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COMPUTER-AIDED TREATMENT OF THERMOGRAVIMETRIC DATA AND CALCULATION OF EFFECTIVE KINETIC PARAMETERS OF THERMAL DECOMPOSITION PROCESSES

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Separate stages of mathematical processing of thermogravimetric data, the difficulties most often encountered, and typical error sources are considered. A complex procedure of automatic acquisition and editing of experimental data, including calculation of effective kinetic parameters, is described and an appropriate algorithm for the 15 BCM-5 microcomputer is presented. The computer calculation of the kinetic parameters of the multistage thermal decomposition of a polyamide fibre is given as an example.

Mathematical treatment of the results of thermogravimetric experiments to determine the effective kinetic parameters of thermal decomposition of materials is a tedious and time-consuming procedure. An error in any of the stages is accumulated and "enhanced" within following stages, and may finally result in unreliable kinetic parameters (KP).

This work deals with the computer-aided complete treatment of thermogravimetric data, beginning with acquisition and reduction of primary information and ending with estimation of the accuracy of the computation results. The method is implemented in a complex program for the 15 BCM-5 microcomputer used as a control computing device in an automatic system including a TGS-1 Perkin–Elmer thermogravimetric system, a Щ 68000 electronic digital voltammeter, a Consul 260.1 printer and three external memory (EM) devices. The block-diagram of the program is shown in Fig. 1.

Let us consider each of the stages in the treatment of thermogravimetric data, the difficulties encountered most often and typical error sources, as well as the implementation of the procedure in the suggested approach.

Acquisition of primary data (weight of test sample w vs. T and time τ)

Within this stage the error stems from the measuring and recording devices and the method of reading w and T (using a ruler, diagram divisions, etc.). The procedure is much easier and the accuracy higher when devices are used which convert a continuous electric signal from the experimental device into discrete digital

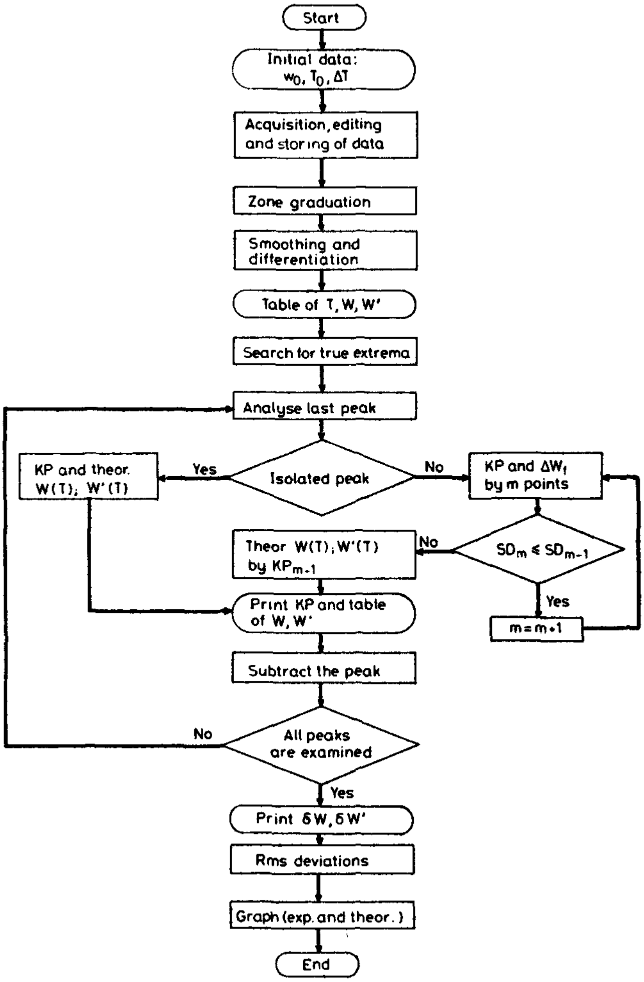

Fig. 1 Block-diagram of thermogravimetric data processing

information printed out, recorded on perforated tape, or stored in the computer or EM. Error may also appear in reducing experimental data to a dimensionless form $W = (w - w_f)/(w_0 - w_f)$, due to inaccurate estimation of the initial (w_0) and final (w_f) weights of a sample. In cases when the process is not completed by the moment the upper temperature limit is reached and the sample weight still decreases, indirect estimation of w_f is questionable and special calculation methods [1] must be used. In this work primary information is collected automatically with the programmable 15 BCM-5 15 calculator, which, in strictly definite time intervals corresponding to a prescribed temperature step ΔT, takes a signal, proportional to the sample weight, from TGS-1 via the Ш 68000 and special interface module, normalizes it and sends it to be stored in one of the EM devices. The maximum number of readings is determined by the EM capacity as 512. Hence, when test material is heated from room temperature to 1270 K, the minimum temperature step is 2 degree if it is necessary to fix the sample weight through the entire heating range. The values of w_0 and w_f are determined as average ones from 10 readings immediately before and after heating. After the experiment, the sample weight are recalculated into relative units, and the computer starts treating the data stored in the EM.

Smoothing and differentiation of the W(T) function

Generally speaking, smoothing is unnecessary in the case of high-quality $W(T)$ curve recording. However for the elimination of random deviations due to experimental "noise" and easier subsequent differentiation, especially in computer-aided treatment of the data, this procedure is desirable.

In some thermogravimetric devices, automatic recording of the weight loss rate curves is provided, but these curves are either insufficiently accurate (e.g. in the derivatograph of MOM, Hungary) or are recorded for another sample of greater weight (e.g. in the TGS-1, Perkin–Elmer, USA).

In the present work, smoothing and differentiation of the set of W_i values $(1 \leqslant i \leqslant 512)$ are performed by a numerical method [2] involving approximation of the group of $(2k + 1)$ equispaced $W(T)$ points (the "window") by the mth power polynomial, and computation of the smoothed W value and its derivative W' at the central window point. In practice, this procedure reduces to estimation of W_i and W_i' via the formula

$$W_i^{(s)} = \frac{1}{N_{s,m,k}(\Delta T)^s} \sum_{l=i-k}^{l=i+k} A_{s,m,l-i} W_l \qquad (1)$$

where $s = 0$ corresponds to smoothing, and $s = 1$ to differentiation, and the convolution integers $A_{s,m,-k}, \ldots, A_{s,m,k}$ and normalizers $N_{s,m,k}$ are found preliminarily for prescribed s, m and k. Obviously, for definite types of dependences, certain optimum values of the parameters m and k exist, depending both on the behavior and the rate of variation of the reference function and on the level and kind of the experimental "noise", when smoothing is rather effective and, at the same time, does not unduly degrade the underlying information. Model calculations made by the author, and the treatment of real thermogravimetric curves, have shown that the optimum window half-width depending on the slope of $W(T)$ may be evaluated from

$$k\Delta T = C \frac{m}{|W'|} \qquad (2)$$

where C is a constant dependent on the sensitivity of the thermobalances, the recorder and other characteristics of the measuring system (in our case $C \approx 10^{-2}$). Since W' changes in a wide range in thermal decomposition processes, and variation of m and k would require changing of the appropriate numerical coefficients in Eq. (1), it is convenient to vary the window half-width due to a multiple change of a temperature step in Eq. (2) at constant m and k.

This procedure is implemented in the program under consideration in the following manner. Before smoothing, preliminary (rough) differentiation of $W(T)$ is performed with some constant step ΔT, and appropriate (maximum for the process) value of the derivative $W'_M(T)$ is estimated. The whole set of W'_i values is then divided into separate zones with

$$(j-1)\frac{|W'_M|}{3} \leqslant |W'_i| \leqslant j\frac{|W'_M|}{3},$$

where $j = 1, 2, 3$ is the coefficient of the zone, and the code $K = j + N_1 \cdot 10^{-3} + N_n \cdot 10^{-6}$, with N_1 and N_n as the numbers of the first and last points, is formed and stored. For instance, if for the points 117 through 193 the rate of weight change is within

$$\frac{|W'_M|}{3} \leqslant |W'| \leqslant 2\frac{|W'_M|}{3}$$

the code 2.117 193 is assigned to this zone. In the simplest case of a one-stage process, the whole set of W'_i values will be divided into 5 zones.

In the course of smoothing and differentiating, the program compares the number of the central window point with the zone code, and estimates, following Eq. (2), the multiplier of the step

$$r = \mathrm{ent}\left(\frac{3Cm}{jk|W'_M|}\right) + 1 \tag{2a}$$

whose value is rounded to the integer on the higher side. In this case, ΔT in Eq. (1) is substituted by $\Delta T' = r\Delta T$, and summation is made within $i - rk = l \leqslant i + rk$. This procedure provides new sets of W, W' and appropriate T values with a variable temperature step and with numbering differing from that of the primary set of $W_i(T)$ values. This enables one to preserve sufficiently detailed information on the most interesting parts of the process curve without loading the EM devices with superfluous information on the flat part of the $W(T)$ curve.

Analysis of process stages and choice of the calculation procedure

The character of a thermal decomposition (the presence of one or several isolated or temperature-overlapping stages) may be judged to a first approximation from the number of peaks and inflexions in the $W'(T)$ curve (DTG). Following this, the appropriate KP calculation procedure is chosen: isolated simple peaks (without inflexions) are calculated as one-stage processes, and irregularly-shaped peaks as multistage processes. It may occur, however, that a DTG peak simple in appearance is poorly described by one set of KP, this corresponding to the presence of two or more highly temperature-overlapping stages. In this case, the calculation must be repeated as for a multistages process.

In the suggested method the stages of the process are analysed in accordance with the program.

To begin with, we must define some of the concepts used. As thermal decomposition involves a decrease in weight, $W'(T) < 0$, maxima and minima *absolute* values of the derivative $|W'|$ are understood by the maxima and minima in the DTG curve. A maximum (minimum) is considered *a true* one provided that: (i) neighbouring minima (maxima) are at least 2 points from it; (ii) the difference between relative weights at a given point and neighbouring like extrema is not less than 5 percent; (iii) the difference between $|W'|$ values at a given point and neighbouring opposite extrema is not less than the "noise" level. If one of conditions (i) or (ii) is violated, the true maximum (minimum) is the highest (lowest) of the competing ones, the other being *false* (associated with residual non-smoothed "noise"). If condition (iii) is violated, the extremum is false.

A true minimum is *zero* if its value is less than the "noise" level (in our case $7 \cdot 10^{-5}$ deg^{-1}). A true maximum is *isolated* if both neighbouring maxima are zero, and *overlapping* if at least one neighbouring true minimum is non-zero.

Following the above concepts, the computer analyses the $W'(T)$ curve, stores the number of true extrema, and starts computing effective KP of the process.

Prediction of the numerical KP values of the entire process or its individual stages

The prediction of the effective KP of simple processes (isolated peaks) involves no difficulties of principle. Numerous methods of calculating these processes [3] via the equation

$$-\frac{dW}{dT} = \frac{Z}{B} e^{-E/RT} f(W), \tag{3}$$

with E and Z as effective activation energy and pre-exponential factor, B as heating rate, and $f(W)$ as the function for the mechanism of the process (whose most common form is $f(W) = W^n$), are based on one or another assumption, and differ in their complexity and accuracy. In the case of computer calculations of KP using the data of one experiment at constant heating rate, it is most expedient to apply the least square method (LSM) to the logarithmic form of this equation. In some situations, correct computation requires consideration of the sample temperature change deviation from the prescribed heating rate due to exo- and endothermic effects [4].

In calculating multistage processes, correct determination of the boundaries of the individual stages is of great importance. Assuming that each stage obeys Eq. (3) and proceeds independently, the calculation may be carried out by the method of successive elimination of stages [5].

These considerations underlie the calculation method described. The prediction of the effective KP of the process or its individual stages starts with the last zero minimum in the direction opposite to the process run. Isolated peaks are calculated as simple stages via Eq. (3), using the LSM for $0.05 < W < 0.95$ (when estimating W for a particular stage, the values of w_0 and w_f are taken at the points of neighbouring zero minima). The resulting KP are used to calculate the theoretical $W(T)$ and $W'(T)$ functions, which are subtracted from the experimental ones, and the calculation goes on, beginning from the last of the remaining zero minima. The overlapping peaks are calculated by the method of successive elimination of stages described in detail in [5]. In this case a minimum error in the KP estimation with a fixed confidence coefficient is the criterion for limiting the calculation domain for the last of the overlapping stages. The calculation is completed with the process onset as the last zero minimum.

Calculation of theoretical $W(T)$ and $W'(T)$ with the resulting KP values and comparison with experiment

Such a comparison must be performed in the final stage of any kinetic calculation. A considerable discrepancy between experimental and theoretical $W(T)$ and $W'(T)$ indicates that an error has been made in at least one of the calculation stages, and the calculated KP do not adequately describe a real process. It should be noted that the coincidence of the calculated and experimental curves gives the only evidence that this particular experiment is described fairly by the calculated KP. The definitive criterion of the correct calculation may be the agreement of the KP values obtained for the material from the results of several experiments at different heating rates or for samples of different weight.

In our case of computer computations this step coincides with the previous one, since, after the calculation of the entire process by the above scheme, the values $\delta W(T)$ and $\delta W'(T)$ rather than the primary smoothed $W(T)$ and $W'(T)$ remain in the EM as a result of subtraction of all calculated stages. $\delta W(T)$ and $\delta W'(T)$ correspond to the deviations of the total calculated functions from the experimental ones and are used to determine the rms deviations characterizing the quality of the whole computation.

The primary data, relative finite weight; codes of all zones; tabulated T, W and W' after smoothing and differentiating over the zones; calculation results for each stage with indications of its type and the fraction of substance participating in it; tabulated T, W and W' for each stage; tabulated residuals $\delta W(T)$ and $\delta W'(T)$; rms deviations and the combined graph of the total calculated and experimental $W'(T)$ illustrating the quality of the description of experimental data in terms of the calculated kinetic parameters, are printed in the course of the computation.

Figure 2 is a graph resulting from the calculation of the multistage thermal decomposition of a polyamide fibre (heating rate 20 deg/min, sample weight 1.471 mg, flowing Ar as ambient medium) using the above program. It is impossible to calculate directly the main process (with a peak at about 833 K, with a 20.2% loss of the initial sample weight), as the end of this process is concealed by two small high-temperature stages with peaks at 948 and 1118 K, when 8.4% and 4.6% of the weight are lost. In themselves, these high-temperature stages are of no interest because of their insignificance, but their calculation and subsequent subtraction are necessary to estimate the finite weight and to calculate the major stage. A negligible peak at about 603 K displays about 1.4% loss of volatiles, while that around 423 K characterizes 5.6% removal of moisture. The effective KP obtained for each stage are given in Table 1. Similar KP values have also been obtained for this material at alternative heating rates.

Table 1 Calculation results for thermal decomposition of polyamide fibre

Parameter	Stage I (moist.)	II (volat.)	III (major)	IV	V
T_{max}, K	424	604	830	948	1118
ΔW, %	5.6	1.4	20.2	8.4	4.6
E, kJ/mol	34.8	33.5	232.5	74.7	165.5
n	0.9	0.4	1.6	0.8	2.3
Z, s^{-1}	$1.76 \cdot 10^{2}$	3.49	$5.94 \cdot 10^{12}$	$4.43 \cdot 10$	$2.46 \cdot 10^{5}$

The coincidence of the calculated and experimental $W(T)$ and $W'(T)$ (Fig. 2) is quite satisfactory. The rms deviation is 0.2 percent in weight while that in weight loss rate is 1.3 percent of its maximum. The temperature scale is seen to be non-uniform, due to the temperature step variations from zone to zone.

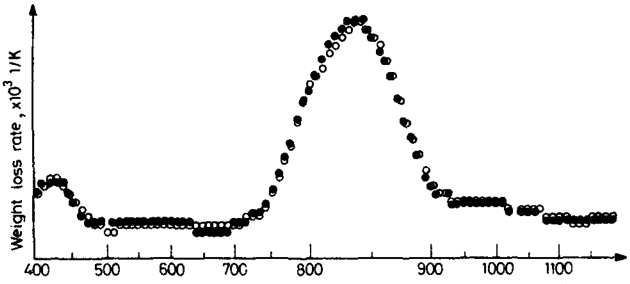

Fig. 2 Experimental (●) and calculated (○) curves of polyamide fibre weight loss rate

The entire calculation by the above program, including primary processing of data and printing of tables and graph, requires between 20 and 50 min, depending on the number of stages. The participation of an operator is unnecessary.

Thus, the application of the automatic thermogravimetric system and the above complex program markedly reduces the time and tediousness of kinetic calculations.

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Zusammenfassung — Verschiedene Phasen der mathematischen Behandlung von thermogravimetrischen Daten, am häufigsten auftretende Schwierigkeiten und typische Fehlerquellen werden erörtert. Das komplexe Verfahren der automatischen Eingabe und Ausgabe experimenteller Daten wird, einschliessliche der Berechnung von effektiven kinetischen Parametern, beschrieben. Ein entsprechender Algorithmus wird für den Mikrokomputer 15 BCM-5 angegeben. Als Beispiel wird die Berechnung der kinetischen Parameter der mehrstufigen thermischen Zersetzung von Polyamidfasern ausgeführt.

Резюме — Рассматриваются основные этапы математической обработки термогравиметрических данных, наиболее часто встречающиеся трудности и типичные источники ошибок. Описывается процедура автоматизированного сбора и обработки экспериментальных данных, включающая расчет эффективных кинетических параметров, и приводится алгоритм программы для микро-ЭВМ 15 ВСМ-5. В качестве примера приводятся результаты машинного расчета многостадийного процесса термического разложения полиамидного волокна.