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Some successes and failures of the methods based on several experiments

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Abstract

The actual kinetics of a solid state reaction cannot be discerned by means of the kinetic analysis of a single TG curve. The cause of this relates to the fact that different kinetic equations appear to fit a set of kinetic data. This paper shows the advantage of a choice of method based on comparing data from several experiments at the same degree of conversion. But this procedure must be carried out with great care. The limitations are discussed.

Keywords: Kinetics; Solid state reaction; TG

1. Introduction

Before the advent of the modern non-isothermal technique, kinetic analyses of heterogeneous reactions were studied by the isothermal method. This method, which is useful in predicting the activation energy, is cumbersome and tedious. The concept of non- isothermal kinetics was outlined as early as 1930 and ever since it has continued to develop rapidly. It is well known that the non-iso methods can be grouped into two classes:

1. Integral methods, utilising weight loss vs. temperature data directly.
2. Differential methods, utilising the rate of weight loss.

The literature contains many long lists of specific equations to test, of both integral and differential forms, including dimensional diffusion, Avrami–Erofeev-type equations, contracting sphere or contracting cylinder, etc. The mathematical formulae of the most frequently cited models are summarised in Table 1. These kinetic model functions

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Table 1
Algebraic expression of the $g(\alpha)$ functions commonly used for reaction kinetics

Mechanism	Symbol	$g(\alpha)$
Random nucleation; unimolecular decay law (first-order)	F1	$-\ln(1-\alpha)$
Phase-boundary-controlled reaction (contracting cylinder)	R2	$2[1-(1-\alpha)^{1/2}]$
Phase-boundary-controlled reaction (contracting sphere)	R3	$3[1-(1-\alpha)^{1/3}]$
Two-dimensional growth of nuclei (Avrami–Erofeev equation)	A2	$[-\ln(1-\alpha)]^{1/2}$
Three-dimensional growth of nuclei (Avrami–Erofeev equation)	A3	$[-\ln(1-\alpha)]^{1/2}$
One-dimensional diffusion	D1	α^2
Two-dimensional diffusion	D2	$(1-\alpha)\ln(1-\alpha)+\alpha$
Three-dimensional diffusion (Jander equation)	D3	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional diffusion (Ginstling–Brounshtein equation)	D4	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

have been derived on the basis of physical-geometrical assumptions of regularly shaped bodies.

In general, it is recognized in the literature that both of the above methods permit the proper determination of the kinetic parameters of solid-state reactions, although opinions differ [1, 2] regarding their usefulness for discriminating the kinetic model followed by the reaction. It has been shown [3, 4] that the phase-boundary- and diffusion-controlled reaction laws cannot be discriminated from a single TG curve by means of integral methods. In a similar way, it has been demonstrated [5] that it is impossible to distinguish, solely on the basis of this integral analysis, between a random nucleation unimolecular decay law (first order) and an Avrami–Erofeev-type model.

The general conclusion is that the actual kinetics of a solid-state reaction cannot be discerned by means of the kinetic analysis of a single thermogravimetric curve. Moreover, it has been pointed out that any theoretical TG curve calculated using a linear heating programme by assuming a particular kinetic law, necessarily fits all the kinetic equations of Table 1 developed for describing a reaction, although the activation energy E obtained is strongly dependent on the kinetic law assumed in performing the calculations. For example, Fig. 1 shows that a unique TG curve can be calculated by assuming three different kinetic models: a random nucleation unimolecular decay law (labelled F1 in Table 1), an Avrami–Erofeev (A2) model and a three-dimensional diffusion law (D3). This example shows that it is impossible to select unambiguously the $g(\alpha)$ function obeyed by the reaction. The problem arises from the fact that in all cases different kinetic equations appear to fit a set of kinetic data and the researchers may not be able to select the most appropriate one.

One way to overcome the above limitation is to abandon classical linearising methods based on the regression coefficient. In many cases, even a good linear relationship is not sufficient proof of the validity of the model. The kinetic evaluation should be made using methods which yield the largest measure of statistical security. But a difficulty arises from the fact that a rigorous application of statistical criteria is only possible if it is assumed that the data have a normal distribution. This problem stresses the importance of the ·several experiments procedure.

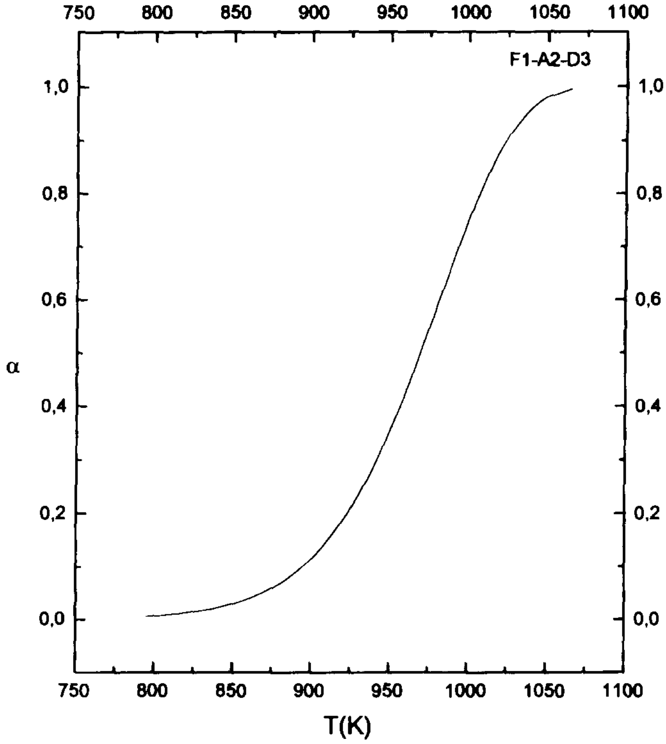

Fig. 1. A single TG curve for three different kinetic models: F1 ($E = 167$ kJ mol^{-1}, $A = 1.6 \times 10^6$ s^{-1}); A2 ($E = 76$ kJ mol^{-1}, $A = 0.12 \times 10^2$ s^{-1}); D3 ($E = 308$ kJ mol^{-1}, $A = 6 \times 10^{12}$ s^{-1}).

The aim of this paper is to show the advantages of the choice of a method, based on the kinetic analysis from several experiments. This procedure includes the advantage of allowing the calculation of the activation energy without prior knowledge of the $g(\alpha)$ function. But this approach has some disadvantages which will be discussed later.

2. Theoretical

The differential and integral forms of a rate equation are generally expressed, respectively, as follows

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = Af(\alpha)\exp(-E/RT) \qquad (1)$$

$$g(\alpha) = \frac{AE}{\beta R}\,p(x) \qquad (2)$$

where $x = E/RT$; $\beta = \mathrm{d}T/\mathrm{d}t$ is the heating rate, $g(\alpha)$ and $f(\alpha)$ are appropriate functions of α, and $p(x)$ represents the integral

$$\int_x^{\infty} \frac{\exp(-x)}{x^2} \mathrm{d}x \qquad (3)$$

A difficulty in non-isothermal kinetic methods is that there is no exact analytical solution of the $p(x)$ function. In order to express this temperature integral, evaluation of $p(x)$ could be done in several ways [6, 7] but if x is sufficiently large (> 20) and the temperature interval for the non-isothermal scan is restricted (< 100 K), Doyle has suggested that $\log p(x)$ is an approximately linear function of x, i.e. of $1/T$

$$\log p(x) = -2.315 - 0.4567\,x \qquad (4)$$

2.1. *Kinetic evaluation from several experiments*

The lack of knowledge of the analytical form of $g(\alpha)$ can be circumvented quite easily by combining Eqs. (2) and (4)

$$\log g(\alpha) = \log \frac{AE}{\beta R} - 2.315 - 0.4567 \frac{E}{RT} \qquad (5)$$

For a number of experiments with different temperature programmes, β, we can write for the same extent of reaction α

$$-\log \beta = 0.4567 \frac{E}{RT} + \text{constant} \qquad (6)$$

The plot of $\log \beta$ vs. $1/T$ for a given value of α must give the activation energy E. Thus we have a method for determining E which does not depend on a knowledge of the analytical form of $g(\alpha)$. This procedure was suggested by Ozawa [8] and Flynn [9] independently. However, an agreement between the values of E calculated from several experiments at different heating rates, which does not depend on a knowledge of the $g(\alpha)$ function, with those obtained from the kinetic analysis of a single TG curve largely depending on the kinetic law obeyed by the reaction, is only achieved when the proper kinetic model has been chosen for carrying out the calculation. Thus a comparison of the kinetic parameters determined by both methods is a very good way of determining the reaction mechanism of solid-state reactions.

2.2. *Some successes and failures of the several experiments procedure*

Let us now examine some successes and failures of non-isothermal kinetics from several experiments. The nice thing about the method of several experiments is that the kinetic law whose form is very difficult to calculate unambiguously can be ignored completely. Moreover, with this isoconversional method we are able to test the kinetic parameter values and to see whether or not they do stay constant over the whole range of α. These represent clear examples of success for this procedure. Another important success is that when competitive and independent reactions proceed concurrently in a system, the nature of the reaction may be revealed by either increasing or decreasing the heating rates [10].

For the correct use of the several experiments procedure, it is necessary to bear in mind the following sine qua non conditions:

1. Use the lowest ranges of heating rates.
2. Fit the data at the same degree of conversion.
3. Test for heating rate dependence of the activation energy.
4. Test for degree of conversion dependence of the activation energy.

For the remainder of this paper, we will discuss some experimental problems in order to investigate the validity or effectiveness of this procedure.

3. Experimental

Sodium bicarbonate (Aldrich) ACS reagent was used. The experiments were performed in a Mettler thermoanalyser connected to nitrogen flowing at 2.5 $cm^3 s^{-1}$.

Samples of calcium carbonate were D'Hemio, r.a. Themogravimetric analysis was carried out in a Mettler thermoanalyser under a vacuum of approx. 2×10^{-5} mbar.

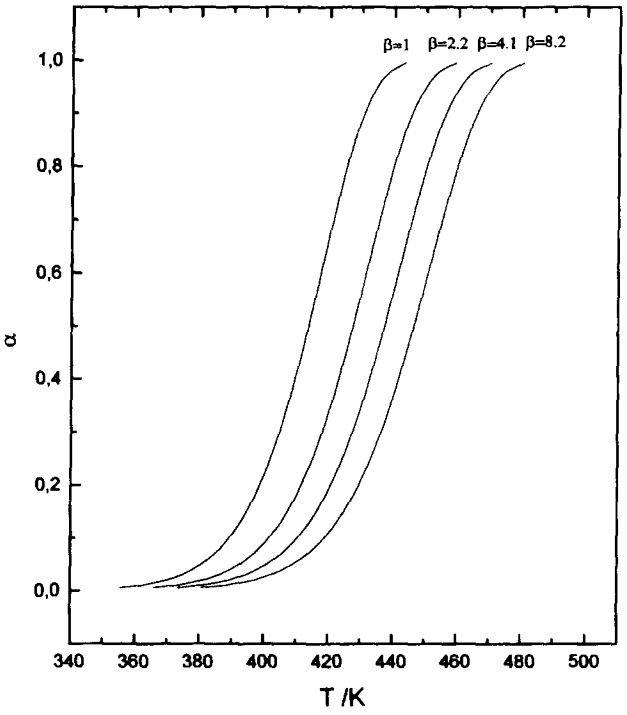

Fig. 2. TG curves for the thermal decomposition of sodium bicarbonate.

All experiments were carried out at different heating rates ranging from 1 to 10.

4. Results and discussion

Fig. 2 shows the series of TG curves at different heating rates for the thermal decomposition of sodium bicarbonate. The isoconversional lines obtained in plotting log β versus the reciprocal of the temperature (Eq. (6)) in Fig. 3, at the same degree of conversion, are all parallel straight lines yielding the same activation energy, as shown in Table 2. We can see that sodium bicarbonate is a case where the activation energy calculated by means of Eq. (6) is dependent neither on the heating rate nor on the degree of conversion. In this particular case, the four suggestions summarised above are fulfilled and it can therefore be expected that the several experiments procedure yields correct values of the kinetic parameters.

The next step of the analysis is the determination of the kinetic law obeyed by the reaction. For this later study, Table 3 shows the activation energy calculated from the kinetic analysis of a single experimental run by means of Eq. (5) at constant heating rate using all the kinetic models of Table 1. This analysis is repeated by using all the experimental TG curves of Fig. 2.

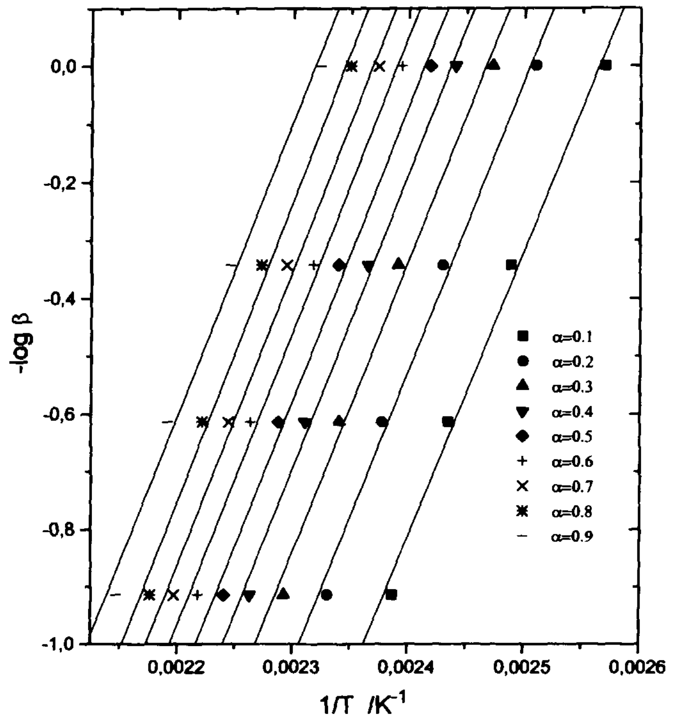

Fig. 3. Isoconversional plots for the thermal decomposition of sodium bicarbonate.

Table 2
Activation energy values of sodium bicarbonate obtained from the kinetic analysis of the isoconversional lines of Fig. 3 by means of Eq. (6)

$E/(\mathrm{kJ\ mol^{-1}})$	α
93.6	0.101
94.0	0.203
93.5	0.310
93.5	0.400
93.7	0.500
94.0	0.602
94.1	0.705
94.3	0.806
94.6	0.900
Mean value: $E = 93.9 \pm 1.5$ kJ mol^{-1}	

Table 3
Activation energy values (kJ mol^{-1}) obtained from the kinetic analysis of individual TG curves of Fig. 2 assuming different kinetic models

Models	$\beta = 1$	$\beta = 2.2$	$\beta = 4.1$	$\beta = 8.2$
R1	75.1	74.8	74.0	76.7
R2	86.9	86.1	84.8	88.9
R3	88.0	89.1	87.3	90.1
F1	**94.1**	**93.9**	**93.4**	**93.2**
A2	47.9	47.0	46.1	49.4
A3	29.7	29.0	28.4	30.5
D1	157.0	156.6	155.1	160.6
D2	170.8	169.9	167.7	174.6
D3	190.0	188.1	185.3	195.1
D4	177.0	175.7	173.4	181.2

A comparison of the results of Table 3 with those previously obtained from the several experiments procedure ($E = 93.9$) shows that a good agreement between the activation energy obtained from both methods is achieved only if it is assumed that the thermal decomposition of sodium bicarbonate fits a first-order kinetic model, labelled F1 in Table 1.

The success of the procedure, in this particular case, arises from the fact that the experimental factors (heating rate, sample size, etc.) do not involve uncertainties in the kinetic analysis and lead to adequate determination of both the activation energy and the reaction mechanism. The results obtained here agree very well with those calculated by Hu et al. [11] and Romero et al. [12].

Let us now examine some failures. One very strong disadvantage of the several experiments procedure is that the scatter of E values is very high when the experimental factors affect significantly the course of the reaction. These deviations are exemplified

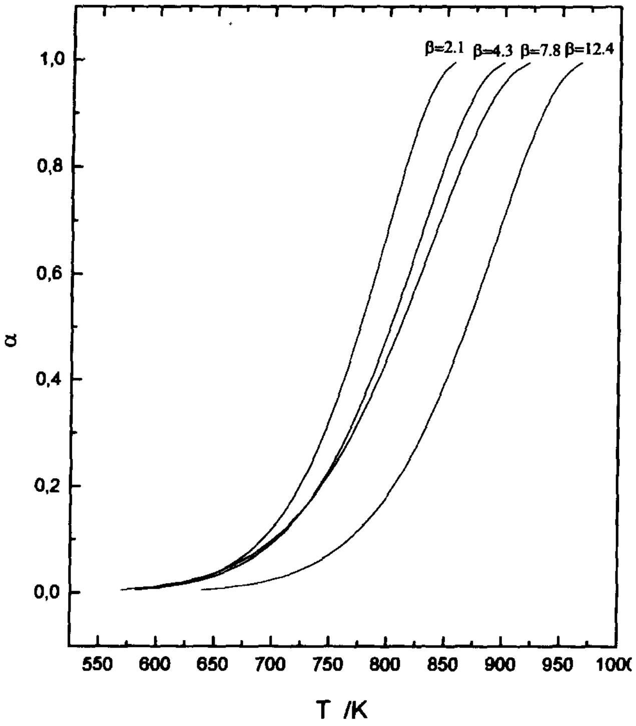

Fig. 4. TG curves for the thermal decomposition of calcium carbonate.

by the reported values of the activation energy of the decomposition of calcium carbonate. This is a model compound which has frequently been studied and for which the activation energy is variably reported to range from 142 to 3828 kJ mol^{-1}. The behaviour of this reaction is dominated by mass and thermal transport problems. Let us examine this case. Fig. 4 shows the TG curves recorded at different heating rates. The isoconversional lines of Fig. 5 obtained by using Eq. (5) show a considerable scatter of the points at the same degree of conversion. The lines obtained are not parallel, which means that the reaction is path-dependent and we are in trouble because the kinetic parameters determined from Eq. (6) are probably in error. In this latter example, which is often the case, all the isoconversional slopes change with both temperature and α. The general suggestions outlined above are not fulfilled and the use of the several experiments procedure is not at all recommended.

5. Conclusion

Non-isothermal kinetics is very popular and useful but presents a significant problem which is that it is impossible to distinguish solely on the basis of the kinetic analysis of a single TG between the kinetic models of Table 1. This stresses the importance of choosing a method based on comparing data from several experiments

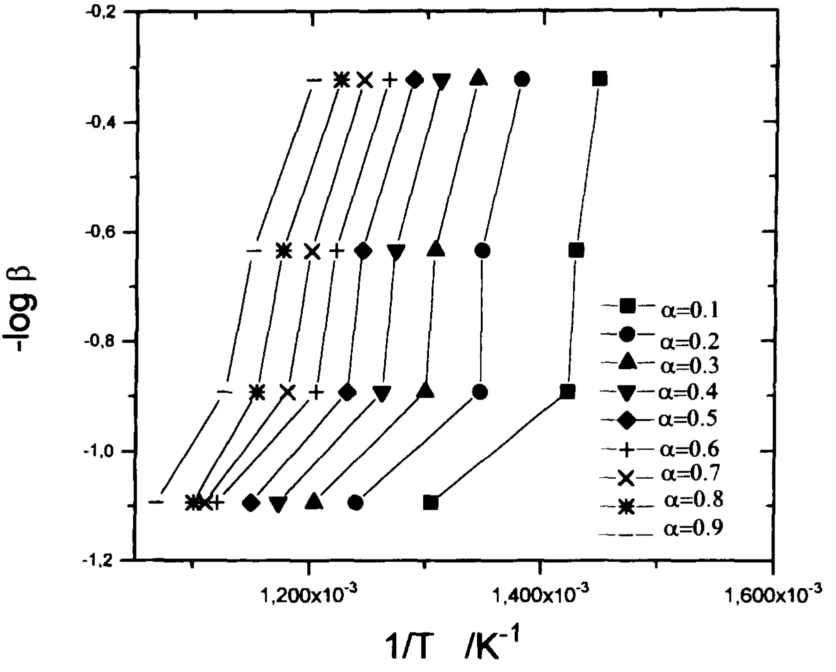

Fig. 5. Isoconversional plots for the thermal decomposition of calcium carbonate.

at the same degree of conversion. The main point of the several experiments procedure is that the kinetic law obeyed by the reaction whose form is very difficult to calculate unambiguously can be ignored completely, but this isoconversional method must be carried out with great care. If the isoconversional lines obtained from Eq. (6) are not parallel, the method is not adequate and will inevitably lead to a wide scatter of results; this is the case for calcium carbonate.

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