Journal of Thermal Analysis, Vol. 5 (1973) 227—237

THE DETERMINATION AND USE OF THE SECOND DERIVATIVE THERMOGRAVIMETRIC FUNCTION (DDTG) AND THE CALCULATION OF THE KINETIC CONSTANTS OF SOME DECOMPOSITION REACTION TYPES

T. SZÉKELY, G. VÁRHEGYI and F. TILL

Research Group for Inorganic Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary

As previously pointed out by the authors, the determination and use of the second derivative thermogravimetric curve (DDTG) permits the accurate calculation of kinetic parameters of simple reactions, using the methods of numerical analysis. Furthermore, the method outlined makes possible the kinetic analysis of some composite reactions which frequently occur in thermoanalytical practice. The cases of independent and competitive reactions are discussed. In the latter the proposed method of evaluation is suitable for the on-line work of a combined thermobalance—mass spectrometer system.

Many doubts have been voiced recently about the adequacy of the rate law of thermal decomposition reactions. It is being discovered that certain systematic errors and experimental deficiencies have led to contradictions between literary data for the kinetic parameters of such reactions and the physical significance attributed to the parameters. Some authors thus prefer to regard all information provided by thermal analysis as purely qualitative from the point of view of kinetics, and query the chances of gaining any real insight into the course of chemical reactions in this way. Much of this scepticism in fact seems to be justified, especially with regard to a large part of the earlier literature on the topic, and in particular on treatment of composite chemical reactions. Even if the latest developments in experimental technique have succeeded in solving some of the conditions (it seems clear, for instance, that we have to accept severe limitations on the amount of sample, heating rate, etc.), the problems of numerical evaluation of the experimental results, despite the attention they have received, still remain practically unsolved. Most of the difficulties devolve on two factors: the first is the choice of an adequate rate law and parameters; the second is the mathematical method of getting these results from the initial experimental data.

The rate law

Šatava [1] Šesták and Berggren [2] have recently given comprehensive summaries of the equations applicable to solid-state decomposition reactions. Most of the rate laws of solid-state chemistry allow the use of an equation formally similar to the following simple expression for elementary reactions with homogeneous kinetics:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n = Ae^{-E/RT}(1 - \alpha)^n . \tag{1}$$

Certain types of self-catalyzed reaction require more complicated functions. Depending on the model used to derive expressions such as (1), definite values may be attributed to n on the basis of a topochemical approach. Deviations from these numbers may result in cases which do not correspond "purely" to one or another model.

In the degradation of polymers an equation similar to (1) often seems appropriate, while for the frequent examples of random degradation it is possible to use either some equation based on statistical considerations, with some necessary simplifications, or else an empirical formula corresponding to a certain extent to these equations. As a rule, the more sophisticated the equation, the more constants have to be determined, and the flexible formula may be fitted to a fairly wide range of curves. Here we reach the central difficulty of kinetic calculations: the problem that the overall conversion is insensitive to the special mathematical form of the rate law; in other words, more than one type of formula often give more or less equally good fits to the experimental results. That is why experimental accuracy cannot be too great, while every caution should be taken in the numerical calculation.

Further difficulties arise when the kinetics cannot be described by any definite number of parameters. Of course, a sufficiently short section of the conversion curve may always be fitted by an equation of type (1) and parameters assigned to this section, but it is then tempting to try to attach physical importance to these parameters, and this may lead us to speak about "changing" mechanisms. In reality, although it is possible that a mechanism may alter in a dramatic way over some given temperature interval and so cause a sudden change in the set of parameters, a continuously changing mechanism is most improbable. It will be shown later that when two simple elementary reactions are competing in the same system, the overall kinetics show a typically "variable" order, energy of activation and pre-exponential factor. Indeed, at the beginning of the reaction, we may even find "negative orders"; obviously, in this case the parameters can have no physical meaning. In most composite cases we have to choose between two or more ways of interpretation, and thus at least two independent experimental methods are needed to permit decision between the possible mechanisms.

As most authors use a simple rate law, such as (1), and this is applicable to a very large number of experimental results, this will be dealt with first, though it should be pointed out that the methods described are not limited to this equation.

Some remarks on methods of calculation used in thermogravimetry

Methods of calculation may be classed as either differential or integral, depending on whether they are based on the differential or integrated form of the rate equation. Integral methods can only be used to fit conversion curves, and then only the curve as a whole, and never parts of it. The main advantage of such procedures is that primary experimental data are used directly, and assumptions or approximations (above all in the chosen mode of integration) are applied only to the approximating function and not to the curve to be reproduced. Their main drawback is that on account of the insufficiency of data, at least one parameter must be assumed in the calculation and changed by trial-and-error until the fit is obtained. Even though this tedious procedure is nowadays simplified by computer and is consequently not too time-consuming, the disadvantage remains that it is inconvenient to apply proper statistical methods, and so the procedure is not a genuine curve-fitting. In addition, it is very hard to estimate the importance of the residual deviation of the theoretical from the experimental curve.

Differential methods have the advantage of being simpler, and at the same time the lack of information is less, since two functions, TG and DTG, are available for which values can be substituted in the rate equation. The main problem in their application is always connected with obtaining the derivative of the conversion function, the DTG. The analogue signal of some recording thermobalance is unsuited for this purpose. An attempt has been made by Schempf et al. [3] to fit the TG curve by a single high-degree polynomial. Such an expression ought essentially to carry out a twofold task: first it should smooth the curve to diminish the influence of experimental scatter, and second, it should approximate the probability function. The fulfilment of the first condition is very important, because differentiation magnifies scatter greatly, while as to the second point the chosen polynomial must approximate the TG function with the least possible distortion, as its derivative is wanted. In fact the two tasks cannot be catered for by one and the same polynomial; indeed, smoothing alone is impossible by a single expression, on account of the great variation in "signal-to-noise ratio" along the curve. One criticism of the frequently used Freeman – Carroll method and its published computerized versions [4] is precisely its inaccuracy.

While many of the differential and some integral methods try to overcome the above deficiencies by the use of more than one TG curve, obtained on different samples by employing different heating rates, it is easy to demonstrate that they do so only at the expense of an increase in error.

In this paper an attempt is made to approach the kinetic problem by a more correct numerical treatment of the thermogravimetric data, and also by using the second derivative function (DDTG) in addition to the first derivative (DTG) and the integral (TG) [6].

New numerical treatment of thermogravimetric results: the DDTG method

As the first and especially the second derivatives are highly sensitive to experimental error, methods with a good smoothing power had to be sought. Basically, the choise rested between two types of methods. According to the first of these the experimental data could be approximated by a function only partly able to follow the fluctuations of the errors, and this smoothing function differentiated. The second possibility is to carry out a numerical differentiation in the usual way (that is the derivatives are substituted by the differential quotient of an interpolating curve), and to smooth the obtained curve. The drawback of both methods is that if smoothing of a sufficient extent is applied, the substituting of the derivative and the smoothing together become a very poorly-defined procedure; it is hard to judge whether the procedure is correct or not, and it is hard to view the influence of the individual factors on the systemic error. For example, the derivative of a well-smoothed curve may be highly distorted in comparison to the function to be obtained, and thus the approximation of the derived function may be poor in spite of the good fit given by the integral function.

The difficulties, however, can be overcome in the following way [5].

Let us take an interval $[a, b]$ and transform it to the interval $[-1, 1]$. We want to define a polynomial $p(x)$ which is the best approximation of the unknown function $\frac{\mathrm{d}y}{\mathrm{d}x}$ in the following sense:

$$\int_{-1}^{+1} \left[\frac{\mathrm{d}y}{\mathrm{d}x} - p(x)\right]^2 \mathrm{d}x = \min . \tag{2}$$

Let us express $p(x)$ by means of Legendre polynomials:

$$p(x) = \sum_{j=0}^{m} a_j P_j(x) . \tag{3}$$

As the Legendre polynomials are orthogonal, the a_j coefficients may be written as:

$$a_j = (j + 0.5) \int_{-1}^{+1} \frac{\mathrm{d}y}{\mathrm{d}x} P_j(x)\, \mathrm{d}x . \tag{4}$$

The $\mathrm{d}y/\mathrm{d}x$ in (4) can be eliminated by partial integration:

$$a_j = (j + 0.5) \left\{ \left[P_j(x) y \right]_{-1}^{+1} - \int_{-1}^{+1} \frac{\mathrm{d}P_j}{\mathrm{d}x} y\, \mathrm{d}x \right\} . \tag{5}$$

If the experimental data y_i are taken sufficiently close together, then the integral included in (5) can be determined by the well-known methods of integrating with weight functions. It is found that the systematic formula-error inherent in the numerical nature of the integration is negligible in comparison to the random error of the experimental fluctuations if we use more than ten base points and polynomials of the second or third degree. As we actually fit an interpolating function onto the y_i points during integrating with weight functions, the procedure outlined above may be regarded as a smoothing of the derivative of the interpolating function by (2) but with the differentiation of the interpolating function eliminated by the integration.

As detailed analysis shows that the random error of the derivative is variable along the interval, a special "sliding and averaging" procedure, which may be performed in different ways depending on the accuracy required, was worked out. The derivation cannot be "automatized" completely, because the operator has to decide the location and length of the intervals, the degree of polynomials, and the mode of "sliding and averaging", taking into account the special features of the experimental curve under evaluation.

By means of this procedure we were able to produce first and second derivatives with a high accuracy.

The following DDTG calculation [6] makes use of these three functions. If (1) is taken to be valid, we may write the second derivative function of the conversion, α, or of the remaining weight fraction $w = 1 - \alpha$, according to

$$\frac{\mathrm{d}^2 w}{\mathrm{d}T^2} = \frac{\mathrm{d}w}{\mathrm{d}T}\left[\frac{E}{RT^2} - \frac{\mathrm{d}w}{\mathrm{d}T}\,\frac{n}{w}\right]. \tag{6}$$

This may be simply transformed to the linear equation

$$I = Kn + \frac{E}{RT^2}, \quad I \equiv \frac{(\mathrm{d}^2 w/\mathrm{d}T^2)\,T^2}{(\mathrm{d}w/\mathrm{d}T)}, \quad K \equiv \frac{(\mathrm{d}w/\mathrm{d}T)T^2}{w}. \tag{7}$$

The residual fluctuation, which is due not to the random accidental vibration of the balance or any other part of the measuring system, but to the non-uniformity of the decomposition itself, may be eliminated by a linear regression analysis of the I vs. K values obtained.

If the method holds, it yields directly the three parameters of (1); if not, it is simple to notice and hence to conclude that a more complicated rate law is appropriate.

Solution of some kinetic problems in composite cases by means of the DDTG function

Equation (7) provides a simple method of linearizing anisothermic (dynamic) thermogravimetric curves that not only allows the correction of experimental curves, but (in contrast to integral methods) may also be applied to a part of the curve; this is of considerable importance in general thermogravimetric techniques in view of the commonness of multi-step decompositions [7]. Provided the successive steps are well separated, they can be treated independently. If neighbouring steps overlap, however, it is often very hard to determine the amounts of substance which actually decompose in each step, since the steps can be separated only in an arbitrary way. If we use the I vs. K diagram, we observe that at the end of the decomposition it always becomes linear, as in this section only the end-reaction takes place.

Let us take as an example a simple two-step reaction with two independent, parallel reactions in which both reactions are of type (1). Denoting the actual weight by g, the weight at the beginning of the reaction by g_0, and writing the different kinetic parameters in the usual way but distinguishing them by the indices 1 and 2 for reactions 1 and 2, we obtain [7]:

$$g^{1-n_2} = A_2E_2(n_2-1)\, g_{02}^{1-n_2}\, p(x_2) + g_{02}^{1-n_2} \tag{8}$$

where $$\frac{E}{RT} \equiv x\,, \quad \frac{\mathrm{d}T}{\mathrm{d}t} = B \text{ and } p(x) = \frac{e^{-x}}{x} - \int\limits_x^{\infty} \frac{e^{-u}}{u}\,\mathrm{d}u = \frac{e^{x}}{x} - Ei\,.$$

In a plot of g^{1-n_2} vs. $p(x_2)$, g_{02} can be found from the intercept, we can obtain A_2 from the slope, as E_2, and n_2 may obviously be calculated from the final linear

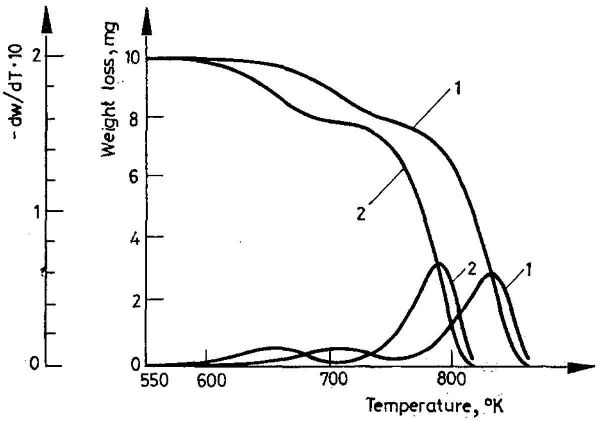

Fig. 1. TG and DTG curves of two independent, parallel reactions. $A_1 = 10^{10}$, $E_1 = 35$ kcal/mole, $n_1 = 1.2$; $A_2 = 10^{15}$, $E_2 = 60$ kcal/mole, $n_2 = 0.8$, Curve 1: $B = 4$ K/min; Curve 2: $B = 0.5$ K/min.

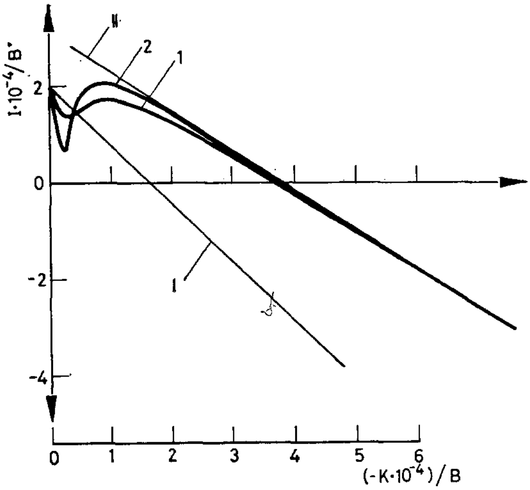

Fig. 2. *I* vs. *K* plot of the reaction of Fig. 1; I and II: part-reactions

part of the curve, since there no other reaction takes place. Fig. 1 shows a typical overlapping two-step TG curve, and Fig. 2 the I vs. K diagram of the same.

The exact kinetic parameters of the first reaction may only be obtained if it is not a very small one. In the latter case we only can "free" the second reaction from the first by this procedure. If both reactions are evaluable, we simply subtract the TG, DTG and DDTG values calculated for the second reaction from the overall data, and thus we are already able to make an I vs. K plot for the first reaction and obtain its kinetic parameters.

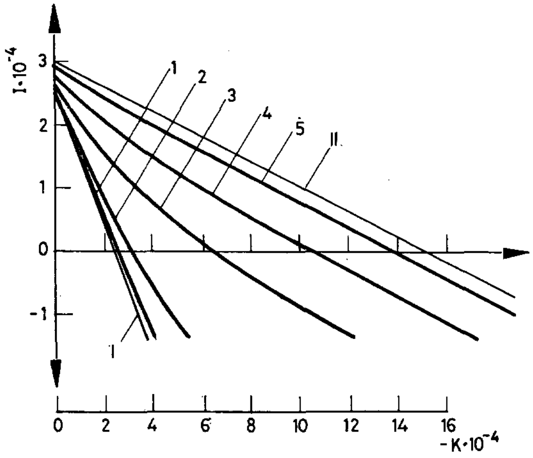

Fig. 3. I vs. K plot of competing case 1. $n_1 = 1.05$; $n_2 = 0.25$; $E_1 = 50$ kcal/mole; $E_2 = 60$ kcal/mole

In the case of competing simple reactions the overall I vs. K plot is essentially never linear, even though parts may appear to be so. We may assign kinetic parameters to these "linear" sections and the corresponding part of the TG curve can be fitted by using them. These parameters may be calculated as usual by a simple linear regression, but they have no real physical meaning.

Taking again a composite reaction produced by two simple competing reactions, we may distinguish three cases, according to Table 1:

Table 1

Case	ΔE	Δn
1	+	+
2	+	–
3	+	0

$\Delta E \equiv E_2 - E_1$, if $E_2 > E_1$

$\Delta n = n_2 - n_1$

The corresponding I vs. K diagrams are illustrated in Figs 3, 4 and 5. In these the $I-K$ lines of the pure component-reactions are denoted by I and II, the competitives by arabics. One of them is held fixed in each set of curves and the pre-exponential factor of the other is varied, producing thus another grade of competition by a different shift of this reaction on the temperature scale. This may be characterized by a simultaneity function, (S), which will be treated later on.

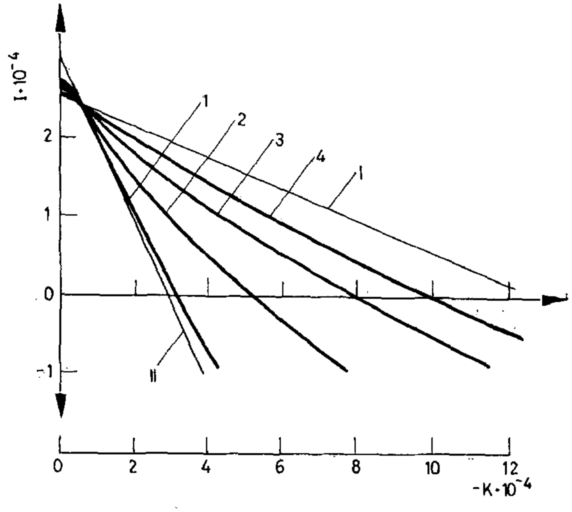

Fig. 4. I vs. K plot of competing case 2. $n_1 = 0.2$; $n_2 = 1.05$; $E_1 = 50$ kcal/mole; $E_2 = 60$ kcal/mole

It is impossible to extract the I vs. K lines of the part reactions from an analysis of TG's of this sort, but the shape of the I vs. K curve of the overall reaction frequently permits us to choose between the three possibilities. If a choice is possible, by a procedure which cannot be outlined here in detail, we can obtain a first estimate of the individual parameters. To determine the parameters more precisely we have to use another, more sophisticated computing procedure. The principle of the least squares for the differences $[(w_i)_{obs} - (w_i)_{calc}]$ would be an appropriate one, but its execution is rather difficult since the equation

$$- dw/dt = A_1e^{-E_1/RTw^{n_1}} + A_2e^{-E_2/RTw^{n_2}} \tag{9}$$

is analytically not integrable. If, however, we have the numerical derivatives of the observed $w(t)$ function with sufficient precision, we may write by the principle of least squares for the derivatives according to (10):

$$\textstyle\sum_i [(dw/dt)_i - (A_1e^{-E_1/RTw_i^{n_1}} + A_2e^{-E_2/RTw_i^{n_2}})] = \min \tag{10}$$

where w_i and $(dw/dt)_i$ stand for the measured data and their numerical derivatives. Since the term in the second round brackets contains the measured values of w_i, it is not equal exactly to the value of the theoretical dw/dt function for the given set of parameters. Its relative deviation, however, is negligible if we have obtained the values of w_i with a small relative error.

Using the I vs. K diagram or assuming the values of n_1 and n_2 from a probable mechanism we have to determine four unknown parameters. In condition (10) the second expression in round brackets is linear in the two pre-exponential factors, and thus we have to change E_1 and E_2 systematically (e.g. by a steepest descent type method), and at given values of E_1 and E_2 we can obtain A_1 and A_2 by the simple linear least squares method.

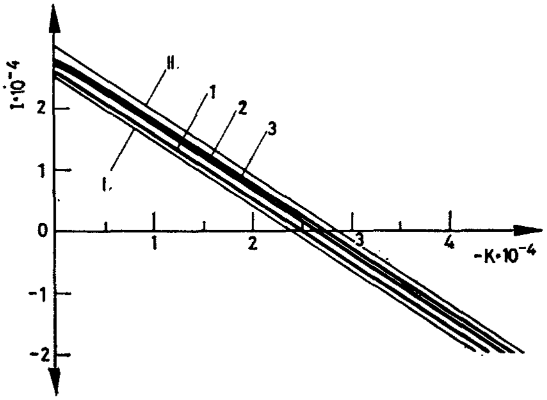

Fig. 5. I vs. K plot of competing case 3. $n_1 = n_2 = 1.05$; $E_1 = 50$ kcal/mole; $E_2 = 60$ kcal/mole

To check the usefulness of the procedure, we integrated (9) numerically for the parameters $E_1 = 41.4$ kcal, $E_2 = 60$ kcal, $A_1 = 10^{10}$ min^{-1}, $A_2 = 10^{16}$ min^{-1}, $n_1 = 0$ and $n_2 = 1.05$. The calculation was performed with a linear, 1°/min heating rate between 675 and 758 °K. The values of w_i and $(dw/dt)_i$ were calculated at fifty different points. By definition $w_0 = 1$. Simulating a case similar to our experiments and to the differentiating method outlined in page 230, the errors were modelized by adding a Gauss-type error to the values of w_i with a standard deviation of $2 \cdot 10^{-3}$, and furthermore two different types of errors to the dw/dt function: a Gauss-type one with standard deviation of $2 \cdot 10^{-4}$ and a sine function with wavelength 20 min and amplitude $2 \cdot 10^{-4}$. (A deviation of this type was observed in our experiments in general.) To study the effect of the errors the calculations were carried out for some greater errors too. The results are shown in Table 2 where the second row corresponds to our real experimental conditions.

If a reliable first estimation should not be possible, or when we have the experimental possibility of measuring individual or relative rates of the simple component-reaction in each case, it is much more accurate to make use of (11), which is a generalized form of (7):

$$I_T = n_2 K_T - \Delta n S K_T + \frac{E_2}{R} - S\frac{\Delta E}{R}, \qquad S \equiv \frac{1}{1+u_T}, \qquad u_T \equiv \frac{w_2'}{w_1'} \qquad (11)$$

where $\Delta E \equiv E_2 - E_1$, $\Delta n = n_2 - n_1$, and the index T refers to differentiation with respect to temperature. For more than two reactions we may use a similar equation,

Table 2

Determination of parameters in the case of competitive reactions

Case	Parameters of the error-simulation			Obtained parameters			
	$\sigma(w)$	$\sigma(dw/dt)$	amplitude	E_1	E_2	log A_1	log A_2
1	0	0	0	41.40	60	10	16
2	$2 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	40.87	60.68	9.86	16.19
3	$2 \cdot 10^{-3}$	$4 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	40.33	61.44	9.73	16.40
4	$2 \cdot 10^{-3}$	$6 \cdot 10^{-4}$	$6 \cdot 10^{-4}$	40.11	62.04	9.69	16.57
5	$2 \cdot 10^{-3}$	$8 \cdot 10^{-4}$	$8 \cdot 10^{-4}$	39.81	62.75	9.62	16.77
6	$2 \cdot 10^{-3}$	$10 \cdot 10^{-4}$	$10 \cdot 10^{-4}$	39.60	63.45	9.57	16.97
7	$2 \cdot 10^{-3}$	0	0	41.12	60.20	9.92	16.06

but with more than one simultaneity function (S). This function has the value of 1 or 0 if only one of the competing reactions plays a role, and 0.5 if the two reactions have just the same rate. As I and K are to be determined from the TG curve of the overall reaction, we have the task only of obtaining further experimental information from the relative rate; this, however, is straightforwardly determined by mass-spectrometry if the two reactions produce different and characteristic products of sufficiently high volatility. It is worth mentioning that the determination of relative rates is easy by mass-spectrometry, but to obtain the overall conversion from the same source is difficult and essentially inaccurate. The use of (11) requires only the relative rates mentioned above and it is easy to combine with overall conversion data, obtained for instance by thermogravimetry

References

1. V. Šatava, Thermochim. Acta, 2 (1971) 423.
2. J. Šesták and G. Berggren, Thermochim. Acta, 3 (1971) 1.
3. J. M. Schempf, F. E. Freeberg, D. J. Royer and F. M. Angeloni, Anal. Chem., 38 (1966) 520.
4. E. S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
   B. Carroll and E. P. Manche, J. Appl. Polymer Sci., 9 (1965) 1895.
5. G. Várhegyi and T. Székely, Acta Chim. Acad. Sci. Hung. (in press).
   G. Várhegyi, Inform. Process. Letters (to be published).
6. B. Lengyel, Kém. Közl., 30 (1968) 271.
   T. Székely, F. Till and Gy. Borossay, Kin. and Mech. of Polyreactions IUPAC (1969) V. 403.
   T. Székely, Chim. Ind. Gen. Chim., 104 (1971) 905.
   B. Lengyel and T. Székely, Monatsh. Chem., 103 (1972) 24.
7. B. Lengyel, T. Székely and G. Garzó, Acta Chim. Acad. Sci. Hung. (in press).
   B. Lengyel, K. A. Andrianov, T. Székely, A. A. Zhdanov, and G. Garzó, Macromol. Chem. (Russ.) in press.

Résumé — L'emploi de la dérivée seconde de la courbe thermogravimétrique, déjà signalé par les auteurs, permet le calcul précis des paramètres cinétiques de réactions simples, à l'aide d'une méthode d'analyse numérique. La méthode qui est décrite permet de plus l'analyse cinétique de plusieurs réactions composites qui constituent un cas souvent rencontré dans la pratique de l'analyse thermique. On discute le cas de réactions indépendantes et celui de réactions compétitives. Pour celles-ci la méthode d'évaluation qui est proposée se prête à l'utilisation combinée d'une thermobalance et d'un spectromètre de masse.

Zusammenfassung — Wie von den Autoren schon früher gezeigt, gestattet die Bestimmung und Anwendung der zweiten derivierten thermogravimetrischen Kurve (DDTG) die genaue Berechnung kinetischer Parameter einfacher Reaktionen durch die Methode der numerischen Analyse. Ferner ermöglicht die beschriebene Methode die kinetische Analyse einiger zusammengesetzter Reaktionen, welche in der thermoanalytischen Praxis häufig vorkommen. Unabhängige und kompetitive Reaktionen werden erörtert. Bei letzteren eignet sich der zur Auswertung vorgeschlagene Weg zur "on-line" Arbeit eines kombinierten Systems bestehend aus Thermowaage und Massenspektrometer.

Резюме — Как было отмечено ранее, определение и использование второй производной термогравиметрической кривой (ДДТГ), при измерении методов числового анализа разрешает надежный расчет кинетических параметров простых реакций. Описанный метод делает возможным кинетический анализ некоторых сложных реакций, часто имеющих место в термоаналитической практике. Обсуждены случаи для независимых и конкурирующих реакций. В последнем случае предлагаемый метод обработки является подходящим при совместной работе комбинированной системы термовесы—масс-спектрометр.