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Approximation of the TG curve through a temperature power series in order to evaluate the non-isothermal kinetic parameters of solid–gas decompositions and degradation

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Abstract

A procedure has been developed for evaluating non-isothermal kinetic parameters based on the development of the degree of conversion in a temperature power series. The procedure was applied to the dehydration of calcium oxalate monohydrate and to the thermooxidative degradation of an unsaturated polyester resin.

Keywords: Calcium oxalate; Non-isothermal kinetic parameters; Solid–gas decomposition; Solid–gas degradation; Temperature power series; TG curve approximation

1. Introduction

The general rate equation in terms of the degree of conversion, time and temperature has the form:

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

where the separation of the functions of temperature and conversion is not rigorously justified [1]. Eq. (1) is the basis of the differential and integral methods used in order to

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evaluate non-isothermal kinetic parameters [2]. Among the methods which do not require the knowledge of the analytical form of f(α) in order to obtain the value of the activation energy, one has to mention the isoconversional ones due to Friedman [3], Ozawa [4] and Flynn–Wall [5]. The main disadvantage of these methods consists in the fact that the second activation parameter, the preexponential factor, cannot be directly evaluated in their framework.

This paper deals with a procedure to evaluate non-isothermal kinetic parameters by means of a differential method which uses TG curves. The procedure is based on approximation of a portion of the TG curve, corresponding to the investigated change, by a temperature power series. From the known analytical form of the TG curve, one can evaluate the reaction rate for various degrees of conversion, α_i, and consequently differential methods for the evaluation of the non-isothermal kinetic parameters can be applied. This procedure is applied to the dehydration of calcium oxalate monohydrate and thermooxidative degradation of a styrenated unsaturated polyester resin.

2. Procedure for evaluating non-isothermal kinetic parameters

In the following we shall consider Eq. (1) as correct, the function $k(T)$ being given by the Arrhenius equation:

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

where A is the preexponential factor, E is the activation energy, T is the temperature (K) and R is the gas constant.

From Eqs. (1) and (2) we obtain:

$$\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \ln A - \frac{E}{RT} + \ln f(\alpha) \tag{3}$$

Thus for $\alpha = \text{const.}$, the plot of $(\ln \mathrm{d}\alpha/\mathrm{d}t)$ versus $(1/T)$ is a straight line whose slope enables the evaluation of the activation energy.

This is, in fact, the principle of Friedman's method [3]. In order to obtain reliable values of the reaction rate, the thermogravimetric curves, in coordinates α, T (the values of α and T being determined with rather high precision) have to be used. For a given range of degrees of conversion we shall try the following approximation:

$$\alpha(T) = \sum_{i=0}^{N} c_i T^i \tag{4}$$

where c_i values are constants and i an integer. In order to determine the constants c_i a fitting program was used [6].

Once the values of c_i are known the reaction rate at the temperature T can be calculated taking into account that:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} \equiv \beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} \tag{5}$$

where β is the heating rate, and according to Eq. (4):

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \sum_{i=1}^{N} ic_i T^{i-1} \tag{6}$$

Thus combining Eqs. (5) and (6) it follows that:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \beta \sum_{i=1}^{N} ic_i T^{i-1} \tag{7}$$

Eq. (7) can be used directly to evaluate the reaction rates and the activation energy with the help of the Friedman method.

Concerning the form of the conversion function which expresses the reaction mechanism, among the procedures suggested for its determination one has to mention that of Dollimore et al. [7, 8] based on the use of DTG ($\mathrm{d}\alpha/\mathrm{d}T$ versus T) curves. In our opinion, the application of such a method to the thermal or thermooxidative degradation of complex materials like polymers can lead to unrealistic values of kinetic parameters. As will be shown in this paper the peak of the DTG curve for the thermooxidative degradation of a polyester resin may correspond to several successive degradation processes.

In this work we suggest another procedure for finding the differential conversion function $f(\alpha)$ which consists in the evaluation of the activation energy using an isoconversional method, like Friedman's, and then the function $f(\alpha)$ which leads to almost the same value of E from the plot ($\ln[(\mathrm{d}\alpha/\mathrm{d}T)/f(\alpha)]$ versus $1/T$).

3. Applications

3.1. The dehydration of calcium oxalate monohydrate

In order to evaluate the activation energy the data shown in Table 1 have been used [9]. These data enabled us to evaluate the activation energy by integration of the rate equation over small changes of variables. It has been shown that the activation energy decreases with the degree of conversion. Some of the results obtained are given in Fig. 1.

In the same figure the values of the activation energy obtained by the Flynn–Wall–Ozawa method are also shown.

Our calculations have shown that for $0.10 \leq \alpha \leq 0.75$ a good approximation of the curves $\alpha(T)$ is given by a fourth degree power series in T with the values of the coefficients c_i given in Table 2. Comparison with the data given in Table 1 shows that the experimentally determined α values are in fairly good agreement with those calculated using the power series. Using the values of c_i, the values of $(\mathrm{d}\alpha/\mathrm{d}t) \equiv \beta(\mathrm{d}\alpha/\mathrm{d}T)$ have been calculated. Fig. 2 shows the curves $\ln(\beta(\mathrm{d}\alpha/\mathrm{d}T))$ versus α which have been used to draw the curves $\ln(\beta(\mathrm{d}\alpha/\mathrm{d}T))$ versus $1/T$ (Fig. 3), from whose slopes we obtain the values of the activation energy ($r \geq 0.998$). According to these results, the values of E decrease from 155.1 kJ mol^{-1} for $\alpha = 0.15$ to 88.8 kJ mol^{-1} for $\alpha = 0.75$. These values (see Fig. 1) agree with those obtained using the Urbanovici–

Table 1
Values of the degree of conversion for the dehydration of calcium oxalate monohydrate determined experimentally and values calculated using power series Eq. (4)

$\beta_1 = 0.987/(\mathrm{K\,min^{-1}})$			$\beta_2 = 2.353/(\mathrm{K\,min^{-1}})$			$\beta_3 = 4.988/(\mathrm{K\,min^{-1}})$			$\beta_4 = 9.573/(\mathrm{K\,min^{-1}})$		
T/K	α_{det}	α_{calc}	T/K	α_{det}	α_{calc}	T/K	α_{det}	α_{calc}	T/K	α_{det}	α_{calc}
412.5	0.10	0.12	420.9	0.10	0.105	425.3	0.10	0.10	430.8	0.10	0.09
414	0.15	0.13	424.5	0.15	0.15	429.5	0.15	0.145	436.5	0.15	0.15
418.4	0.20	0.20	428.1	0.20	0.20	434	0.20	0.21	441	0.20	0.21
420	0.25	0.23	430.5	0.25	0.24	437	0.25	0.25	444	0.25	0.25
422.8	0.30	0.30	433.1	0.30	0.30	440.2	0.30	0.31	447.6	0.30	0.31
424.8	0.35	0.36	435.5	0.35	0.355	442	0.35	0.34	450	0.35	0.35
426.2	0.40	0.40	437.2	0.40	0.40	445.3	0.40	0.41	453.2	0.40	0.405
427.8	0.45	0.45	439.2	0.45	0.45	447	0.45	0.45	455	0.45	0.44
429.2	0.50	0.50	441	0.50	0.51	449.2	0.50	0.50	458	0.50	0.50
430.5	0.55	0.55	442.5	0.55	0.55	450.8	0.55	0.54	460	0.55	0.54
431.9	0.60	0.61	443.8	0.60	0.595	455.1	0.60	0.60	462.4	0.60	0.60
433	0.65	0.66	445.5	0.65	0.65	455	0.65	0.65	464.5	0.65	0.65
434	0.70	0.70	446.6	0.70	0.69	456.8	0.70	0.70	466.2	0.70	0.69
434.5	0.75	0.72	448	0.75	0.74	458.5	0.75	0.75	469	0.75	0.76

Table 2
The values of the constants c_i in the power series $\alpha(T) = \sum_{i=0}^{N} c_i T^i$ for dehydration of calcium oxalate monohydrate

$\beta/(\mathrm{K\,min^{-1}})$	c_0	$c_1 \times 10^3$	$c_2 \times 10^6$	$c_3 \times 10^8$	$c_4 \times 10^{10}$	r[a]
0.987	39.3069	−58.56	−239.80	−9.3790	11.172	0.9989
2.353	66.5702	−252.01	−9.1845	69.158	−3.2935	0.9998
4.988	6.2344	2.0978	−27.550	−27.547	5.9074	0.9996
9.573	−49.4300	303.96	−447.33	−41.462	10.086	0.9995

[a] The correlation coefficient of the power series.

Segal method [9], but are lower than those obtained using Flynn–Wall–Ozawa method.

For the dehydration of calcium oxalate monohydrate it has been shown [10, 11] that the activation energy is correlated with the preexponential factor through the compensation effect. The problem of evaluation of the preexponential factor as well as of the compensation parameters for this system is discussed elsewhere [11].

3.2. *The thermooxidative degradation of a styrenated unsaturated polyester resin*

The analysis of the thermogravimetric data for the thermooxidative degradation of polymeric materials raises the following problems:

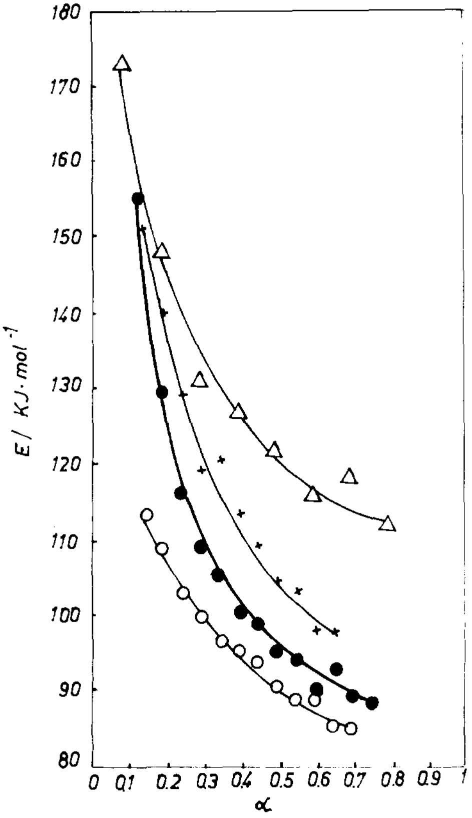

Fig. 1. The curve $E(\alpha)$ for the dehydration of calcium oxalate monohydrate. Methods of evaluating the activation energy according to: ○ Urbanovici and Segal for $\beta_1 = 0.987\ \mathrm{K\ min^{-1}}$ and $\beta_2 = 2.353\ \mathrm{K\ min^{-1}}$; + Urbanovici and Segal for $\beta_2 = 2.353\ \mathrm{K\ min^{-1}}$ and $\beta_3 = 4.988\ \mathrm{K\ min^{-1}}$; △ Flynn–Wall–Ozawa; ● Friedman (power series).

(1) to find the analytical form of the differential conversion function, $f(\alpha)$, as well as the range of variables in which this function describes the degradation;
(2) to find the dependence of the kinetic parameters on the heating rate;
(3) to find the dependence of the kinetic parameters on the degree of degradation

In order to find the power form of $f(\alpha)$, the isothermal degradation of polymeric materials should also be investigated. The results of such long experiments in conjunction with those obtained under non-isothermal conditions led to the correct form of $f(\alpha)$ for the proper range of experimental variable changes.

In order to illustrate these statements we have investigated the thermooxidative degradation of a styrenated unsaturated polyester resin (resin A).

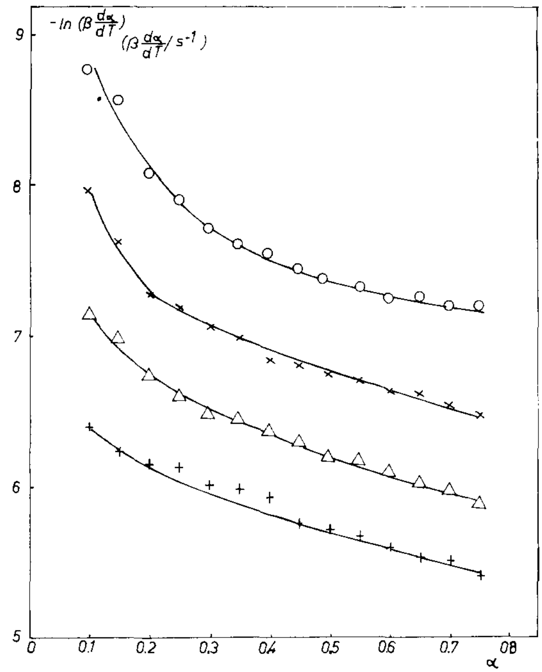

Fig. 2. The curves $\ln(\beta(d\alpha/dT))$ versus α for the dehydration of calcium oxalate monohydrate ○ $\beta = 0.987\ \mathrm{K\ min^{-1}}$; × $\beta = 2.353\ \mathrm{K\ min^{-1}}$; △ $\beta = 4.988\ \mathrm{K\ min^{-1}}$; + $\beta = 9.573\ \mathrm{K\ min^{-1}}$.

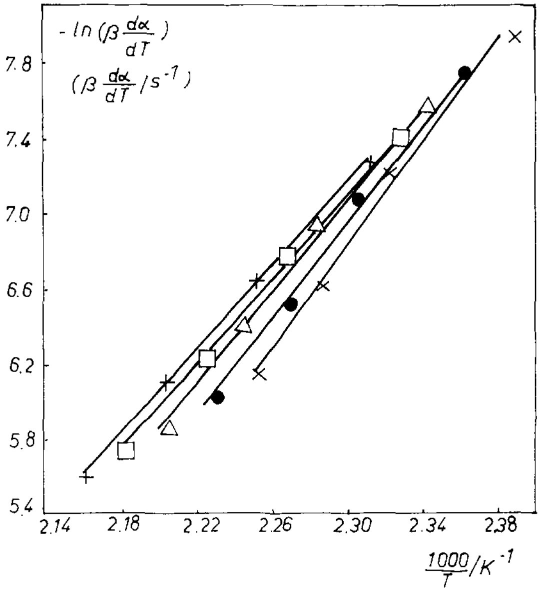

Fig. 3. The straight lines $\ln(\beta(d\alpha/dT))$ versus $1/T$ for the dehydration of calcium oxalate monohydrate × $\alpha = 0.20$; ● $\alpha = 0.30$; △ $\alpha = 0.40$; □ $\alpha = 0.50$; + $\alpha = 0.60$.

4. Experimental

Resin A, a highly reactive unsaturated polyester, Nestrapol 450, manufactured by Polycolor–Bucharest (Romania), was used as raw material. This resin contains 65% (weight percentage) unsaturated polyester formed from maleic anhydride, phthalic anhydride and propylene glycol and 35% styrene (0.51 mol styrene per 100 g unsaturated polyester; ≈ 1.72 mol styrene per gram-equivalent double bonds in the polyester). The characterization of the resin Nestrapol 450 gave the following results: density 1.135 g cm^{-3}; acidity index 30.7 mg KOH g^{-1}; hydroxyl index 16.0 mg KOH g^{-1}.

The resin was prepared by block-copolymerization in the presence of 1% *t*-butyl perbenzoate (16 h at 80°C + 1 h at 90°C + 2 h at 100°C). A thermosetting resin was obtained by this procedure.

The results concerning the isothermal and non-isothermal thermooxidative degradation of a similar material are reported in another paper [12].

The isothermal degradation of resin A was investigated using a WSU oven in which the temperature was kept constant with a precision of ± 2°C.

The heating curves of the powdered samples were obtained with a Q-1500D MOM Budapest-type Paulik–Paulik–Erdey derivatograph in static air atmosphere in the temperature range 20–500°C at the heating rates: 0.68, 1.45, 2.97, 5.95 and 12.20 K min^{-1}.

5. Results and discussion

5.1. *The isothermal degradation of resin A*

Fig. 4 shows the weight loss (%) versus ageing time isotherms at 190°C, 200°C, 210°C and 220°C.

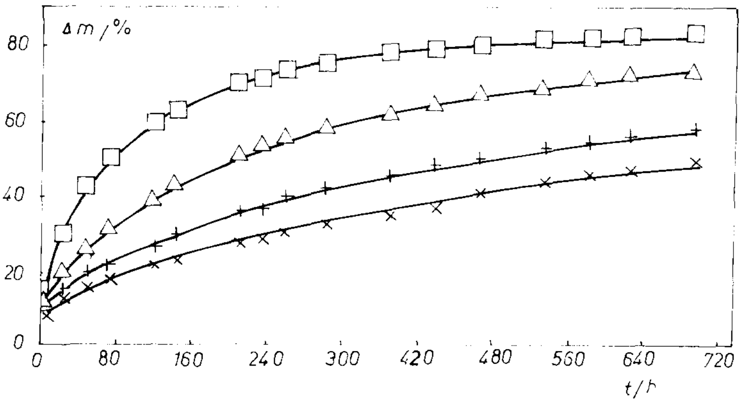

Fig. 4. The isotherm of weight loss of the resin A. × 190°C; + 200°C; △ 210°C; □ 220°C.

The inspection of these curves shows that for all the temperatures, after an initial period characterized by a fast weight loss ($t < 3$ h) a relatively slow degradation occurs.

As will be shown subsequently from the non-isothermal data, the fast initial weight loss is followed by a slower degradation which ends at $\Delta m \approx 35\%$. The kinetic parameters of this latter reaction will be determined.

For the kinetic analysis of the data obtained under isothermal conditions we assume Eqs. (1) and (2) to be valid. The degree of conversion can be written in term of weight loss, Δm, as follows:

$$\alpha = \frac{\Delta m}{\Delta m_{\max}} \tag{8}$$

where $\Delta m_{\max}$ is the total weight loss in the process of interest.

The integration of Eq. (1) leads to :

$$\ln t = \ln F(\Delta m) - \ln A + \frac{E}{RT} \tag{9}$$

$$\text{where: } F(\Delta m) = \frac{1}{\Delta m_{\max}} \int_{\Delta m_0}^{\Delta m} \frac{\mathrm{d}(\Delta m)}{f\left(\dfrac{\Delta m}{\Delta m_{\max}}\right)}$$

where Δm_0 is the initial weight loss.

For $\Delta m =$ const. the plot of $\ln t$ versus $1/T$ should be a straight line the slope of which enables the evaluation of the activation energy. Fig. 5 shows the three straight lines obtained for $\Delta m = 20\%$, $\Delta m = 25\%$ and $\Delta m = 30\%$.

For $20\% \leq \Delta m \leq 35\%$, the values of the activation energy located in the range $140.4(\pm 7.1)\,\mathrm{kJ\,mol^{-1}}$–$151.7(\pm 15.0)\,\mathrm{kJ\,mol^{-1}}$ ($r > 0.99$) can be considered practically constant.

The following relationship which can be derived from Eqs. (1), (2) and (8):

$$\ln\left(\frac{\mathrm{d}(\Delta m)}{\mathrm{d}t}\right) = \ln A(\Delta m_{\max}) f\left(\frac{\Delta m}{\Delta m_{\max}}\right) - \frac{E}{RT} \tag{10}$$

was used to evaluate the activation energy. This parameter can be obtained from the slope of the straight line $\ln(\mathrm{d}(\Delta m)/\mathrm{d}t)$ versus $1/T$ at $\Delta m =$ const. The degradation rate, $\mathrm{d}(\Delta m)/\mathrm{d}t$, was evaluated considering the development:

$$\Delta m = \sum_{i=1}^{N} b_i t^i \tag{11}$$

for $N = 4$. For all the isothermal curves the development in power series gave $r > 0.999$. For $20\% \leq \Delta m \leq 35\%$, the values of E are in the range $158.0(\pm 16.0)\,\mathrm{kJ\,mol^{-1}}$–$160.1$ $(\pm 16.0)\,\mathrm{kJ\,mol^{-1}}$ ($r > 0.985$). These values are in satisfactory agreement with those obtained from the straight lines of $\ln t$ versus $1/T$.

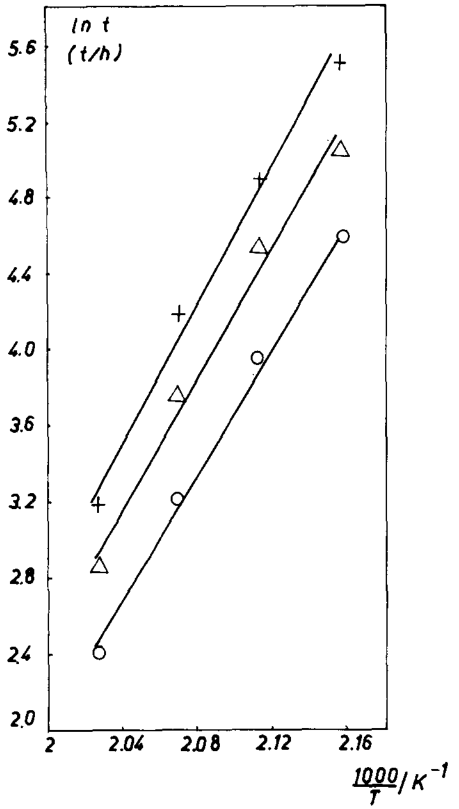

Fig. 5. The straight lines ln t versus $1/T$ for the isothermal degradation of the resin A. ○ $\Delta m = 20\%$; △ $\Delta m = 25\%$; + $\Delta m = 30\%$.

For $15\% \leq \Delta m \leq 35\%$ the following form of the differential conversion function will be considered:

$$f(\alpha) = \alpha^{-n} \equiv \left(\frac{\Delta m}{\Delta m_{\max}}\right)^{-n} \tag{12}$$

where $1 \leq n \leq 2$. This function is characteristic of diffusion-limited reactions [2, 13] ($n = 1$, unidimensional diffusion or parabolic law; $n = 2$, cubic law).

From Eqs. (9) and (12) it turns out that:

$$(\Delta m)^{n+1} = (\Delta m_0)^{n+1} - (n+1)(\Delta m_{\max})^{n+1} k t_0 + (n+1)(\Delta m_{\max})^{n+1} k t \tag{13}$$

The analysis of the experimental data showed that for $n = 1.0$ and $n = 1.1$, plots of $(\Delta m)^{n+1}$ versus t are straight lines with $r > 0.999$ (Figs. 6 and 7).

Taking into account Eqs. (2) and (13), plots of $\ln[(n+1)k(\Delta m_{\max})^{n+1}]$ versus $1/T$ for $n = 1.0$ and $n = 1.1$ have been drawn (Fig. 8). From the parameters of the so obtained

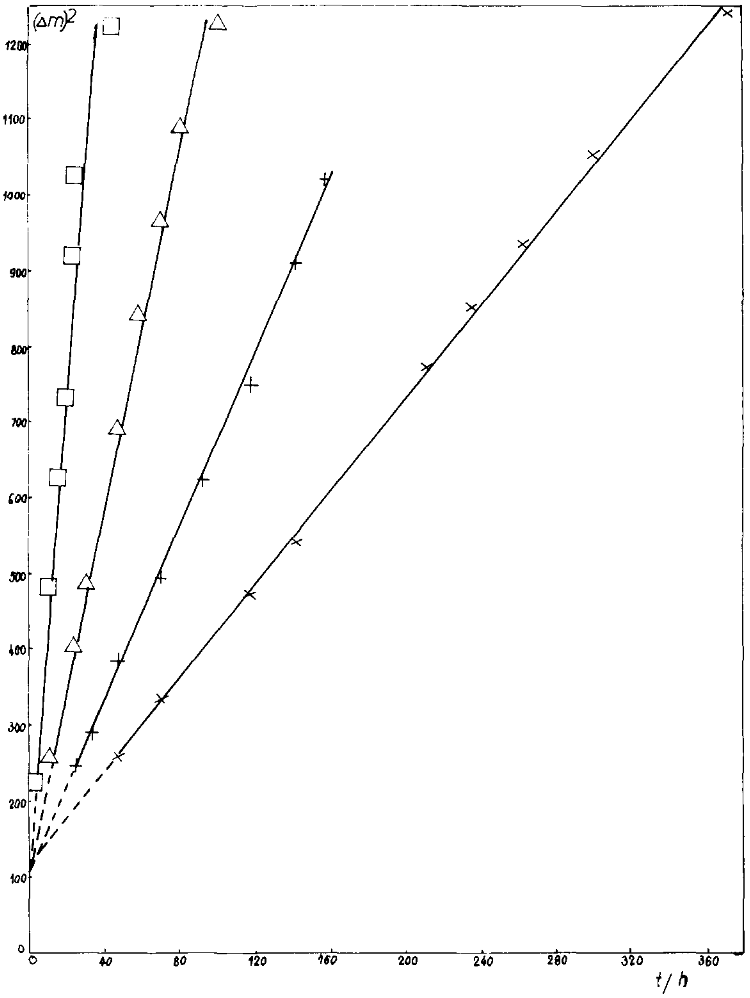

Fig. 6. The verification of Eq. (12) for the isothermal degradation of the resin A, $n = 1$. × 190°C; + 200°C; △ 210°C; □ 220°C.

straight lines the values of E and $A(\Delta m_{\max})^{n+1}$ have been evaluated (Table 3). One has to notice that the same values of E have been obtained in both the cases. The value lies in the range obtained with the help of the isoconversional methods applied to the isothermal data. We interpret these results as proof of the form of Eq. (12) for $f(\alpha)$.

5.2. *The non-isothermal degradation of resin A*

Fig. 9 shows the TG, DTG and DTA curves obtained at a heating rate $\beta = 2.97\,\mathrm{K\,min^{-1}}$; similar curves were obtained for other heating rates. The curves show that in the

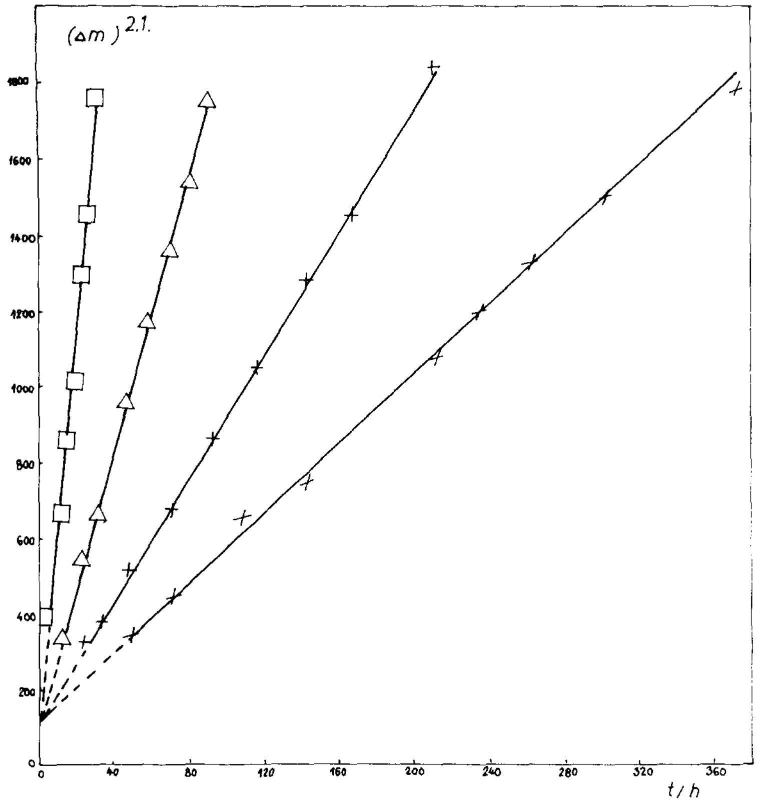

Fig. 7. The verification of Eq. (12) for the isothermal degradation of the resin A. $n = 1.1$. × 190°C; + 200°C; △ 210°C; □ 220°C.

Table 3
Values of the kinetic parameters for the isothermal degradation of resin A

n	$E/(\mathrm{kJ\,mol^{-1}})$	$\ln A(\Delta m_{\max})^{n+1}$ $(A(\Delta m_{\max})^{n+1}\,\mathrm{s})$	r[a]
1.0	150.1 ± 13.0	31.22 ± 3.26	0.9892
1.1	150.1 ± 13.0	33.00 ± 3.25	0.9892

[a] r is the correlation coefficient of the linear regression corresponding to the plot of $\ln[(n+1)k(\Delta m_{\max})^{n+1}]$ values versus $1/T$, (Fig. 8).

temperature range 20–500°C the following successive thermodegradation processes occur: an initial change I with 8.5% weight loss; an exothermic change II for which the weight loss reaches 36%; and a third change noted by III. The total weight loss of 78–80% is practically the same as that obtained under isothermal conditions at 220°C (see Fig. 4).

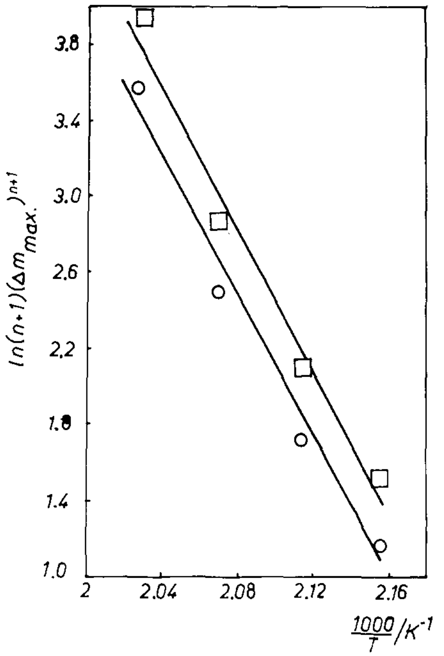

Fig. 8. The Arrhenius straight line for the isothermal degradation of resin A. ○ $n = 1$; □ $n = 1.1$.

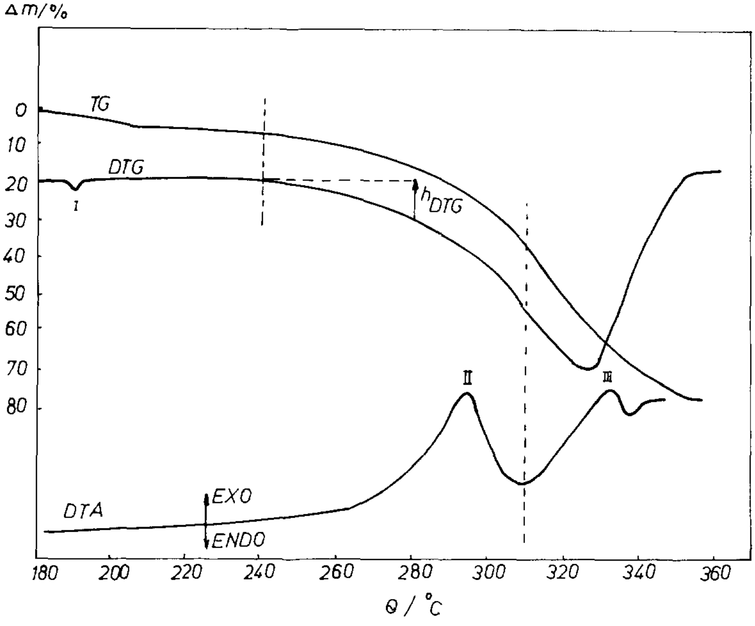

Fig. 9. The derivatogram of resin A in static air atmosphere at $\beta = 2.97\ \text{K min}^{-1}$.

The initial change corresponds to the fast initial weight loss observed for isothermal degradation. Considering that in Eq. (13) $t_0 \approx 0$, from the intercept of the straight lines $(\Delta m)^{n+1}$ versus t (see Figs. 6 and 7) it turns out that $9.0\% \leq \Delta m \leq 10.5\%$, i.e. values which are relatively close to the non-isothermal value.

The exothermic change II is delimited by the beginning of the change of the degradation rate after the peak I in the DTG curve and the beginning of the change II in the DTA curve. In order to determine that the change II corresponds to a thermooxidation, the thermal analysis curves of the resin A have been recorded in an oxygen atmosphere. A derivatogram similar to that from Fig. 9 was obtained but with more intense DTA peaks. It was also noticed that the TG and DTG curves were shifted toward lower temperatures ($\Delta T \approx -15$ K) with respect to the same curve obtained in air.

For $15\% \leq \Delta m \leq 35\%$ the Flynn–Wall–Ozawa diagrams for isoconversional conditions [5] have been recorded using local heating rates for $10\,\text{K} \leq \Delta T < 15\,\text{K}$ (Fig. 10).

The inspection of these diagrams shows that the degradation mechanism of resin A depends on the heating rate. For $\beta < 1.45\,\text{K min}^{-1}$ the kinetic parameter values are different from those obtained at $1.45\,\text{K min}^{-1} \leq \beta \leq 12.20\,\text{K min}^{-1}$ (the linear portion of the Flynn–Wall–Ozawa diagram). For this linear portion the values obtained for activation energy are listed in Table 4.

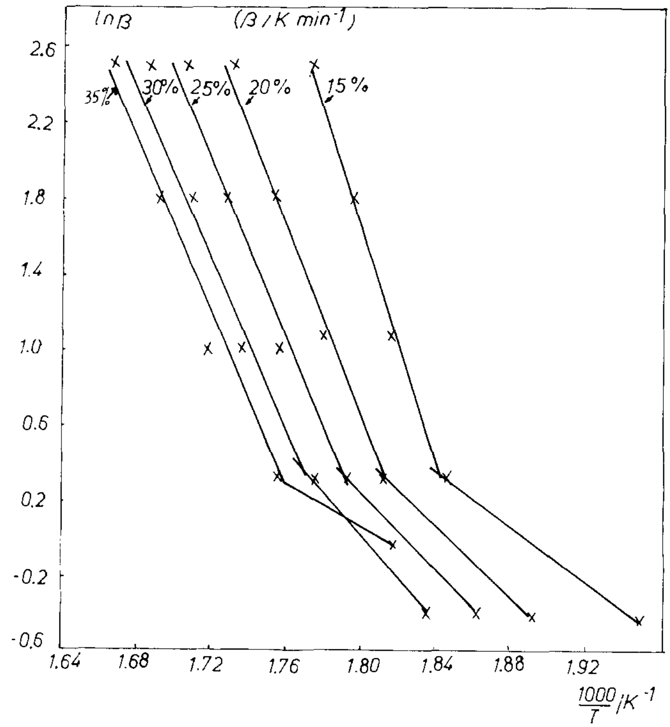

Fig. 10. Flynn–Wall–Ozawa isoconversion diagram for the thermal degradation of resin A.

Table 4
The values of the activation energy for various weight losses of the resin A determined with the help of isoconversional methods for 1.45 K min^{-1} $\leq \beta \leq$ 12.20 K min^{-1}

Δm %	Flynn–Wall–Ozawa		Friedman with h_{DTG}		Friedman power series	
	E/(kJ mol^{-1})	r	E/(kJ mol^{-1})	r	E/(kJ mol^{-1})	r
15	194.4 ± 22.0	0.9835	201.9 ± 14.0	0.9954	221.1 ± 24.0	0.9860
20	196.9 ± 14.5	0.9964	197.7 ± 10.0	0.9977	199.0 ± 15.5	0.9941
25	188.9 ± 17.3	0.9921	186.8 ± 13.8	0.9957	187.3 ± 17.6	0.9912
30	184.3 ± 17.5	0.9913	177.2 ± 17.1	0.9915	183.5 ± 13.8	0.9944
35	185.2 ± 14.6	0.9937	178.9 ± 10.0	0.9979	185.2 ± 15.9	0.9927

One can notice that for 15% $\leq \Delta m \leq$ 35%, E is practically constant (185 kJ mol^{-1}–197 kJ mol^{-1}). The values of E are higher than those obtained for the isothermal degradation.

The activation energy was also evaluated using the isoconversional method of Friedmann [3]. In order to use this method, Eq. (3), where α was transcribed in weight loss terms, (Eq. (8)) has been used. Thus the working equation has the form:

$$\ln\left(\frac{\mathrm{d}(\Delta m)}{\mathrm{d}t}\right) \equiv \ln\left(\beta\frac{\mathrm{d}(\Delta m)}{\mathrm{d}T}\right) = \ln A\Delta m_{\max} + \ln f\left(\frac{\Delta m}{\Delta m_{\max}}\right) - \frac{E}{RT} \tag{14}$$

The $\ln(\beta(\mathrm{d}(\Delta m)/\mathrm{d}T))$ have been evaluated:

(1) From the DTG curve, $\beta(\mathrm{d}(\Delta m)/\mathrm{d}T)$ being directly proportional to the ordinate of h_{DTG} (see Fig. 9);
(2) From the TG curve, considering that Δm can be developed in a fourth degree temperature power series.

Fig. 11 shows the Friedman diagram $\ln h_{\mathrm{DTG}}$ versus $1/T$ for 15% $\leq \Delta m \leq$ 35%. The analysis of this diagram confirms that for $\beta <$ 1.45 K min^{-1} the values of the kinetic parameters differ from those obtained for 1.45 K min^{-1} $\leq \beta \leq$ 12.20 K min^{-1} (the linear portion of the diagram). The values of the activation energy obtained for the linear portion of the diagram $\ln h_{\mathrm{DTG}}$ versus $1/T$ are listed in Table 4.

In order to evaluate the differential ratio $(\mathrm{d}(\Delta m)/\mathrm{d}t)$, from the TG curve, Δm was developed in a power series of T. The coefficients of the series for the heating rates at which the derivatograms have been recorded and 15% $\leq \Delta m \leq$ 35% are given in Table 5. The values of Δm calculated using these series are practically the same as those determined experimentally. Then $\ln(\beta(\mathrm{d}(\Delta m)/\mathrm{d}T))$ values have been calculated with these values of c_i. Fig. 12 shows the curves $\ln(\beta(\mathrm{d}(\Delta m)/\mathrm{d}T))$ versus Δm which have been used in order to draw the curves $\ln(\beta(\mathrm{d}(\Delta m)/\mathrm{d}T))$ versus $1/T$ (Fig. 13). The diagram from Fig. 13 shows also that for $\beta <$ 1.45 K min^{-1}, the kinetic parameter values differ from those obtained for 1.45 K min^{-1} $\leq \beta \leq$ 12.20 K min^{-1} (the linear portion of the diagrams). The values of the activation energy obtained for the linear portion of the

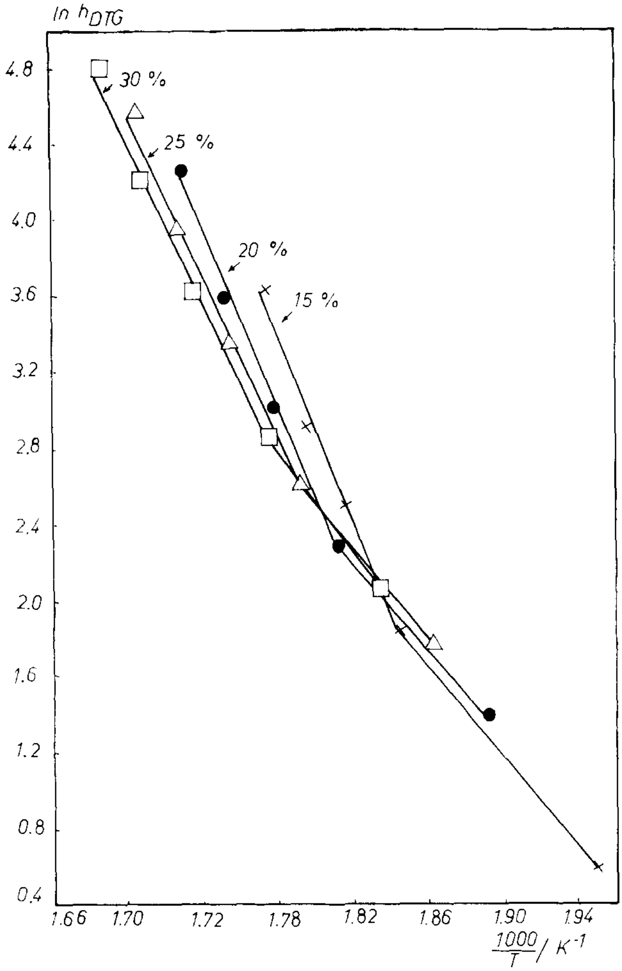

Fig. 11. Friedman diagram (ln h_{DTG} versus $1/T$) for the thermal degradation of resin A.

Table 5
The values of the constants c_i from the power series for change II of resin A

$\beta/(\mathrm{K\,min^{-1}})$	$c_0 \times 10^{-2}$	$c_1 \times 10^{2}$	$c_2 \times 10^{3}$	$c_3 \times 10^{6}$	$c_4 \times 10^{9}$	r
0.68	8.5083	−292.19	−4.9554	−11.631	13.413	0.9992
1.45	9.3584	−149.57	−1.8020	−2.6161	9.6870	0.9993
2.97	4.9629	−1.0760	−1.7320	−6.2126	11.823	0.9999
5.95	7.9150	−99.430	−3.1101	1.8050	4.4635	0.9994
12.20	9.1918	−194.50	−1.3920	2.1546	2.4575	0.9994

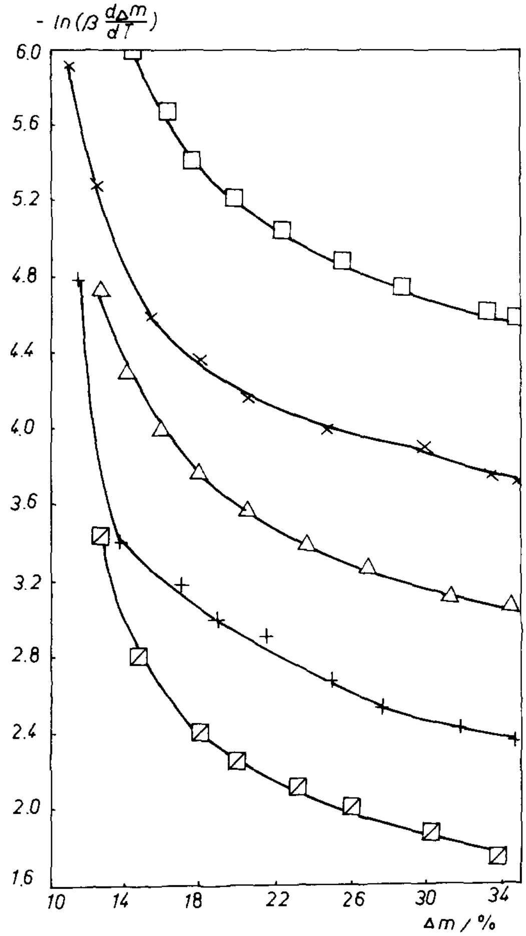

Fig. 12. The curves $\ln(\beta/(d(\Delta m)/dT))$ versus Δm for the thermal degradation of resin A. □ 0.68 K min^{-1}; × 1.45 K min^{-1}; △ 2.97 K min^{-1}; + 5.95 K min^{-1}; ⧄ 12.20 K min^{-1}.

curves of $\ln(\beta(d(\Delta m)/dT))$ versus $1/T$ are shown in Table 4. The value of E obtained using this method for $\Delta m = 15\%$ is higher than the values obtained using the other methods and exhibits a rather high error. This is because of the higher errors of reaction rate evaluation which are inherent to the lower boundary of the weight loss range.

Table 4 shows that the values of the activation energy determined with the help of the three isoconversional methods are in rather good agreement. The correctness of the method which uses power series of T is justified by the agreement of the results obtained by using the two variants of the Friedman method (using the DTG curves and the power series of temperature for Δm).

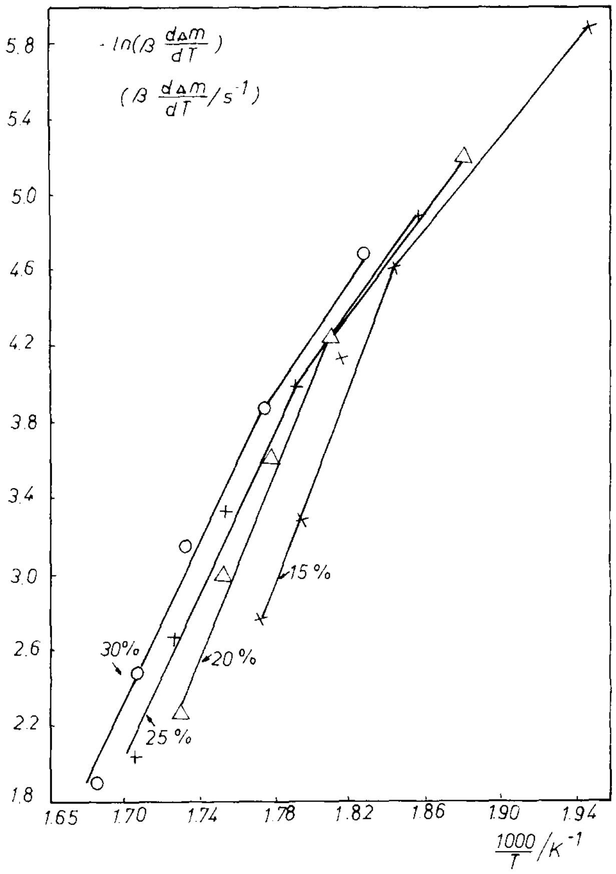

Fig. 13. Friedman diagram ($\ln(\beta(\mathrm{d}(\Delta m)/\mathrm{d}T))$ versus $1/T$) for the thermal degradation of resin A.

Considering that for the non-isothermal degradation, the differential conversion function f(α) is given by Eq. (12), from Eq. (14) one obtains:

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

Thus, the plot $\ln(\beta(\mathrm{d}(\Delta m)/\mathrm{d}T))+n\ln(\Delta m)$ versus $1/T$ should be a straight line with parameters which enable the evaluation of E and $\ln(A(\Delta m_{\max})^{n+1})$. Such straight lines for the thermogram obtained at $\beta = 0.68$ K min^{-1}, and values of n located in the range 1.0–1.5, are shown in Fig. 14. The values obtained for E and $\ln(A(\Delta m_{\max})^{n+1})$ are listed in Table 6. One can notice that the values of E for the considered range of n lie in the range of activation energy values obtained with the help of various methods for isothermal conditions. One can also notice that for $\beta = 0.68$ K min^{-1}, the E values are

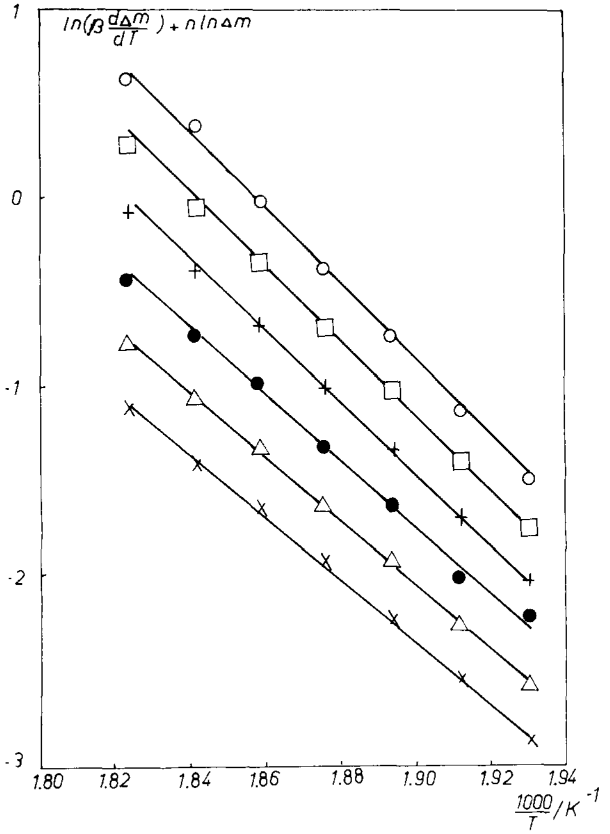

Fig. 14. The straight line $[\ln(\beta(d(\Delta m)/dT)) + n\ln(\Delta m)]$ versus $1/T$ corresponding to the TG curve obtained at $\beta = 0.68\ K\ min^{-1}$. × $n = 1.0$; △ $n = 1.1$; ● $n = 1.2$; + $n = 1.3$; □ $n = 1.4$; ○ $n = 1.5$.

Table 6
The values of the kinetic parameters for the non-isothermal degradation of the resin A (the thermogram was recorded at $\beta = 0.68\ K\ min^{-1}$)

n	$E/(kJ\ min^{-1})$	$\ln A(\Delta m_{max})^{n+1}$ $(A(\Delta m_{max})^{n+1} s)$	r
1.0	136.7 ± 1.9	28.97 ± 0.43	0.9995
1.1	142.5 ± 1.7	30.57 ± 0.39	0.9996
1.2	148.4 ± 1.7	32.19 ± 0.34	0.9997
1.3	153.8 ± 1.2	33.76 ± 0.32	0.9998
1.4	159.7 ± 1.2	35.36 ± 0.29	0.9998
1.5	165.1 ± 1.2	36.95 ± 0.27	0.9999

lower than those obtained with the help of isoconversional methods for 1.45 K min^{-1} $\leq \beta \leq$ 12.20 K min^{-1}. For $n = 1.0$ and $n = 1.1$, the values of $\ln(A(\Delta m_{\max})^{n+1})$ obtained from thermogravimetric data ($\beta = 0.68$ K min^{-1}) are in good agreement with those obtained from isothermal data (see Table 3). Thus, as expected, the non-isothermal kinetic parameter values obtained for the lowest value of the heating rate are close to the values obtained from isothermal data.

For 1.45 K $\mathrm{min}^{-1} \leq \beta \leq$ 12.20 K min^{-1} we have shown that if $\Delta m = \text{const.}$, the Flynn–Wall–Ozawa and Friedman plots are straight lines. Thus in this range of heating rates the degradation mechanism does not change. Considering that under such conditions Eq. (15) is still valid, for $T = \text{const.}$ the plot $\ln(\beta(\mathrm{d}(\Delta m)/d\,T))$ versus $\ln(\Delta m)$ should be a straight line, the slope of which enables the evaluation of n. In such a way it has been found that in the considered range of heating rates, $1.3 \leq n \leq 1.5$ ($r > 0.985$). For this range of n, from the parameters of the straight line $\ln(\beta(\mathrm{d}(\Delta m)/\mathrm{d}\,T))$ versus $1/T$, the non-isothermal kinetic parameter values of the degradation have been obtained. Such straight lines for $\beta = 2.97$ K min^{-1} are shown in Fig. 15. Similar straight lines have been obtained for other heating rates. The values of the so obtained non-isothermal kinetic parameters are listed in Table 7. For all the n values a slight decrease of E values with increasing heating rate can be noticed. A comparison of the results

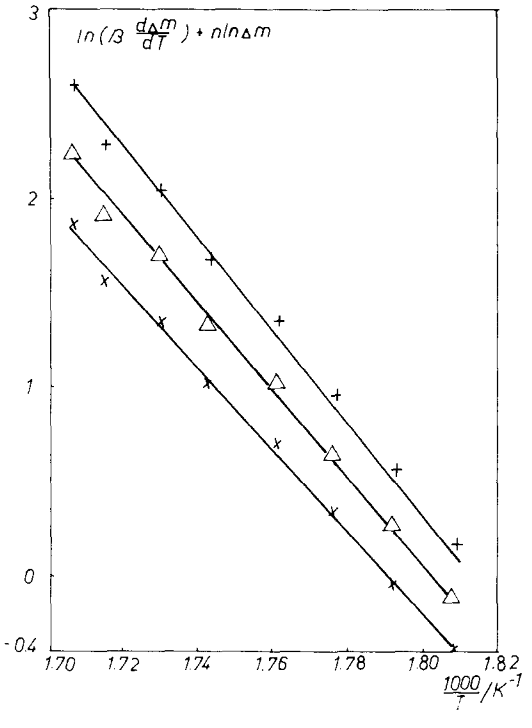

Fig. 15. The straight line $[\ln(\beta(\mathrm{d}(\Delta m)/\mathrm{d}\,T)) + n\ln(\Delta m)]$ versus $1/T$ corresponding to the TG curve obtained at $\beta = 2.97$ K min^{-1}. × $n = 1.3$; △ $n = 1.4$; + $n = 1.5$.

Table 7
The values of the kinetic parameters for the non-isothermal degradation of resin A for 1.45 K min^{-1} $\leq \beta \leq$ 12.20 K min^{-1}

β/(K min^{-1})	E/(kJ mol^{-1})	ln $A(\Delta m_{\max})^{n+1}$ ($A(\Delta m_{\max})^{n+1}$ s)	r
n = *1.3*			
1.45	188.5 ± 4.6	40.83 ± 0.59	0.9987
2.97	178.1 ± 4.6	38.45 ± 0.98	0.9983
5.95	170.1 ± 1.7	36.89 ± 0.31	0.9998
12.20	165.5 ± 2.5	36.17 ± 0.51	0.9996
n = *1.4*			
1.45	196.9 ± 5.0	42.92 ± 1.07	0.9987
2.97	185.6 ± 4.2	40.32 ± 0.96	0.9985
5.95	177.2 ± 1.5	38.70 ± 0.30	0.9998
12.20	173.0 ± 2.5	38.00 ± 0.53	0.9996
n = *1.5*			
1.45	204.8 ± 50	45.00 ± 1.09	0.9988
2.97	192.7 ± 4.2	42.18 ± 0.94	0.9987
5.95	184.3 ± 1.5	40.51 ± 0.30	0.9998
12.20	180.2 ± 2.5	39.83 ± 0.54	0.9996

given in this table with those obtained with the help of the isoconversional method (Table 4) shows that for $n = 1.4$ and $n = 1.5$, the values of E are in a quite good agreement.

6. Conclusions

A method has been developed for evaluating non-isothermal kinetic parameters from thermogravimetric data based on the development of the degree of conversion in a temperature power series. A procedure to find the form of the differential function of conversion was suggested.

The proposed method for non-isothermal kinetic analysis leads to values of the kinetic parameters in fairly good agreement with those obtained using other methods.

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