SOME PROBLEMS CONCERNING THE EVALUATION OF NON-ISOTHERMAL KINETIC PARAMETERS
Solid-gas decompositions from thermogravimetric data

P. Budrugeac[1], Alice Luminita Petre[2] and E. Segal[3]*

[1]EUROTEST-S.A., Splaiul Unirii 313, Sector 3, Bucharest, 73204
[2]'I. G. Murgulescu' Institute of Physical Chemistry of the Romanian Academy
Splaiul Independentei 202, 77208, Bucharest
[3]Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest
Bd. Republicii, Nr. 13, Bucharest, Romania

Abstract

The validity of isoconversional methods used to evaluate the activation energy is discussed. The authors have shown that the Flynn-Wall-Ozawa and Friedman methods give results that agree with each other only if the activation energy does not change with the degree of conversion. A criterion for the reaction mechanism as expressed by the differential conversion function is suggested too.

Keywords: non-isothermal kinetics, thermogravimetry

Introduction

In order to estimate the non-isothermal kinetic parameters from thermogravimetric data the general isothermal rate equation is used in terms of the degree of conversion (α):

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

The dependence of the rate constant on the temperature, $k(T)$, is given by the Arrhenius equation:

$$k(T) = A\exp\left(-\frac{E}{RT}\right) \tag{2}$$

where A is the preexponential factor, E is the activation energy and R is the gas constant.

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* Author to whom all correspondence should be addressed.

In order to evaluate the activation parameters A and E and to establish the right form of the differential function of conversion, $f(\alpha)$, various methods have been suggested [1]. Among them isoconversional methods are to be mentioned which permit estimation of the activation energy without the knowledge of the analytical form of the conversion function $f(\alpha)$ [2-5].

Various other procedures have been suggested to determine the analytical form of $f(\alpha)$ [6-16].

In this paper some considerations concerning the applicability of isoconversional methods will be presented. On the basis of a critical analysis of the procedures suggested in order to determine the analytical form of $f(\alpha)$, a criterion for finding it will also be presented. The isoconversional methods as well as the criterion for $f(\alpha)$ will be applied to a set of simulated thermogravimetric data, the dehydration of calcium oxalate monohydrate and the thermooxidative degradation of an unsaturated polyester resin.

On the isoconversional methods for estimating the activation energy

As previously stated, isoconversional procedures permit estimation of the activation energy without knowledge of the form of $f(\alpha)$.

The method suggested by Friedman [2] is based on the following equation that can be easily derived from relationships (1) and (2):

$$\ln \frac{d\alpha}{dt} = \ln A f(\alpha) - \frac{E}{RT} \qquad (3)$$

For $\alpha = $ const. (isoconversion) the plot of $\ln d\alpha/dt$ vs. ($1/T$) for various heating rate should be a straight line from whose slope the activation energy can be calculated. In order to apply Friedman's method one needs the values of the reaction rate $d\alpha/dt$ that can be obtained from the DTG curves. In some cases, like the thermal degradations of polymeric materials, the DTG curves exhibit significant noise/signal ratios. Under such conditions the precision of estimation of $d\alpha/dt$ values is considerably reduced. The $d\alpha/dt$ values can be obtained with satisfactory precision by approximating TG curves with a power series in T [17].

The method suggested by Ozawa [3] and independently by Flynn and Wall [4, 5] is based on the following equation which is derived from the integral form of (1), taking into account the Arrhenius Eq. (2) and the Doyle approximation [18] for the temperature integral:

$$\ln\beta \cong \ln \frac{AE}{R} - \ln F(\alpha) - 5.331 - 1.052 \frac{E}{RT} \qquad (4)$$

where β is the heating rate and $F(\alpha)$ is the integral conversion function.

For $\alpha = \text{const.}$, using thermal curves recorded at various heating rates, one can plot the $\ln\beta$ values vs. $(1/T)$. From the slope of the straight line obtained the activation energy can be calculated.

Concerning the isoconversional methods, according to Ozawa [19], the only assumption used in order to derive Eq. (3) on which Friedman's method is based, is the validity of Eqs (1) and (2). Thus the method exhibits a high degree of reliability although it requires the values of the degree of conversion as well as those of the reaction rate for various temperatures.

Obviously the methods of Friedman and Flynn-Wall-Ozawa, when applied to the same set of thermogravimetric data, should lead practically to the same values of the activation energy. A more rigorous relationship between the activation energy values estimated using the Flynn-Wall-Ozawa (E_{FWO}) and the Friedman (E_{FR}) methods can be derived from Eqs (3) and (4), taking into account that for a linear heating program

$$\frac{d\alpha}{dt} \equiv \beta \, \frac{d\alpha}{dT} \, . \tag{5}$$

Thus, from Eqs (3) and (5) one obtains

$$\frac{d\ln\beta}{d(1/T)} = -\frac{E_{FR}}{R} - \frac{d(\ln d\alpha/dT)}{d(1/T)} \tag{6}$$

Correspondingly, from (4) it follows that for $\alpha = \text{const.}$,

$$\frac{d\ln\beta}{d(1/T)} = -1.052 \, \frac{E_{FWO}}{R} \tag{7}$$

Eqs (6) and (7) lead to

$$E_{FR} = E_{FWO} + 0.052 E_{FWO} - R \, \frac{d(\ln d\alpha/dT)}{d(1/T)} \tag{8}$$

As the relative error in the value of activation energy should not exceed ±10%, the following condition of agreement between the values of E_{FR} and E_{FWO} should be fulfilled:

$$\frac{|0.052 E_{FWO} - B|}{E_{FWO}} \leq 0.1 \tag{9}$$

where:

$$B = R \, \frac{d(\ln d\alpha/dT)}{d(1/T)} \tag{10}$$

From (9), the following condition can be written for the change of B in such a way that the values of E_{FR} and E_{FWO} agree with each other:

$$-0.048E_{FWO} \leq B \leq 0.152E_{FWO} \qquad (11)$$

If the activation energy, E, and the preexponential factor, A, do not change with the degree of conversion, the conditions for the validity of Eq. (4) which is the basis of the Flynn-Wall-Ozawa method are fulfilled. That is the reason why we expect that under such conditions inequalities (11) should be fulfilled. But, as it is well known for many thermal decompositions and thermooxidative degradations of solids, the activation energy changes with the degree of conversion [20–23]. For these cases a compensation relationship has been evidenced between the activation energy and the preexponential factor:

$$\ln A = aE + b \qquad (12)$$

where a and b constants. Thus, as E depends on α, A should depend on α, too. The integration of Eq. (1) for $A = A(\alpha)$ and $E = E(\alpha)$ is not possible because under such conditions one cannot separate the temperature integral from the conversion integral. Thus, if $A = A(\alpha)$ and $E = E(\alpha)$, the Flynn-Wall-Ozawa method cannot be used. As far as the Friedman method is concerned, this leads to correct values for the activation energy, as the rate equation need not be integrated. Thus, for $A = A(\alpha)$ and $E = E(\alpha)$, one expects B values outside the range required by (11).

A criterion for determining the analytical form of the differential conversion function from TG data

The mechanism of solid-gas decompositions or thermal degradations is expressed by the conversion function $f(\alpha)$. Obviously, the values of the activation parameters depend on the analytical form of $f(\alpha)$. In order to find the conversion function, the following procedures have been suggested:

• The function $f(\alpha)$ should have the same analytical form as the corresponding function obtained from isothermal data [6–10].

• The optimal form of $f(\alpha)$ corresponds to the best linearization of the equation from which the activation parameters are obtained [11–13].

• The analytical form of $f(\alpha)$ is the one that leads to the same value of the preexponential factor A, for various linear heating rates [14].

• The analytical form of $f(\alpha)$ can be obtained from the DTG curve [15, 16].

The first procedure requires the isotherms of weight loss recorded at three temperatures at least. The main disadvantage of this procedure consists in the long time necessary for the experiments (hundreds of hours of isothermal heat-

ing). It has to be mentioned that in some cases the values of the parameters of $f(\alpha)$ obtained under isothermal conditions agree with the corresponding values obtained under non-isothermal conditions, but only for low heating rates.

As far as the second procedure is concerned, it has to be mentioned that for quite different analytical forms of $f(\alpha)$, correlation coefficients of linear regression higher than 0.99 are obtained. Under such conditions one cannot be sure whether lower values of the correlation coefficient are due to the improper choice of $f(\alpha)$ or to the experimental errors inherent to the measurements of thermogravimetric curves.

Concerning the third procedure one has to state that, due to the experimental errors, the A values are not rigorously constant for various heating rates but they are within the same order of magnitude. On the other hand, for several analytical forms of $f(\alpha)$ it is possible to find the A values within the same order of magnitude.

Finally, the use of DTG curves in order to obtain the analytical form of $f(\alpha)$ (the fourth procedure) is not always recommendable, especially for thermal or thermooxidative degradation of some polymeric materials. As shown by us earlier [17], one DTG peak obtained during the thermooxidative degradation of an unsaturated polyester resin corresponds to more than one overlapping consecutive reactions.

In this work we suggest another procedure for finding the analytical form $f(\alpha)$ and the mechanism of thermal or thermooxidative degradation. Taking into account that the activation energy can be obtained by means of an isoconversional method without the knowledge of $f(\alpha)$, we will consider such a value as correct. On the other hand, from Eqs (3) and (5) we get:

$$\ln \frac{d\alpha/dT}{f(\alpha)} = \ln \frac{A}{\beta} - \frac{E}{RT} \qquad (13)$$

i.e. the plot $(\ln(d\alpha/dT)/f(\alpha)$ vs. $1/T)$ is linear with a slope of E/R.

Thus, from various analytical forms of $f(\alpha)$ used in (13), the correct one leads to an activation energy which is close to the isoconversional value. The main advantage of this procedure consists in the fact that improper analytical forms of $f(\alpha)$ lead to significant differences between the two values of the activation energy. The disadvantages of this procedure come from the limitation of isoconversional methods. Thus, the procedure cannot be used if the activation parameters depend on the degree of conversion.

Applications

The criterion of agreement between E_{FWO} and E_{FR} (Eq. (11)) will be applied to thermogravimetric data from reference [14], for the dehydration of calcium oxalate monohydrate and for the thermooxidative degradation of an unsaturated

polyester resin (resin A). For the first and third cases, where the activation energy is constant, the analytical form of $f(\alpha)$ will be obtained by help of the criterion suggested in the previous paragraph.

Simulated thermogravimetric data from reference [14]

The data have been generated for:

$$f(\alpha) = 1-\alpha; \ E = 83.6 \text{ kJ mol}^{-1}; \ A = 1.67 \cdot 10^{10} \text{ s}^{-1}$$

and for the heating rates: 1, 2, 5, 10, 20, 50 and 100 K min^{-1}.

Using the Flynn-Wall-Ozawa and the Friedman methods, the activation energy was estimated in the range of conversion of 0.1–0.6. In order to apply Friedman's method, the TG curves were approximated with a fourth degree polynomial in T (the correlation coefficient of the polynomial for all the heating rates used was 0.9999).

The values of the activation energy calculated using this procedure are listed in Table 1. The data in the table indicate a good agreement between E_{FWO} and E_{FR}.

Table 1 Activation energy values estimated by means of the Flynn-Wall-Ozawa and the Friedman methods; checking relationship (11) for thermogravimetric data from [14]

| α | Flynn-Wall-Ozawa | | Friedman | | B Eq. (10)* | B_{max} Eq. (11) | E_{FR} Eq. (8) |
| | E_{FWO} | r | E_{FR} | r | | | |
	kJ mol^{-1}		kJ mol^{-1}		kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
0.1	84.4	0.9999	84.4	0.9999	$0 \leq B \leq 5.8$	12.8	83.0–88.8
0.2	84.6	0.9999	83.6	0.9999	$5.4 \leq B \leq 5.8$	12.8	83.1–83.6
0.3	84.8	0.9999	83.6	0.9999	$5.6 \leq B \leq 5.8$	12.9	83.3–83.6
0.4	84.8	0.9999	83.6	0.9999	$5.4 \leq B \leq 6.3$	12.9	82.9–83.8
0.5	84.8	0.9999	84.0	0.9996	$4.8 \leq B \leq 6.3$	12.9	82.9–84.4
0.6	84.8	0.9999	84.0	0.9997	$4.0 \leq B \leq 6.3$	12.8	82.9–85.2

* The ranges of values in columns 6 and 8 are due to the deviations from linearity of the $\ln d\alpha/dT$ vs. $1/T$ plots.

Actually for $\alpha > 0.1$, E_{FWO} is slightly higher than E_{FR}.

In order to estimate the constant B from Eq. (10), $\ln d\alpha/dT$ was approximated by a fourth degree polynomial of $1/T$. For all the heating rates, values of correlation coefficients higher than 0.996 were obtained. In Table 1, the maximum values of B according to Eq. (11) are also listed. In the same Table the values of E_{FR} calculated from E_{FWO} and B suing Eq. (8) are given, too. One can notice that for the entire range of conversions considered, the criterion of agreement between E_{FWO} and E_{FR} according to Eq. (11) is fulfilled. Besides the

values of α corresponding to the boundaries of the range for which the $\ln d\alpha/dT$ values exhibit higher errors, the values of E_{FR} calculated by means of Eq. (8) are close to the values of E_{FR} obtained by application of Friedman's method. This result agrees with Ozawa's observation [19] that Friedmans' method is highly reliable since the activation energy is obtained without the approximations used to estimate the temperature integral. This is the reason why the last two terms in the right-hand side of Eq. (8) may be considered as corrections of the activation energy determined using Flynn-Wall-Ozawa method.

Table 2 Analytical forms of the conversion function

Mechanism	Code	$f(\alpha)$
Avrami-Erofeev ($m=2$)	AE2	$(1 - \alpha)[-\ln(1 - \alpha)]^{1/2}$
Diffusion mechanism	D1	α^{-1}
	D2	$[-\ln(1 - \alpha)]^{-1}$
Reaction order	R1	$1 - \alpha$
	R1.5	$(1 - \alpha)^{1.5}$

In order to check the criterion for determining the mechanism suggested by us, the analytical forms of $f(\alpha)$ listed in Table 2 were considered. For all these differential functions of conversion, the straight lines $\ln (d\alpha/dT)/f(\alpha)$ vs. $(1/T)$ were plotted and from the slopes the corresponding values of E were estimated. The results obtained for the heating rates of 1 and 10 K min^{-1} are listed in Table 3.

Table 3 Values of activation energy obtained from the slope of the straight line $\ln(d\alpha/dT)/f(\alpha)$ vs. $(1/T)$ for the reaction mechanism listed in Table 2

Mechanism	$\beta = 1$ K min^{-1}		$\beta = 10$ K min^{-1}	
	E/kJ mol^{-1}	r	E/kJ mol^{-1}	r
AE2	42.6	0.9967	41.4	0.9958
D1	127.8	0.9947	127.9	0.9956
D2	143.8	0.9978	143.0	0.9985
R1	86.9	0.9992	86.1	0.9990
R1.5	105.7	0.9976	102.2	0.9967

For all the heating rates the values obtained for E, corresponding to each reaction mechanism as expressed by $f(\alpha)$ agree. Although for all the considered mechanisms satisfactory values were obtained for the correlation coefficient ($r>0.994$) have been obtained, the best value of the correlation coefficient corresponds to model R1. There are significant differences among the E values

obtained for various mechanisms and the values of E agree with those obtained by means of isoconversional methods only for mechanism R1. It is to be noted that R1 is the mechanism used to simulate the thermogravimetric data [14].
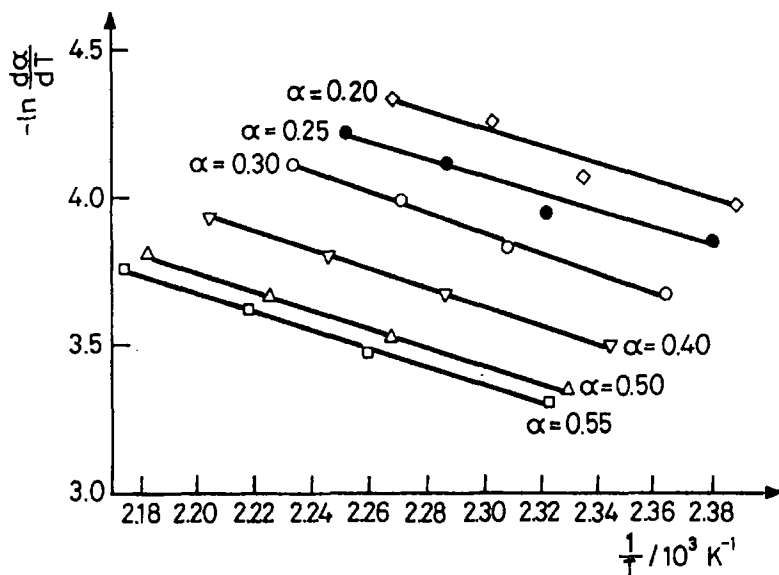

Fig. 1 ln$d\alpha/dT$ *vs.* (1/T) plots for the dehydration of calcium oxalate monohydrate

Dehydration of calcium oxalate monohydrate

Thermogravimetric data from [21] for heating rates of 0.987; 2.353; 4.988 and 9.573 K min^{-1} were used. The activation energies were estimated by means of the Flynn-Wall-Ozawa and the Friedman methods using values of the degree of conversion in the range 0.20–0.55. Like in the previous case, the method described in [17] was used to evaluate $d\alpha/dT$. By approximating the TG curve with a polynomial of fourth degree in T, the found values of the correlation coefficient were higher than 0.9989. The values obtained for the activation energy are listed in Table 4. The activation energy decreases with the degree of conversion and $E_{FWO}>E_{FR}$. It was shown that for the considered range of heating rates ln $d\alpha/dT$ depends linearly on (1/T) (Fig. 1). In Table 4 the B values obtained from the slopes of the straight lines shown in Fig. 1 as well as the maximum value of B corresponding to condition (11) are also given. Thus, for the dehydration of calcium oxalate monohydrate the condition of agreement between E_{FWO} and E_{FR} values is not fulfilled. This is due to the change of E with the degree of conversion and hence to the fact that under these conditions the Flynn-Wall-Ozawa method leads to erroneous results. The data in Table 4 also suggest that the use of Eq. (8) leads to E_{FR} values closer to those obtained by

Table 4 Activation energy values estimated by means of the Flynn-Wall-Ozawa and the Friedman methods; checking relationship (11) for the dehydration of calcium oxalate

	Flynn-Wall-Ozawa		Friedman				
α	E_{FWO}	r	E_{FR}	r	B Eq. (10)	B_{max} Eq. (11)	E_{FR} Eq. (8)
	kJ mol^{-1}		kJ mol^{-1}		kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
0.20	148.0	0.9974	129.6	0.9997	25.7	22.5	130.0
0.25	137.9	0.9976	115.4	0.9983	25.1	21.0	120.0
0.30	131.2	0.9980	109.1	0.9990	28.2	19.9	109.8
0.40	127.5	0.9990	105.7	0.9991	26.7	19.4	107.4
0.50	122.1	0.9978	101.6	0.9974	26.3	18.6	102.1
0.55	120.0	0.9980	101.4	0.9976	26.3	18.2	99.9

Table 5 Activation energy values estimated by means of the Flynn-Wall-Ozawa and the Friedman methods; checking relationship (11) for the thermooxidative degradation of resin A

	Flynn-Wall-Ozawa		Friedman				
Δm/	E_{FWO}	r	E_{FR}	r	B Eq. (10)	B_{max} Eq. (11)	E_{FR} Eq. (8)
%	kJ mol^{-1}		kJ mol^{-1}		kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
20	196.9	0.9964	199.0	0.9941	$18.4 < B < 28.8$	29.9	178.3–188.7
25	188.9	0.9921	187.3	0.9912	$20.3 < B < 23.1$	28.7	175.6–178.4
30	184.3	0.9913	183.5	0.9944	$13.8 < B < 24.7$	28.0	169.1–180.0
35	185.2	0.9937	185.2	0.9927	$16.8 < B < 22.8$	28.1	172.0–178.0

direct application of Friedman's method. Thus, in this case the last two terms in the right-hand side of Eq. (8) represent significant corrections of E_{FWO}.

Consequently, the suggested criterion for obtaining $f(\alpha)$ cannot be applied in this case.

Thermooxidative degradation of an unsatured polyester resin (resin A)

The results concerning the isothermal and non-isothermal degradation of resin A have been presented in a previous paper [17]. It has been shown that for heating rates of 1.45; 2.97; 5.95 and 12.20 K min^{-1} the Flynn-Wall-Ozawa and the Friedman plots are linear and the weight losses, Δm, are within the range of 15–35%. The activation energies determined by means of the Flynn-Wall-Ozawa and the Friedman methods are listed in Table 5. In the same Table are given the ranges of B values calculated by means of Eq. (10), the maximum value of B which results from (11), as well as the E_{FR} values calculated according to relationship (8). The condition of agreement between E_{FWO} and E_{FR} given by (11) is fulfilled. The errors which are inherent for a complex system like

resin A are reflected by the relatively broad range of B values calculated by means of Eq. (10) as well as by the relatively significant differences between E_{FR}, obtained from E_{FWO} and B, and the value determined directly. Nevertheless, the differences between the E_{FR} values and the E_{FR} values determined directly are acceptable as they are less than 10%. Thus, for resin A, the values of E_{FWO} and E_{FR} are in satisfactory agreement.

Isothermal studies of the thermooxidative degradation of resin A [17] have shown that $f(\alpha)$ has the form:

$$f(\alpha) = \alpha^{-n} \equiv \left(\frac{\Delta m}{\Delta m_{max}}\right)^{-n} \tag{14}$$

where $n \geq 1$ and Δm_{max} is the maximum weight loss in the considered change.

Conversion function (14) describes a diffusional mechanism. Obviously, the same analytical form of the conversion function should be valid for the non-isothermal degradation. In order to determine the value of n for 1.45 K min^{-1} $\leq \beta \leq 12.20$ K min^{-1}, we applied the procedure suggested by us using the following equation which is obtained from (13) and (14):

$$\ln\left[(\Delta m)^n \frac{d\Delta m}{dT}\right] = \ln \frac{A(\Delta m_{max})^{n+1}}{\beta} - \frac{E}{RT} \tag{15}$$

Table 6 Values of E obtained from the slope of the straight line $\ln[(\Delta m)^n\, d\Delta m/dT]$ vs. $(1/T)$ for the thermooxidative degradation of resin A

$\beta/$ K min^{-1}	$n=1$ $E/$ kJ mol^{-1}	r	$n=1.1$ $E/$ kJ mol^{-1}	r	$n=1.2$ $E/$ kJ mol^{-1}	r
1.45	151.3	0.9987	159.7	0.9988	167.8	0.9988
2.97	145.0	0.9980	159.7	0.9977	166.1	0.9978
5.95	144.2	0.9994	155.7	0.9997	162.9	0.9998
12.2	132.9	0.9982	140.0	0.9983	147.1	0.9984

$\beta/$ K min^{-1}	$n=1.3$ $E/$ kJ mol^{-1}	r	$n=1.4$ $E/$ kJ mol^{-1}	r	$n=1.5$ $E/$ kJ mol^{-1}	r
1.45	188.5	0.9987	196.9	0.9987	204.8	0.9988
2.97	178.1	0.9983	184.3	0.9985	192.7	0.9987
5.95	170.2	0.9998	177.2	0.9998	184.3	0.9998
12.2	165.5	0.9996	173.0	0.9996	180.2	0.9996

The E values were estimated for $1.0 \le n \le 1.5$ from the slopes of the straight lines $\ln[(\Delta m)^n d\Delta m/dT]$ vs. $(1/T)$. The results obtained are listed in Table 6. The inspection of this table shows that:

– for all the n values, correlation coefficients close to unity were obtained;
– the E values increase with n;
– the E values decrease slightly with the heating rate.

Comparison of the values of E listed in Table 6 with values of E obtained using isoconversional methods listed in Table 5 shows that for $n = 1.4$ and $n = 1.5$ one obtains a satisfactory agreement. Thus, the thermooxidative degradation of resin A occurs according to a diffusional mechanism described by the conversion function (14) with $1.4 \le n \le 1.5$.

Conclusions

1 The applicability of the Flynn-Wall-Ozawa and the Friedman isoconversional methods used to evaluate the activation energy was discussed.

2 The agreement between the results provided by the two methods is satisfactory, if the activation energy does not depend on the degree of conversion.

3 If the activation energy depends on the degree of conversion one has to use Friedman's method which does not require integration of the rate equation.

4 A criterion was suggested for finding the analytical form of the conversion function.

5 The presented theoretical considerations were checked for three sets of thermogravimetric data.

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