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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA; DISCRIMINATION OF INTEGRAL MODELS

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ABSTRACT

A novel procedure is presented for the discrimination of kinetic models and evaluation of kinetic parameters from thermogravimetic (TG) data. A constant temperature and constant conversion kinetic analysis is explained from TG curves and the relation between TG data and constant temperature and constant conversion data is developed. These relationships enable us to study separately the influence of α and T in the kinetic model. This procedure was tested against theoretical data and was found to be satisfactory. Advantages of this method are: it is relatively simple to use, it allows the user readily to discern whether the data deviate from the kinetic model ($\alpha - t$) or whether the deviation takes place under the influence of temperature on the kinetic parameters.

INTRODUCTION

A solid decomposition takes place by a heterogeneous reaction. In this kind of reaction, the initial solid leads to another solid and gaseous products; a kinetic analysis of decompositions must take into account phenomena such as chemical reaction mass and heat transfer, etc. [1]. Values of composition and temperature in a solid matrix are given by the simultaneous coupling of chemical rate and internal and/or external heat and mass transfer.

A description of the reaction as a function of variables such as fluid temperature and solid conversion using a kinetic model based on different steps requires knowledge of structural changes in the solid matrix and the kinetics of different processes.

Models developed to describe this kind of reaction differ greatly in their assumptions and details, depending on whether they emphasize chemical mechanisms or associated physical processes, but they usually introduce some simplifications:

—The temperature has the same value at all the points in the solid matrix and the external fluid (isothermal analysis).

—There are not interfacial gradients of composition and temperature.

—The observed rate of decomposition is the rate of the slower step; boundary reaction rate, fluid products diffusion rate or nucleation rate.

—The kinetic behaviour is the same throughout the transformation.

The validity of these simplifications depends on the reaction and on how the decomposition has been carried out. It has often been found that kinetic parameters depend on variables such as initial mass of solid, particle size, etc. which are not included in the model. In these cases assumptions of the model do not agree with experimental results.

Discrimination of kinetic models has been carried out for isothermal and non-isothermal data. It is clear that the non-isothermal method, usually $T = T_0 + \beta t$ has many advantages to justify this kind of experimental and theoretical work, but the method introduces new complications in the kinetic analysis [2].

The continuous variation of the external temperature can lead to a temperature gradient in the solid matrix [3]. It is known that the variations in conversion and temperature during a non-isothermal run make it possible to change a reaction mechanism or controllant step during a decomposition run [4]. Discrimination of kinetic models using the best fit of experimental data to the model is very difficult in a non-isothermal run, because the major influence of the temperature change can mask the minor influence of the conversion change in the decomposition rate [5].

In this work these different points of view have been considered in order to present a new method to discriminate between integral models for non-isothermal data. Many procedures have been reported for thermal decomposition of solids by TG. These methods have tried to estimate kinetic parameters (A, E) for a simple model using maximization of rate, multiple heating rates, variable heating rate, integration of the rate equation, etc. In this paper we present a novel procedure for discrimination of kinetic models based on the separation of the temperature and conversion influence on the reaction rate.

THEORETICAL BASIS AND METHOD DEVELOPMENT

The kinetic equation of a decomposition under isothermal conditions, can be expressed by

$$\frac{d\alpha}{dt} = K_{Ti} f(\alpha) \tag{1}$$

Upon integrating under isothermal conditions

$$\int \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = K_{T\mathrm{i}} \int \mathrm{d}t \tag{2}$$

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

$$\alpha = \mathrm{IF}(K_{T\mathrm{i}}, t) \tag{3}$$

where, IF is the isothermal function.

Experiments taking place under non-isothermal conditions follow the equation

$$\int \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \int A\ \mathrm{e}^{-E/RT} \mathrm{d}t \tag{4}$$

Upon integrating, a relation between conversion and time can be obtained for non-isothermal conditions

$$\alpha = \mathrm{NIF}(T, t) \tag{5}$$

where NIF is the non-isothermal function.

In thermogravimetry a linear relation between temperature and time is usually taken

$$T = T_0 + \beta t \tag{6}$$

From eqns. (5) and (6), the temperature and conversion can be followed for each heating rate, as is shown in Fig. 1. In this figure, data from eqn. (3) are always in a parallel plane to the α–t, which intersects the T-axis at the temperature of the isothermal course (T_i). The model discrimination using

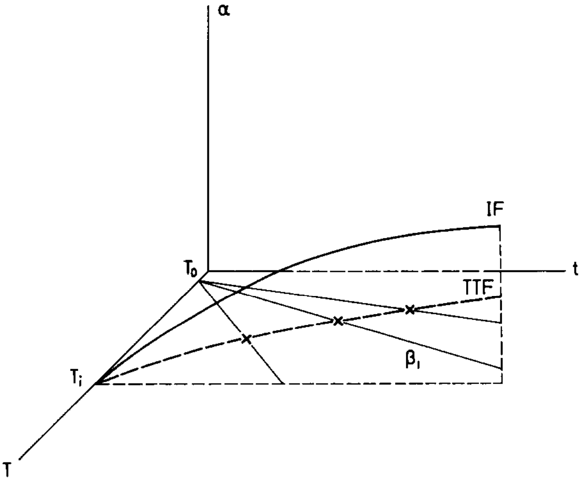

Fig. 1. Isothermal function (IF) at T_i and intersections of the non-isothermal curves at different heating rates by a T_i plane.

eqn. (3) can be performed by separating the influence of the composition and temperature. When eqns. (4) and (5) are used the discrimination must be performed simultaneously for the two variables, temperature and conversion and it is very difficult to fit the best kinetic model.

Non-isothermal data coming from different heating rates can be plotted and taking points which have the same conversion or temperature, the kinetic model can be separately analysed as a function of composition and temperature.

Non-isothermal data at constant temperature

By intersecting non-isothermal curves in a plane perpendicular to the T-axis, at point T_i, different conversion values, a number of points equal to the non-isothermal runs are obtained. The equation, which must describe these points is the following

$$\alpha = \mathrm{TTF}(T_i, t) \tag{7}$$

where TTF is the temperature transform function. From eqns. (4) and (6) [6]

$$\int \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \int A\ \mathrm{e}^{-E/RT} 1/\beta_i \mathrm{d}T \tag{8}$$

Taking into account the relation between t and β_i and using eqn. (8), data for eqn. (7) will be obtained. Equation (7) can be transformed into an isothermal curve

$$\alpha = \mathrm{IF}(K'_{Ti}, t) \tag{9}$$

where

$$K'_{Ti} = \frac{\int_{T_0}^{T_i} A\ \mathrm{e}^{-E/RT} \mathrm{d}T}{T_i - T_0} \tag{10}$$

In this way an isothermal analysis of the α–t data can be performed using eqn. (9); these data can be fitted by a kinetic model, which gives the relation between α and t under isothermal conditions. It is only necessary to know the value of K'_{Ti}, given by eqn. (10).

Non-isothermal data at constant conversion

By intersecting the non-isothermal curves in a plane perpendicular to the α-axis, points with the same conversion can be obtained

$$\alpha_i = \alpha\mathrm{TF}(T, \alpha) \tag{11}$$

where αTF is the α transform function. From eqns. (2) and (4) at the same value of α_i

$$\int \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \int A\ \mathrm{e}^{-E/RT}\mathrm{d}t \tag{12}$$

Equation (12) can be transformed to the isothermal

$$\mathrm{g}(\alpha_i) = K'_{Ti}t \tag{13}$$

where

$$K'_{Ti} = \frac{\int_0^t A\ \mathrm{e}^{-E/RT} 1/\beta_i \mathrm{d}t}{t} \tag{14}$$

and by using a constant heating rate in each experiment

$$K'_{Ti} = \frac{\int_0^t A\ \mathrm{e}^{-E/RT}\mathrm{d}t}{T - T_0} \tag{15}$$

TABLE 1

Conversion and temperature at different heating rates

β (°C min^{-1})	0.5	1	2	5	10	20
T(K)	α					
460	0.009	0.002				
470	0.040	0.010	0.003			
475	0.080	0.021	0.005			
480	0.154	0.041	0.010	0.001		
485	0.283	0.080	0.021			
490	0.479	0.150	0.040	0.006	0.002	
495	0.717	0.271	0.076		0.003	
500	0.910	0.453	0.150	0.024	0.006	0.002
505	0.989	0.679	0.248			
510	1	0.880	0.411	0.081	0.021	0.005
515		0.980	0.623			
520		0.999	0.831	0.247	0.068	0.018
525			0.960	0.400		
530			0.997	0.598	0.204	0.055
535			1	0.800	0.305	
540				0.940	0.504	0.161
545				0.992	0.702	
550				1	0.874	0.404
555					0.970	0.585
560					0.997	0.775
565					1	0.916
570						0.983
575						0.999

and from eqns. (13) and (15)

$$\frac{1}{t}=\frac{A}{g(\alpha_i)}\frac{\int_{T_0}^{T}e^{-E/RT}dT}{T-T_0} \tag{16}$$

This result enables us to obtain the activation energy and pre-exponential factor.

TESTING OF THE METHOD

The present method was tested using theoretical data, a decomposition reaction with a KEKAM equation ($n=2$), where $E=30$ kcal mol^{-1} and A $=6\times10^{11}$ min^{-1}, α–t data were obtained for six different heating rates, numerical integration of $\int\exp(-E/RT)dt$ was carried out by using Simpson's rule ($T_0=300$ K $\Delta T=1$ K). Results are shown in Table 1.

Analysis at constant temperature

For a given value of T, taking into account that $t=(T-T_0)/\beta_i$, pairs of α–t values as heating rates are obtained. The relation between α–t is given by eqn. (8), where K'_{Ti} has been estimated according to eqn. (10). In this way a g(α) function can be obtained and different kinetic models can be fitted as shown in Fig. 2. Linear regression of $(-\ln(1-\alpha))^{1/2}$ leads to the kinetic

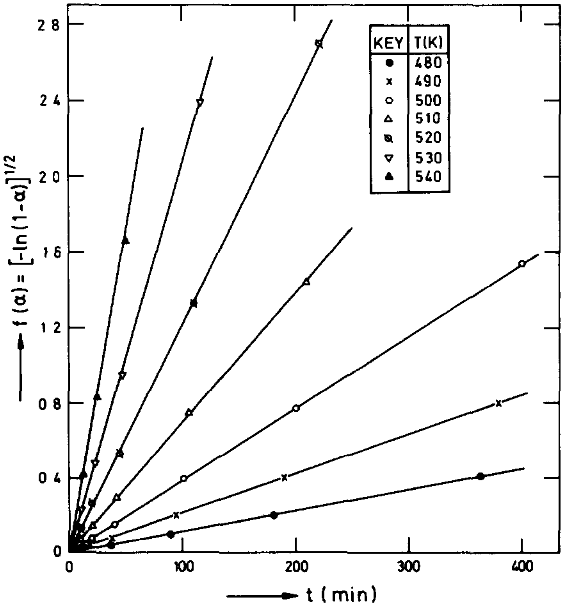

Fig. 2. Determination of the α-function at different temperatures.

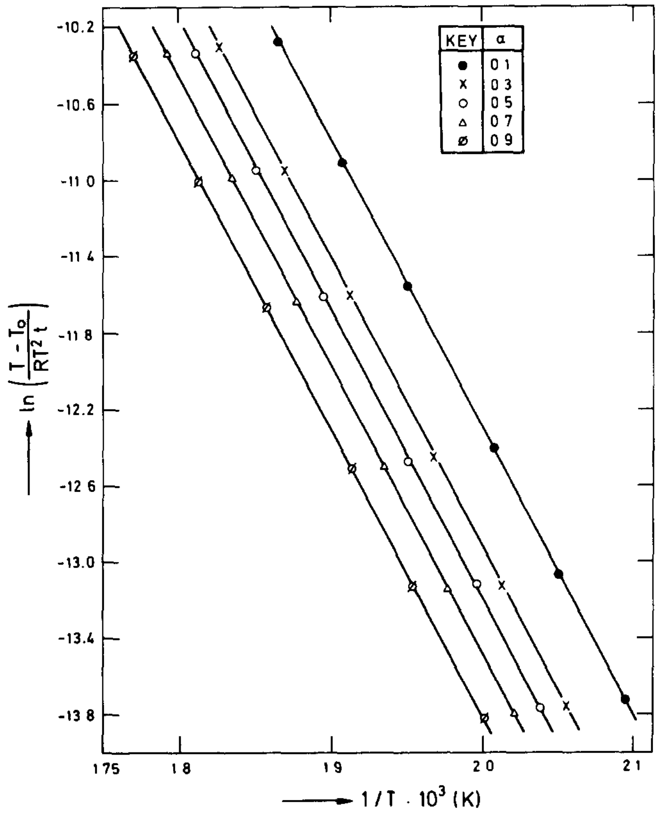

Fig. 3. Activation energy at different conversion levels.

constant at 7 different temperatures from 480 K to 540 K. The activation energy and pre-exponential factor are obtained from these results, taking

$$1-\frac{2RT}{E}+6\left(\frac{RT}{E}\right)^2-\ldots=1 \tag{17}$$

Analysis at constant conversion

Using the TG curves, for a given value of α, t values are obtained for each heating rate, taking into account β_i and T, α–t pairs are obtained.

α values of 0.1, 0.3, 0.5, 0.7 and 0.9 are taken, and by applying eqns. (15) and (16)

$$\frac{T-T_0}{RT^2t}=\frac{A/E}{g(\alpha)}\exp(-E/RT) \tag{18}$$

Results for this equation are shown in Fig. 3 and the least squared fit for the different curves at α constant leads to an activation energy and pre-exponential factor in agreement with the initial values.

REFERENCES

1 J. Szekely, J.W. Evans and H.Y. Sohn, Gas–Solid Reactions, Academic Press, New York 1976.
2 A. Dutta and M.E. Ryan, Thermochim. Acta, 33 (1979) 87.
3 J. Mu and D.D. Perlmutter, Chem. Eng. Sci., 35 (1980) 1645.
4 Gy Pokor, S. Gal and E. Pungor, Thermochim. Acta, 33 (1978) 259.
5 J.M. Criado, J. Therm. Anal., 19 (1980) 381.
6 L. Reich and S.S. Stivala, Thermochim. Acta, 53 (1982) 121.