 974.
- 18 M. Paul, *J. Am. Chem. Soc.*, 72 (1950) 3813.
- 19 J. Šesták, *Thermochim. Acta*, 28 (1979) 197.
- 20 A.L. Draper, *Thermochim. Acta*, 1 (1970) 345.
- 21 J. Šesták, *J. Therm. Anal.*, 16 (1979) 503.
- 22 K. Heide, *Dynamische Thermische Analysenmethoden*, VEB Grundstoffindustrie, Leipzig, 1979.