

DERIVATOGRAPH-C—A MICROCOMPUTER-CONTROLLED SIMULTANEOUS TG, DTG, DTA, TD AND EGA APPARATUS

Part II. A simple method of estimating kinetic parameters

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A simple method has been developed for the estimation of formal kinetic parameters: the microcomputerized Derivatograph-C automatically calculates the virtual n , E and $\log A$ parameters of simple reactions.

The view is becoming increasingly widely held that conventional thermoanalytical curves obtained in the course of dynamic heating programs are not suitable for the reliable estimation and interpretation of the parameters of the Arrhenius model. This is due partly to physico-chemical and partly to mathematical causes.

For example, it is a common experience that the physico-chemical content of estimated reaction kinetic parameters is very poor. The processes of heterogeneous reactions leading to equilibrium, i.e. the courses of the conventional thermoanalytical curves which constitute the basis of the calculations, are characteristic of the experimental conditions rather than of the reactions themselves. For decades we have consistently pointed out this experimentally-proved finding [1-9], and have often emphasized its consequences as concerns kinetic calculations [8-14].

It is well known too that the values of parameter-triplets calculated by various calculation methods from the results of a given experiment differ considerably. Earlier, while seeking the cause of this, we found [11-14] that, due to the nature of the mathematical methods applied, such values can be calculated only with a significant uncertainty.

Despite this, we are ready to accept the justification of kinetic calculations if these are interpreted formally and are carried out for practical purposes. Independently

of whether they have a physico-chemical meaning and whether their values are fictive, kinetic parameters may be suitable for the numerical characterization of the material investigated and for comparison of samples examined in series. For example, a correlation may be sought between the virtual parameters of the decomposition reactions of ceramic raw materials or plastics and their technological or physical properties.

These considerations led us to develop a parameter-estimating method and to construct the Derivatograph-C (described in Part I [15] of this series), which is suitable for the performance of such calculations.

It was not new perceptions and theoretical considerations that induced us to develop the new calculation method, but rather the limited memory capacity of the Derivatograph-C [9, 15, 16]. We attempted to devise a calculation as simple as possible with software as short as possible, without making any concessions as regards accuracy.

In the development of the parameter-estimating method, we started from the following considerations. The uncertainty arising from the badly conditioned nature of the model, i.e. the large deviation of the estimated parameters, can be reduced significantly if the projection method is applied. This means that with the help of a mathematical operation one of the parameters, e.g. the pre-exponential factor A , is eliminated, while another one, e.g. the reaction order n , is determined in advance with another method. In this way, the three-parameter model becomes a one-parameter model. The eliminated A can subsequently be determined in the knowledge of the two other parameters already estimated.

With the Derivatograph-C, the procedure is simple. In the TG curve (Fig. 1) projected on the display by means of the cursor, the beginning (C_0) and end (C_e) of the curve must be indicated. Thereafter, when the appropriate key on the keyboard is pressed, the calculation is performed. In a few seconds, the computer writes out on the display the values of n , E and $\log A$. These are calculated in accordance with the following principle.

The computer first calculates the value of n by the Kissinger method [17] on the basis of the section of the DTG curve between weights C_0 and C_e and times t_0 and t_e . Then, within this time interval, the computer selects the temperature (T_1 and T_2) and weight (C_1 and C_2) values relating to the half values of the DTG curve (h_1 and h_2) and, using the natural logarithmic form of the Arrhenius equation (Eqs (1) and (2)), calculates the value of E :

$$\ln h_1 = \ln A - E/RT_1 + n \ln (1 - \alpha_1) \quad (1)$$

$$\ln h_2 = \ln A - E/RT_2 + n \ln (1 - \alpha_2) \quad (2)$$

where

$$\alpha_i = \frac{C_i - C_0}{C_e - C_0} \quad (i = 1, 2) \quad (3)$$

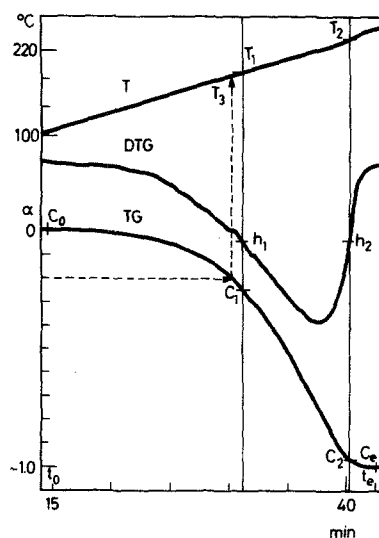


Fig. 1 T, TG and DTG curves of calcium oxalate monohydrate

If (2) is subtracted from (1) and rearrangement is made for E :

$$E = \frac{n [\ln(1 - \alpha_1) - \ln(1 - \alpha_2)]}{(1/T_1 - 1/T_2)} \cdot R \quad (4)$$

For the calculation of $\log A$, the temperature value (T_3) relating to the conversion degree 0.2 is used, together with the already estimated values of E and n .

Our examinations with simulated curves reveal that curves for various reaction orders run together up to a conversion of 0.2. Thus, up to this point the process represented by the TG curve may be regarded from the aspect of the estimation of $\log A$ as a zero-order reaction, whereby the formula used for the calculations becomes significantly simpler:

$$\log A = \log \left[0.2 \frac{R}{E} \cdot e^{x(x^2 + 2x)} \right] + \log G \quad (5)$$

where

$$x = \frac{E}{R \cdot T_3} \quad (6)$$

The equation (Eq. (5)) used here for the calculation of $\log A$ is actually a simplified form of the Doyle approximation [18], well known in the literature.

The method yields acceptable results only for one-step processes, i.e. if the DTG curve indicates overlapping processes of several steps, the calculated reaction kinetic parameter-triplet has no sense.

Table 1 Kinetic parameters of the dehydration of calcium oxalate monohydrate

No.	Order of reaction, n	Activation energy, E	Pre-exp. factor, $\lg A$
1	0.65	91.0	9.10
2	0.73	98.0	9.81
3	0.71	92.0	9.44
4	0.70	92.7	9.59
5	0.67	95.3	9.85
6	0.68	97.3	9.96
7	0.67	99.9	10.32
mean value	0.69	95.2	9.65
stand. deviation	± 0.03	± 3.1	± 0.41

Sample weight: between 81–88 mg, heating rate: 5 deg·min⁻¹, sample holder: open crucible, atmosphere: air

We checked the reliability of this method by using the estimated parameter-triplets to simulate curves in the manner described earlier [11] compared these with the measured curves. The curves were found to fit well.

It should be emphasized that, for a given decomposition step of a given material, a reproducible kinetic parameter-triplet (Table 1) is obtained only if the parallel measurements are carried out under strictly identical experimental conditions. It must also be emphasized that the values of kinetic parameters calculated with the Derivatograph-C cannot be compared with parameter values estimated by means of other methods: as we established earlier, due to the badly conditioned nature of the model, the values of the estimated parameters also depend on the calculation method applied. Accordingly, the results obtained by various methods may exhibit significant differences [11].

List of notations

- h_i ($i = 1, 2$) = value of the derived weight change (dm/dt) at the selected points (mg min⁻¹)
- α_i ($i = 1, 2$) = degree of conversion at the selected points
- $\log A$ = common logarithm of the pre-exponential factor
- E = activation energy (kJ mol⁻¹)
- n = virtual reaction order
- T_i ($i = 1, 2, 3$) = temperatures relating to the given points (K)
- C_i ($i = 0, 1, 2$ and e) = measured weight at the given points (mg)
- G = rate of linear heating (deg min⁻¹)
- R = universal gas constant (kJ mol⁻¹ deg⁻¹)
- t_i ($i = 0, e$) = times relating to the given points (min).

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