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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA
XXIX. Remarks on the 'many curves' methods

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Abstract

Four many curves methods, viz. calculation techniques based on Eqs (30), (31), (34) and (36), respectively, for deriving kinetic parameters from several TG curves recorded with different heating rates are tested on two sets of theoretical TG curves. The maximum reaction rate temperature and conversion, as well as the approximate formulae used for their calculation are discussed. Some aspects of the kinetic compensation effect are analysed. The final conclusion is that the use of the many curves methods is not reasonable.

Keywords: isokinetic relations, kinetic compensation effect, nonisothermal kinetics, thermogravimetry

Introduction

Generally in thermogravimetry (TG)

$$\text{A (solid)} \rightarrow \text{B (solid)} + \text{C (gas)} \tag{1}$$

type heterogeneous reactions are studied under non-isothermal conditions, by using a certain temperature program

$$T = \varphi(t) \tag{2}$$

The kinetics of reaction (1) may be studied by using two types of approximations, viz. model approximations and homogeneous formalism approximations. In the former case an attempt is made to derive kinetic equations by taking into account the nucleation, the growth of the germs, advance of the reaction interface, diffusion of the product etc. [1–7]. In the latter one the formalism of homogeneous kinetics is applied, by presuming that the reaction rate, defined by means of the conversion α, might be given as the product of an apparent rate constant, depending on T and of a certain conversion function, i.e.

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$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{3}$$

Concerning the temperature dependence of k, most frequently the validity of an Arrhenius type relation is presumed:

$$k = Z\exp\{-E/RT\} \tag{4}$$

and very often the conversion function is presumed to be that of an n-th order homogeneous reaction:

$$f(\alpha) = (1 - \alpha)^n \tag{5}$$

By using a linear temperature program

$$T = T_o + qt \tag{6}$$

i.e. a constant heating rate q, from relations (3)–(6) the following rate equation is obtained:

$$\frac{d\alpha}{dt} = \frac{Z}{q}\exp\{-E/RT\}(1 - \alpha)^n \tag{7}$$

As shown [8–9], this equation is based upon several completely arbitrary hypotheses, which cannot be justified from theoretical point of view and their use may be accepted only because the actual mechanism of reaction (1) is too complicated to be properly modelled.

According to Eq. (7), from kinetic point of view reaction (1) may be characterized by means of three parameters, viz. Z, E and n, frequently called frequency or pre-exponential factor, activation energy and reaction order, respectively. A considerable number of calculation technique has been developed in order to derive these parameters from TG data. For this purpose Eq. (7), its derivative, or its integrated form are used and parameters are obtained by means of various linearization or curve fitting methods [9–11]. Obviously, the physical meaning of the kinetic parameters derived cannot be the same as in homogeneous kinetics. Nevertheless, many authors believe that E means an activation energy, that Z is somehow correlated to the activation entropy of reaction (1) and many attempts are made to give the mechanism of the chemical reaction on the basis of the kinetic parameters derived from TG data. In our early papers [12] we also gave similar interpretations, but later we realized the erroneous character of these speculations.

From mathematical point of view the above mentioned procedures mean the use of a variational method, by chosing a family of functions, containing 3 variational parameters and by determining the parameter values ensuring the minimum deviation of experimental points from the theoretical curve. Consequently, the so-called kinetic parameters Z, E and n have no clear physical meaning and they do not characterize the chemical reaction itself, but only the whole complexity of processes occurring during the pyrolysis under the given experimental conditions. Thus, kinetic parameters derived depend very much upon procedural variables as heating rate [13–21], sample weight [13, 22–26] etc. Generally, both Z and E values derived from TG curves decrease with increasing heating rate [13–22], but n values increase [19–22].

Although the apparent kinetic parameters do depend on the heating rate, there were developed a considerable number of methods [27–37], called by us 'many curves' methods [9–10], using several TG curves recorded under different experimental conditions, mainly at different heating rates. Some of them are based on relations valid for a constant conversion value. These methods give different E values for different conversions, i.e. they seem to indicate a conversion dependence of the kinetic parameters. Since the basic relations of many such procedures [e.g. (27), (31), (32)] are obtained by presuming that E does not depend on α, a contradiction appears, which have been tried to be avoided [37].

In the present paper several many curves methods are analysed and tested on simulated TG curves.

Construction of theoretical TG curves

The basic presumption of the majority of many curves methods is the independence of kinetic parameters from heating rate. This is why in series 1 of TG curves the same Z, E and n values have been used. In order to construct TG curves corresponding to different heating rates, the integrated form of Eq. (7) has been used, which may be written as [38]:

$$g(\alpha) = \frac{ZE}{Rq}p(x) \tag{8}$$

where $g(\alpha)$ stands for the conversion integral, i.e. in the case of an n-th order reaction

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{(1-\alpha)^n} = \begin{cases} \frac{1}{1-n}[1-(1-\alpha)^{1-n}] & \text{if } n \neq 1 \\ -\ln(1-\alpha) & \text{if } n = 1 \end{cases} \tag{9}$$

and $p(x)$ means the exponential integral

$$p(x) = -\int_\infty^x \frac{e^{-x}}{x^2}\,\mathrm{d}x \quad \text{with} \quad x = E/RT \tag{10}$$

In our procedure $p(x)$ values have been calculated for different α values, by means of Eq. (8). Tabulated exponential integrals [39] have been used to obtain the corresponding x value and eventually the temperature T has been calculated accordingly to (10).

In series 2 more 'real' TG curves have been constructed by taking into account that integral methods, using Eq. (8), indicate a systematic decrease of Z and E, and increase of n with increasing heating rate, as mentioned above. Meanwhile, Z and E values obey a linear kinetic compensation law [20–22]:

$$\mathrm{lg}Z = a + bE \tag{11}$$

This indicates the existence of an isokinetic temperature T_i, since if in the case of a series of pyrolysis processes there is a temperature T_i at which the rate constant exhibits the same value k_i, Eq. (4) yields:

$$\mathrm{lg}Z = \mathrm{lg}k_i + \frac{1}{2.303RT_i}E \tag{12}$$

From the experimentally found compensation parameters b we concluded that generally the isokinetic temperature is very close to $T_{0.1}$, i.e. to the temperature at which one has $\alpha=0.1$ and the parameters a indicate $\mathrm{lg}k_i$ values close to -3 [22–26, 40–44]. This is why in simulating TG curves of series 2 we took E values decreasing with increasing q, n values increasing with increasing q and Z values have been calculated by means of Eq. (12) by taking $\mathrm{lg}k_i=-3$ and $T_i=423$ K, the latter one being equal to $T_{0.1}$ in the series 1 for $q=10$ K min^{-1}.

The kinetic parameters used for the construction of TG curves are collected in Table 1. The same table contains also the $T_{0.1}$ values, as well as the conver-

Table 1 Kinetic parameters and characteristics of the theoretical TG curves

		q/K min^{-1}					
		1	3	5	10	15	20
E/kJ	1	120	120	120	120	120	120
	2	210	180	150	120	100	85
lg$Z$	1	12	12	12	12	12	12
	2	22.965	19.256	15.547	11.837	9.364	7.510
n	1	1	1	1	1	1	1
	2	0.1	0.4	0.7	1.0	1.3	1.6
$T_{0.1}$	1	397.62	409.37	415.06	423.04	427.84	431.32
	2	413.26	419.20	422.47	427.47	431.98	436.13
α_{423}	1	0.655	0.297	0.186	0.099	0.066	0.053
	2	0.402	0.166	0.108	0.071	0.052	0.040

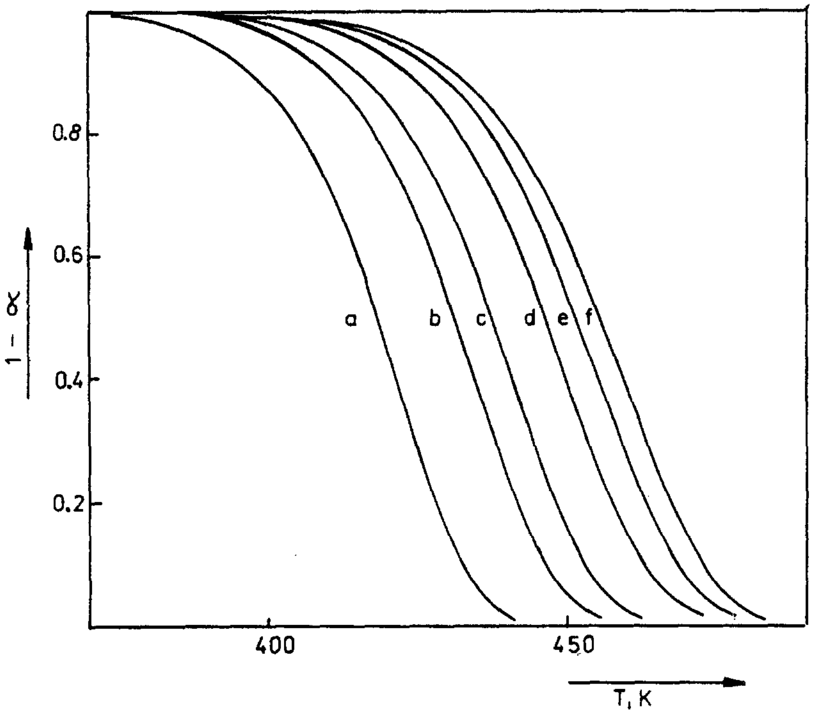

Fig. 1 Theoretical TG curves of series 1. E=120 kJ, lg$Z$=12, n=1. q (in K min^{-1}): a – 1; b – 3; c – 5; d – 10; e – 15; f –20

sion values at the isokinetic temperature, i.e α_{423}. Theoretical TG curves of series 1 and 2 are presented in Figs 1 and 2, respectively.

The maximum of the reaction rate

The temperature T_m and the conversion α_m corresponding to the maximum reaction rate are used to derive kinetic parameters from TG curves recorded with different heating rates. Obviously, under dynamic temperature conditions T_m and α_m correspond to the condition

$$\frac{d^2\alpha}{dT^2} = 0 \tag{13}$$

By presuming that kinetic parameters Z, E and n are independent of q, but are functions of α, derivation of Eq. (7) with respect to T and with the extremum condition (13), yields the following equation

$$\frac{E}{RT^2} = \left(\frac{d\alpha}{dT}\right)_m \left[\frac{n}{1-\alpha_m} - \frac{1}{Z}\left(\frac{dZ}{d\alpha}\right)_m + \frac{1}{RT_m^2}\left(\frac{dE}{d\alpha}\right)_m - \ln(1-\alpha_m)\left(\frac{dn}{d\alpha}\right)_m\right] \tag{14}$$

where the lower index m of the derivatives indicates that their value corresponds to $T=T_m$ and $\alpha=\alpha_m$, respectively.

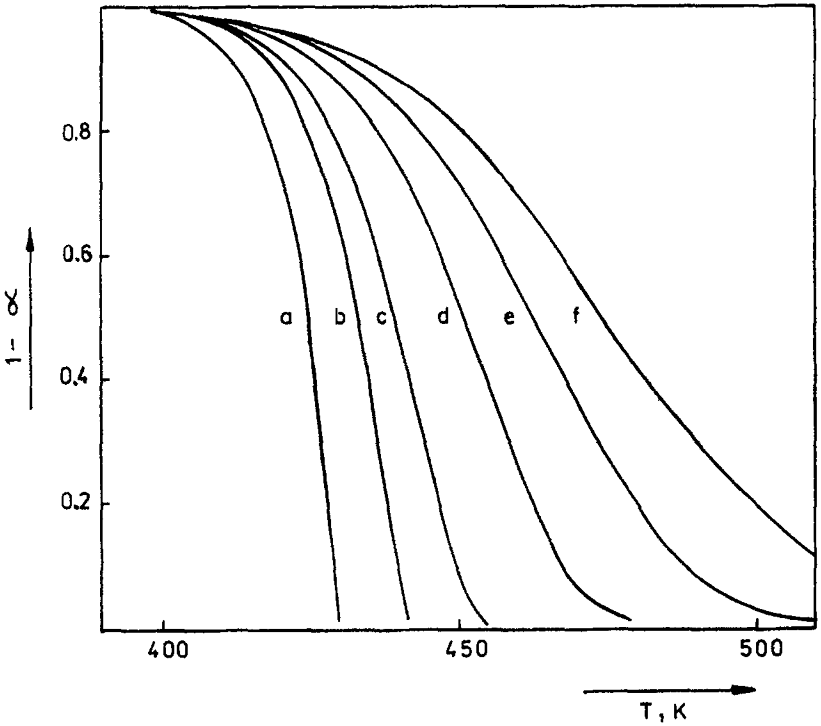

Fig. 2 Theoretical TG curves of series 2. E, lg$Z$, n – see Table 1. q (K min^{-1}): a – 1; b – 3; c – 5; d – 10; e – 15; f –20

Since at the construction of both series of TG curves, 1 and 2, the kinetic parameters have been presumed not to vary with α, in our case Eq. (14) becomes

$$\frac{E}{RT^2}=\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_m\frac{n}{1-\alpha_m}=n\,\frac{Z}{q}\exp\{-E/RT_m\}(1-\alpha_m)^{n-1} \tag{15}$$

This relation allows us to obtain both T_m and α_m. For this purpose the left hand side and the right hand and side of the equation

$$\lg\frac{E}{RT^2}=\lg\frac{nZ}{q}+(n-1)\lg(1-\alpha)-\frac{E}{2.303RT} \tag{16}$$

have been calculated for various α values. Their graphical plot *vs.* T gave T_m as the intersection of two curves. The α_m and T_m values obtained by means of this procedure are presented in Table 2.

Table 2 α and T values corresponding to the maximum reaction rate

		q/K min^{-1}					
		1	3	5	10	15	20
α_m	1	0.612	0.611	0.611	0.610	0.610	0.610
	2	0.920	0.774	0.681	0.610	0.553	0.505
T_m	1	421.73	434.92	441.33	450.33	455.76	459.69
	2	426.04	434.11	442.36	463.94	485.04	510.50

For the calculation of α_m several approaches have been proposed. These are based on approximate expressions for the exponential integral. Since the exponential integral cannot be solved exactly, many formulae have been proposed to approximate this integral [45–47]. Most of them are of the general form:

$$p(x) = x^{-r}e^{-x}Q(x) \tag{17}$$

where $Q(x)$ stands for a series or for a rational expression, i.e. the ratio of two polynomials. In the case of the Schlömlich expansion [48] one has $r=1$ and

$$Q(x) = \frac{1}{x+1} - \frac{1}{(x+1)(x+2)} + \frac{1}{(x+1)(x+2)(x+3)} - \cdots \tag{18}$$

The asymptotic expansion corresponds to $r=2$ and

$$Q(x) = 1 - \frac{2!}{x} + \frac{3!}{x^2} - \frac{4!}{x^3} + \cdots + (-1)^n \frac{(n+1)!}{x^n} + \cdots \tag{19}$$

By introducing the expression (17) with $r=2$ into Eq. (8), one obtains [49]:

$$\frac{E}{RT^2} = \frac{Z}{q} \exp\{-E/RT\} \frac{Q(x)}{g(\alpha)} \tag{20}$$

For the maximum reaction rate, combination of Eqs (20) and (15) gives

$$Q(x_m) = n(1-\alpha_m)^{n-1} g(\alpha_m) \tag{21}$$

By taking into account Eq. (9), one has:

$$1-\alpha_m = \exp\{-Q(x_m)\} \qquad \text{if } n=1$$

$$1-\alpha_m = \left[1 + \frac{Q(x_m) - nQ(x_m)}{n}\right]^{\frac{1}{n-1}} \qquad \text{if } n \neq 1 \tag{22}$$

Let us consider the asymptotic expansion (19). It may be written as

$$Q(x)=\sum_{i=1}^{\infty}(-1)^{i-1}A_i(x) \quad \text{with } A_i(x)=\frac{i!}{x^{i-1}} \tag{23}$$

This infinite series can be truncated after a certain number of terms. Let us denote by $Q_n(x)$ the expression obtained with the first n terms, i.e.

$$Q_n(x)=\sum_{i=1}^{n}(-1)^{i-1}A_i(x) \tag{24}$$

$Q_{10}(x)$ has been found to be a very good approximation of $p(x)$ if $x>15$ [50], but for small x values it may be even divergent [51].

As a matter of fact, (23) is always divergent. It is obvious that $A_i(x)>A_{i+1}(x)$ if $i<x-1$, but if $i=x-1$

$$A_i(x)=\frac{(x-1)!}{x^{x-2}} \text{ and } A_{i+1}(x)=\frac{x!}{x^{x-1}}=\frac{(x-1)!}{x^{x-2}} \quad \text{i.e. } A_i(x)=A_{i+1}(x)$$

Let us denote $x-1=d$. Thus, $A_{x-1}(x)=A_x(x)=A_d(x)$ and the symbol d indicates that the series becomes divergent from this term on, since $A_i(x)<A_{i+1}(x)$ if $i>d$.

Due to the divergency of (19), the best approximation of $p(x)$ will be obtained with $Q_d(x)=Q_{x-1}(x)$, i.e. (17) becomes

$$p(x)=x^{-2}e^{-x}Q_d(x) \tag{25}$$

Since in (24) the sign of the terms alternates, it is obvious that the error of $Q_n(x)$ with respect to $Q_d(x)$ will be

$$[Q_d(x)-Q_n(x)]<A_n(x) \tag{26}$$

if $n<<d$. With increasing x the $A_d(x)$ value decreases very rapidly, as seen from Table 3. Frequently, this enables us to obtain good approximations of $Q_d(x)$ even by taking $Q_n(x)$ with $n<d$. In order to obtain a clear picture of this possibility, we calculated the x values for which $A_n(x)$, i.e. the maximum error of $Q_n(x)$, attains the following values: 10^{-1}, 10^{-3} and 10^{-5}, respectively. These x values are given in Table 4 for small n values. From this table one can see e.g. that by taking the first 5 terms of (19), errors will be less then 0.1% if $x>14.841$. A more complete picture is offered by Fig. 3. The full line curves pass through the n–x pairs corresponding to $A_n(x)$ values equal to 10^{-1}, 10^{-3} and 10^{-5}, respectively. The dotted line corresponds to $n=d$, for which $A_n(x)$ values are given in Table 3.

Table 3 Dependence of $A_d(x)$ upon x

x	$\lg A_d(x)$	x	$\lg A_d(x)$	x	$\lg A_d(x)$
2	0	10	–2.812	45	–16.664
3	–0.176	15	–4.349	50	–18.766
4	–0.426	20	–6.333	60	–22.991
5	–0.717	25	–8.360	70	–27.233
6	–1.033	30	–10.413	80	–31.489
7	–1.369	35	–12.484	90	–35.756
8	–1.717	40	–14.569	100	–40.030

Table 4 x values for which $A_n(x)$ attains certain values

n	$A_n(x)$		
	10^{-1}	10^{-3}	10^{-5}
1	20	2000	200000
2	7.746	77.460	774.60
3	6.218	28.845	133.89
4	5.886	18.612	58.857
5	5.908	14.841	37.279
6	6.078	13.094	28.210

From Fig. 3 it is obvious that the asymptotic expansion is useless if x is small. For example, the error of $Q_n(x)$ will be higher than 0.1% if $x<11.481$, whatever n value would be chosen. On the other hand, for very high x values even the $Q_1(x)=1$ approach may be acceptable. The accuracy of the $Q_n(x)$ approaches with $n=1$, 2 and 3 are illustrated in Fig. 4. The dotted line indicates the correct value

$$Q_r(x) = x^2 e^x p(x) \tag{27}$$

$Q_d(x)$ is practically equal to $Q_r(x)$ if $x>10$, but for smaller x values considerable differences may arise. This is obvious from Fig. 4 where $Q_d(x)$ values are indicated for several low x values.

By using the very rough approximation $Q_1(x_m)=1$, relations (22) become [52, 53]

$$1 - \alpha_m = \begin{cases} e^{-1} & \text{if } n = 1 \\ n^{1/1-n} & \text{if } n \neq 1 \end{cases} \tag{28}$$

Similarly, with

$$Q_2(x_m) = 1 - \frac{2}{x_m} = 1 - \frac{2RT_m}{E}$$

one obtains [52, 54]:

$$1 - \alpha_m = \begin{cases} \exp\left[\frac{2RT_m}{E} - 1\right] & \text{if } n = 1 \\ \left[\frac{E + 2\,(n-1)RT_m}{nE}\right]^{\frac{1}{n-1}} & \text{if } n \neq 1 \end{cases} \tag{29}$$

The actual dependence of α_m upon x_m is expressed by (22), with $Q(x_m) = Q_r(x_m)$. The value of the approaches (28) and (29) may be judged on the base of Fig. 5 in which α_m is plotted *vs.* x_m for a first order reaction.

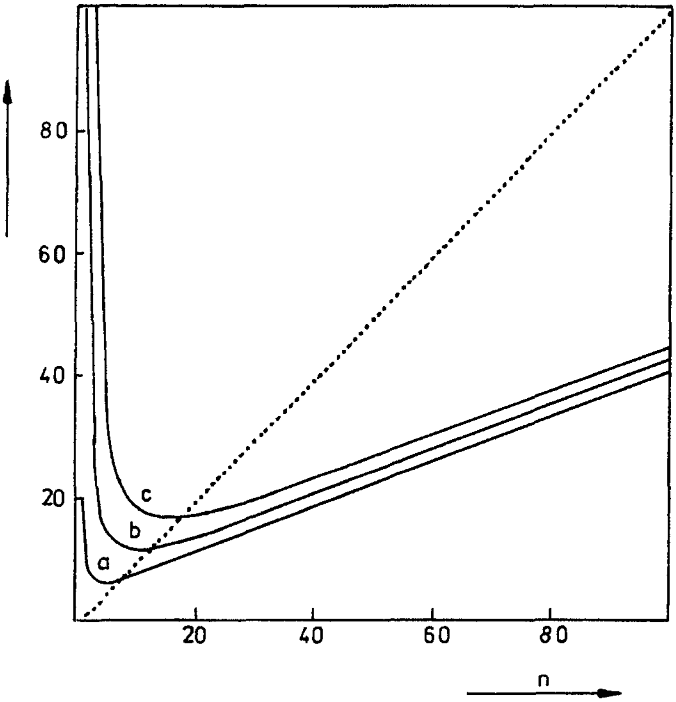

Fig. 3 x *vs.* n plot corresponding to $A_n(x)$ equal to: a – 10^{-1}; b – 10^{-3}; c – 10^{-5}

The above approaches have been used to calculate α_m values for the simulated TG curves of series 1 and 2. Results are presented in Table 5. As seen, the approach (29) is quite good. Since in our case $20 < x_m < 60$, this is not surprising. By comparing the values obtained on the basis of the $Q_r(x_m)$ values with those presented in Table 2, a very good agreement is observed.

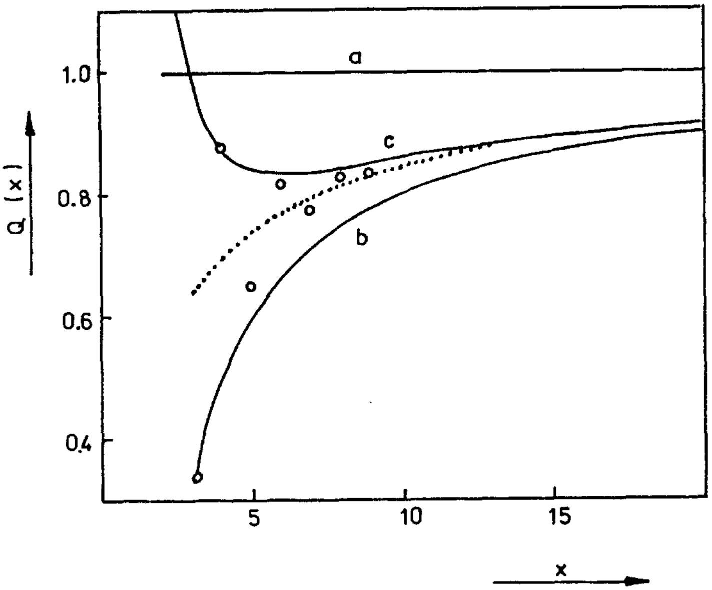

Fig. 4 Accuracy of the $Q_n(x)$ approaches. $a - n=1$; $b - n=2$; $c - n=3$. Dotted line: $Q_r(x)$. Circles: $Q_d(x)$ for $x=3, 4, 5, 6, 7, 8, 9$

The maximum rate temperatures T_m observed at different heating rates may be used to derive kinetic parameters. One of the methods proposed [27] uses the rate Eq. (7) written for T_m. By taking logarithms, a rearrangement yields:

$$\lg\left[q\left(\frac{d\alpha}{dT}\right)_m (1-\alpha_m)^{-n}\right] = \lg Z - \frac{E}{2.303RT_m} = A + BT_m^{-1} \qquad (30)$$

Consequently, the plot of the left hand side *vs.* $1/T_m$ will be linear if the correct n value is chosen. One has $\lg Z=A$ and $E=-2.303RB$. Testing of this method on the TG curves of the series 1 yields for $n=1$ an excellent linearity with a corre-

Table 5 α_m values for the TG curves of series 1 and 2

Series	Approach	q/K min^{-1} 1	3	5	10	15	20
1	(28)	0.6321	0.6321	0.6321	0.6321	0.6321	0.6321
	(29)	0.6100	0.6093	0.6089	0.6084	0.6081	0.6079
	(22)	0.6118	0.6112	0.6109	0.6105	0.6102	0.6101
2	(28)	0.9226	0.7828	0.6954	0.6321	0.5829	0.5431
	(29)	0.9199	0.7728	0.6800	0.6082	0.5498	0.4999
	(22)	0.9200	0.7743	0.6810	0.6102	0.5532	0.5052

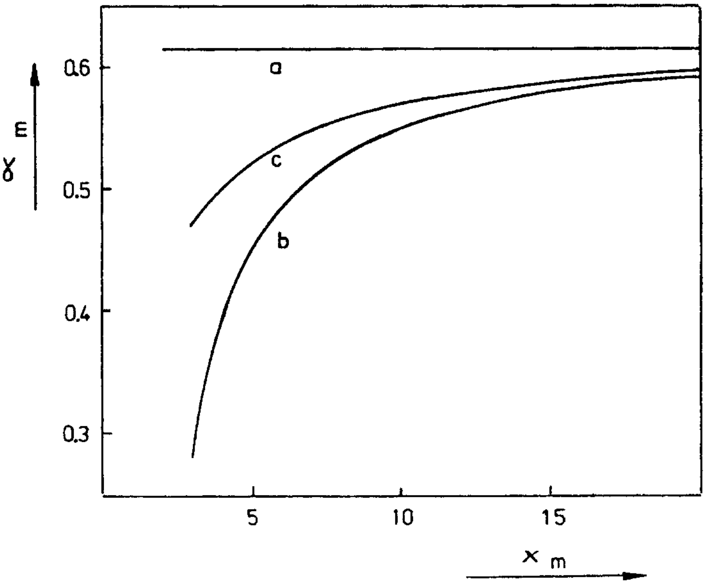

Fig. 5 Maximum rate conversions for $n=1$, calculated by means of: a – approach (28); b – approach (29); c – actual values, (22) and $Q_r(x_m)$

lation coefficient $r>0.999999$. The kinetic parameters derived are exactly the 'input data', i.e. those used for the construction of the TG curves, viz. $E=120$ kJ, $\lg Z=12$.

Another possibility is offered by the relation (15), which may be written in the following logarithmic form:

$$\lg\left[\frac{q}{T_m^2}\frac{(1-\alpha_m)^{1-n}}{n}\right]=\lg Z-\lg\frac{E}{R}-\frac{E}{2.303RT_m} \tag{31}$$

Obviously, the plot of the left hand side *vs.* $1/T_m$ allows us to derive the kinetic parameters, viz. n as the value ensuring the best linearity of the plot, E from the slope of the straight line and $\lg Z$ from the ordinate intercept. Testing of the procedure on the series 1 leads to the following results:

for $n=1$ $r>0.999999$; $E=119.84$ kJ; $\lg Z=11.98$

As seen, the agreement with the 'input data' is very good.

Both procedures have been used to derive kinetic parameters from the TG curves of series 2. Results are presented in Table 6. It is obvious, that with both procedures an acceptable linearization can be performed, especially with Eq. (30). The kinetic parameters obtained differ very much from each other and they are very far from the arithmetical mean of the 'input data', given in Table 1.

Table 6 Kinetic parameters derived from series 2 of TG curves by using T_m values

Eq.	n	E/kJ	lg$Z$	r
(30)	0.27	52.63	3.89	0.993
(31)	1.9	22.64	–0.10	0.977
mean	0.85	140.8	14.41	

One may conclude, that the above two procedures of deriving kinetic parameters from the maximum rate temperatures observed at different heating rates can give reliable results only if the kinetic parameters do not depend on heating rate, at least at α_m. In the case of the method based on Eq. (31), kinetic parameters must not depend on α either, since their independence of α has been postulated at the derivation of Eq. (7).

Differential methods

Procedures using Eq. (7) are called differential methods [32, 52]. It is worth mentioning that Eq. (30) is also a variant of Eq. (7), but the above given method is rather a second derivative method since implies T_m and α_m. One of the differential many curves methods [28] consists in measuring the reaction rate and temperature at the same conversion α_i, by using three different heating rates, and deriving the kinetic parameters by solving the system of three equations having the form

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\alpha_i,s} = \frac{Z}{q_s}\exp\left\{-\frac{E}{RT_s}\right\}(1-\alpha_i)^n$$

which may be written as

$$\lg Z - \frac{E}{2.303RT_s} + n\lg(1-\alpha_i) = \lg\left[q_s\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\alpha_i,s}\right] \quad \text{with } i=1,2,3 \qquad (32)$$

At the first sight this procedure seems to be interesting, but the determinant of the system (32) is equal to zero

$$D = -\frac{E\lg(1-\alpha_i)}{2.303R}\begin{vmatrix} 1 & 1/T_1 & 1 \\ 1 & 1/T_2 & 1 \\ 1 & 1/T_3 & 1 \end{vmatrix} \qquad (33)$$

Therefore, deriving of lg$Z$, E and n values from T–dα/dT pairs, obtained for α=const. is not possible. Actually, at α=const. only E and $\lg[Z(1-\alpha)^n]$ can be obtained. But for this, from mathematical point of view, the use of only two heating rates would be sufficient.

Since in the case of deriving n parameters from n experimental points results are very much affected by experimental errors, we preferred to use a linearization procedure [29]. Eq. (7) may be written as

$$\lg\left(q\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) = \lg[Z(1-\alpha)^n] - \frac{E}{2.303RT} = A + BT^{-1} \tag{34}$$

For α=const. the first term of the right hand side is constant, if n, Z and E are thought to be independent of q. Therefore, the plot of the left hand side *vs.* T^{1} must give a straight line, irrespective of n. E is obtained from the slope B of the straight line and $A=\lg[Z(1-\alpha)^n]$. This procedure has been tested on TG curves of series 1 for different α values. In all cases an excellent linearization was obtained with $r>0.999999$ and the slope of the straight line gave exactly $E=120$ kJ. The A value depends on α, but by taking $n=1$, one obtains $\lg Z=12$ for every α.

Table 7 Kinetic parameters derived for series 2 by means of Eq.(34)

α	E/kJ	$\lg[Z(1-\alpha)^n]$	r	$\lg Z$	n
0.1	124.5	12.27	0.959	18.82	95.8
0.2	83.9	7.34	0.939	13.55	63.0
0.3	65.2	5.12	0.922	10.47	43.9
0.4	50.9	3.45	0.907	8.28	30.3
0.5	40.3	2.21	0.882	6.58	19.8
0.6	31.8	1.22	0.839	5.20	11.2
0.7	21.9	0.04	0.767	4.02	3.9
0.8	10.7	–1.29	0.568	3.01	–2.4
0.9	–3.9	–3.08	0.329	2.11	–0.8

By applying the same procedure with TG curves of series 2, the results presented in Table 7 are obtained. Obviously, for low α values an acceptable linearity was obtained, exhibiting the rapid decrease of E with increasing α. At higher α values the linearity is very poor and one obtains even negative 'activation energy' values. With increasing α the product $Z(1-\alpha)^n$ also decreases rapidly, suggesting a dependence of Z on α. Since at α=const. it is impossible to obtain Z by means of Eq. (34), the following procedure has been used. From the $\lg[Z(1-\alpha)^n]$ values given in Table 7 for two 'neighbouring' α values, e.g. for 0.4 and 0.5, $\lg Z$ and n values were calculated and they were assigned to their arithmetical mean 0.45. By constructing $\lg Z$ *vs.* α and n *vs.* α curves, the values given in Table 7 have been obtained by means of graphical interpolation or extrapolation (in the case of the extreme α values).

Integral methods

Integral methods use Eq. (8) for deriving kinetic parameters. One of the integral many curves methods is a linearization procedure [32], based on the following approach of the exponential integral:

$$-\lg p(x) \approx 2.315 + 0.4567x \tag{35}$$

which gives errors less than 0.2 if $14<x<71$. As mentioned above, in the case of the TG curves used in this paper $20<x<60$, i.e. applying of the approach (35) is completely reasonable.

By combining Eqs (8) and (35) one obtains

$$\lg q = \lg\frac{ZE}{R} - \lg g(\alpha) - 2.315 - 0.4567\frac{E}{RT} = A + BT^{-1} \tag{36}$$

If $\alpha=\text{const.}$ and Z, E and n are thought to be independent of q, (36) will be the equation of a straight line, allowing us to derive the activation energy E. This method has been tested on TG curves of the series 1 for different α values. In all cases an excellent linearity was obtained, corresponding to $r>0.999999$. The E values derived were very near to the 'input data', viz. 120.5 kJ for $\alpha=0.1$ and 121.0 kJ for $\alpha=0.9$, showing a systematic increase with increasing α. This slight error is due to the approximate validity of (35).

By applying the same method with TG curves of series 2, E values vary very much with α, as seen from Table 8. Linearity of the $\lg q$ *vs.* $1/T$ plots was quite good.

Table 8 Kinetic parameters derived for series 2 by means of Eq.(36) for $\alpha=\text{const.}$

α	E/kJ	A	r	lg$Z$	n
0.1	186.7	23.14	0.987	27.0	180
0.2	135.4	16.17	0.977	20.2	82
0.3	114.2	13.30	0.972	14.9	33
0.4	101.5	11.59	0.967	13.0	21
0.5	91.4	10.24	0.964	11.3	14
0.6	82.6	9.08	0.963	10.1	10.1
0.7	75.0	8.08	0.960	9.0	7.45
0.8	67.3	7.08	0.957	7.9	5.40
0.9	58.2	5.92	0.040	7.0	4.08

As far as the lg$Z$ and n values are concerned, these cannot be derived from experimental data for $\alpha=\text{const.}$ For the determination of n the graphical plot of

$\lg g(\alpha)$ *vs.* $\lg q$ has been proposed [32] for T=const. Equation (36) may be written as

$$\lg g(\alpha) = \lg \frac{1}{1-\mathrm{n}}\left[1-(1-\alpha)^{1-\mathrm{n}}\right] = \lg \frac{ZE}{R} - 2.315 - 0.4567\frac{E}{RT} - \lg q =$$

$$= A - \lg q \quad \text{if } n \neq 1 \tag{37}$$

and the above mentioned plot yields a straight line if for the calculation of $g(\alpha)$ the correct n value was used and if n, E and $\lg Z$ values do not depend either on q or on α. The slope of the straight line will be equal to -1.

Testing of this procedure on TG curves of series 1 showed an excellent linearity (r>0.9999) if $g(\alpha)$ was calculated for n=1 and the slope of the $\lg g(\alpha)$ *vs.* $\lg q$ plot was e.g. equal to -0.98 by using α values corresponding to T=450 K.

Table 9 n values derived for series 2 by means of Eq.(36) for T=const.

T	n_B	r_B	n_r	r_m	Numb. points
420	7.27	0.973	–5.48	0.99952	6
425	1.91	0.986	–1.44	0.99976	6
430	1.53	0.997	–1.53	0.99990	5
435	0.10	0.999	–0.59	0.99998	5
440	–0.01	0.000	–0.09	0.99999	5
445	–0.18	0.999	0.33	0.99999	4
450	–0.20	0.996	0.47	0.99999	4
455	–0.34	0.989	0.54	0.99999	4
460	–0.56	0.998	0.57	0.99999	3

With series 2 the same procedure exhibited a dependence of n on T. Generally, the n value ensuring the best linearity did not give -1 for the slope of the straight line. This is why two n values have been derived and given in Table 9, viz. the n value for which the slope of the plot is equal to -1 (denoted by n_B), and the n value ensuring the maximum correlation coefficient $r=r_m$ (this one is denoted by n_r). Both n_B and n_r values are presented in Table 9, together with the corresponding correlation coefficients r_B and r_m, respectively. The last column indicates the number of 'experimental' points processed. It is obvious that both n_B and n_r values vary very much with increasing T, viz. the former decreases and the latter one increases. Consequently, the apparent kinetic parameters do vary not only with T, but also with α.

In order to derive n and $\lg Z$ for different α=const. values, let us consider the constant A of Eq. (36) for α_1 and for $\alpha_2=\alpha_1+0.1$ by presuming $n\neq 1$:

$$\begin{aligned} A_1 &= \lg Z + \lg \frac{E_1}{R} - 2.315 - \lg \frac{1}{1-n}\left[1-(1-\alpha_1)^{1-n}\right] \\ A_2 &= \lg Z + \lg \frac{E_2}{R} - 2.315 - \lg \frac{1}{1-n}\left[1-(1-\alpha_2)^{1-n}\right] \end{aligned} \qquad (38)$$

Let us presume as a first approach, that both lgZ and n are practically constant in such a narrow α interval. By eliminating lgZ from the system (38), one obtains

$$\frac{1-(1-\alpha_1)^{1-n}}{1-(1-\alpha_2)^{1-n}} = \exp[A_2 - A_1 + \lg(E_1/E_2)] \qquad (39)$$

The right hand side of Eq. (39) is easily calculated from the first two columns of Table 8. Thus, an n value may be derived by means of Eq. (39), which may be assigned to $\alpha=\alpha_1+0.05$. The corresponding lgZ value is calculated by means of Eq. (38). Eventually, plots of n *vs.* α and lgZ *vs.* α, allows us to obtain graphically n and lgZ values, respectively, for the α values indicated in Table 8. Results are presented in the last two columns of Table 8.

Discussion and conclusions

Testing of four many curves methods, based on Eqs (30), (31), (34) and (36), respectively, shows that in the case of ideal TG curves, corresponding to kinetic parameters n, Z and E, which do not depend on heating rate (series 1), these methods allow us to derive kinetic parameters exactly equal to the 'input' ones.

In the case of theoretical TG curves, more close to the real ones, exhibiting a dependence of kinetic parameters on heating rate (series 2), the kinetic parameters derived by means of the same methods, do not agree with each other, as seen from Tables 6–8. Moreover, with Eqs (33) and (36) one obtains that n, Z and E depend very much on α. From mathematical point of view it is not surprising that by constructing theoretical TG curves with n, Z and E parameters depending on q and independent of α, methods based on the hypothesis, that they are independent of q, lead to their dependence on α. Since experimental results show that modification of the heating rate modifies the shape of the TG curves, it seems to be more reasonable to presume the dependence of kinetic parameters on heating rate, than their dependence on conversion.

The mathematical correctness of the four methods tested is not of the same degree. All of them are based on the hypothesis, that n, E and Z do not depend on q. In the case of Eq. (34) no further presumptions are needed. Thus, in some respect this method is equivalent with the single curve methods, which postulate that n, E and Z do not depend on α. The other 3 methods imply one more hypothesis, viz.

Equation (30) is valid if n, E and Z have the same value at α_m, although the latter depends on q.

Equation (31) is obtained by performing a derivation in the assumption, that n, E and Z do not depend on α either.

Equation (36) is based on an integration performed with the same condition that n, E and Z do not depend on α, and even this method 'reveals' the most clearly the dependence on α of the kinetic parameters. In this respect it is interesting to compare the correlation coefficients given in Tables 7 and 8. The 'correct' Eq. (34) ensures a very poor linearity, and the 'erroneous' Eq. (36) gives a good one.

Table 10 Isokinetic parameters derived from E and Z values presented in Tables 7 and 8

Tables	$\lg k_i$	T_i/K	r
7	1.508	380.09	0.9946
8	–3.126	320.97	0.9958

Table 11 Rate constants and conversions at the apparent isokinetic temperatures

	q/K min^{-1}					
	1	3	5	10	15	20
$\lg k_{380.09}$	–5.904	–5.489	–5.074	–4.660	–4.383	–4.175
$\lg \alpha_{380.09}$	–3.387	–3.383	–3.113	–2.906	–2.731	–2.581
$\lg k_{320.97}$	–11.222	–10.047	–8.872	–7.698	–6.915	–6.328
$\lg \alpha_{320.97}$	–8.854	–8.092	–7.056	–6.089	–5.406	–4.875

Since both E and $\lg Z$ seem to decrease with increasing α, the validity of an (11) type linear compensation law may be tested. By using the kinetic parameters given in Tables 7 and 8, a good linearity was observed, allowing us to derive the isokinetic parameters k_i and T_i, accordingly to Eq. (12). Results are presented in Table 10. It is obvious, that the linearity is very good. But what kind of 'compensation' occurs here? In the case of kinetic compensation effect some modifications in the structure of the reagent, in the composition of the catalyst, or in working conditions are responsible for the variation of activation parameters. In our case only the conversion α varies and the effect is a completely apparent one. It is indeed more correct to take it for a 'mathematical' compensation effect as in [37]. On the other hand, no real rate constant takes the k_i value at the isokinetic temperature. The real rate constants in the case of TG curves of series 2, at the T_i values given in Table 10, are presented in Table 11, together with the corresponding α values. As seen, the real rate constants are much less than those indicated for T_i in Table 10 and they do not indicate an isokinetic character at all, since their value varies with the heating rate, with more than an order of magnitude at 380.09 K and almost with 5 orders of magnitudes at 320.97 K. The corresponding α values are so small, that we preferred to give their logarithms. It is interesting to compare them with the α values given in Table 1 for the real isokinetic temperature $T_i=423$ K.

On the basis of the above results we conclude that although the physical meaning of the apparent kinetic parameters n, E and Z, derived by means of the single curve methods it not clear, generally they are able to give a good description at least of a single TG curve and their dependence on working conditions might give useful pieces of information concerning the pyrolysis process. On the contrary, the many curves methods are based on hypotheses which are in disagreement with experimental data and the parameters derived by means of these methods depend very much on the calculation procedure used and they do not allow us even to describe the TG curves. They give some parameters, which are much more unrealistic than those obtained with single curve methods (e.g. negative 'activation energy', reaction order $n>100$) and which cannot be correlated with anything. In our view the use of many curves methods has no reason.

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