

KINETIC ANALYSIS OF ADDITIVELY OVERLAPPING REACTIONS. PART 1. DESCRIPTION OF AN OPTIMIZATION METHOD AND ITS USE FOR THE SEPARATION OF PEAKS

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ABSTRACT

The determination of kinetic parameters for additively overlapping TG steps is possible only by fitting model equations (e.g., phase-boundary reactions) to the non-standardized weight step by means of non-linear optimization. A general condition of this procedure is the reproducibility of a conversion curve from a partial interval. Calculations carried out with theoretical and with erroneous values have shown that it is highly dependent upon the dispersion of the measured values and upon the position and length of the interval. In general, it is to be considered that the maximum must be involved in the evaluation. An increase in dispersion of the data can be compensated for by the evaluation of an enlarged partial interval.

The findings obtained have been applied to the evaluation of additively overlapping reactions by the use of the procedure described. A general condition of a successful separation of the peaks is the existence of an overlapping-free interval including the maximum for only one of the overlapping partial reaction steps.

INTRODUCTION

The determination of kinetic parameters from non-overlapping reactions (single peaks) is successful for both standardized and non-standardized conversion curves. The best fit of the experimental curve to the theoretical one for various time laws can be found by the use of non-linear optimization procedures (NLO) [1].

In practice, however, overlapping reactions (multiple peaks) are often encountered for which the beginning and/or the end of the peaks cannot be determined. In these cases, the kinetic evaluation of additively overlapping single peaks is rendered possible only by evaluating the non-standardized conversion curve by the use of NLO, which requires the determination of the parameters to be performed in a partial interval. Therefore, the boundary conditions under which a total reaction step can be reproduced by evaluating a partial interval need to be known.

After the optimization procedure has been applied (simplex method), as described in this paper, an answer to this question is given by systematic calculations based on theoretical conversion curves for a phase-boundary reaction. With a differing amount of overlapping of several reaction steps, the kinetic parameters of single peaks can be determined and, thus, the separation of the peaks can be found.

DETERMINATION OF KINETIC PARAMETERS BY THE USE OF THE SIMPLEX METHOD

For the determination of kinetic parameters under non-isothermal conditions several methods have been described in the literature, all based on the fundamental kinetic equation

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

using the Arrhenius equation

$$k = k_0 e^{-E/RT} \quad (2)$$

Potential errors resulting from the use of a standardized conversion curve, α , and the linearization of eqn. (1) for the determination of E and k_0 have been given earlier [1]. Based on a non-standardized weight curve, the determination of kinetic parameters by the use of a non-linear optimization procedure is described. The simplex method has proved to be suitable for this purpose [2].

The procedure starts from the fundamental kinetic equation (1) using phase-boundary reactions for $f(\alpha)$

$$-\frac{dTG}{dT} = \frac{k_0^*}{q} [TG(T) - TG_E]^n e^{-E/RT} \quad (3)$$

where $k_0^* = k_0 G_V^{1-n}$, $q =$ heating rate ($^{\circ} \text{ min}^{-1}$). It is the aim of the procedure to determine the parameters E (activation energy), k (frequency factor), n (order of reaction), $G_V = TG_0 - TG_E$ (loss in weight), in such a way that eqn. (4) is valid

$$\frac{1}{m-1} \sum_{i=1}^m [DTG(T_i)_{\text{exp.}} - DTG(T_i)_{\text{theor.}}] \rightarrow \min \quad (4)$$

where $m =$ number of measured points on each TG curve, i.e., the payoff function

$$S^2 = Z(E, n, T_M, G_V) \quad (5)$$

is to be minimized.

Using T_M instead of k_0 and $\ln k_0$ for optimization eliminates the dependence existing between E and k_0 . E and T_M having been determined, the

value of k_0 can always be calculated from the equation

$$\ln k_0 = \ln E + E/(RT_M) - \ln(RT_M^2) \quad (6)$$

The use of the simplex method requires a starting matrix, the so-called initial simplex, to be established. Initially, starting parameters are determined from magnitudes that are known or can be read from the curve. The height, $DTG(T_M)$, and position, T_M , of the peak can be obtained from the DTG curve. The loss in weight is given by the TG curve and n by the asymmetry of the DTG curve. According to Kissinger [3], E is obtained from

$$E = DTG(T_M) \frac{RT_M^2}{G_V} n^{-(n/1-n)} \quad (n \neq 1) \quad (7)$$

It is to be pointed out that these initial values are only starting points of the optimization procedure and, thus, do influence the convergence behaviour. However, the great uncertainty of these values (e.g., overlapping of reactions) does not impair the application of the method. The matrix is set up as follows

$$\begin{pmatrix} S & E & T & n & G_V \\ y_1 & E & T & n & G_V \\ y_2 & E_1 & T & n & G_V \\ y_3 & E_1 & T_1 & n & G_V \\ y_4 & E_1 & T_1 & n_1 & G_V \\ y_5 & E_1 & T_1 & n_1 & G_{V_1} \end{pmatrix}$$

In order to establish in advance the direction of the optimization process, it is expedient to vary the parameters in such a way that for the residual dispersion the following order exists: $y_1 > y_2 > y_3 > y_4 > y_5$. This procedure results in a diminution of the iteration number by 1/3 as compared with a random variation of the parameters (multiplication by factors, addition of constant values).

POSSIBILITIES OF REPRODUCING THE TOTAL REACTION STEP FROM PARTIAL INTERVALS

On the basis of theoretical conversion curves calculated by eqn. (3) it is shown that the reproduction of a total weight curve from a partial interval is generally possible. There are limitations due to the length and position of the interval as well as the dispersion of the measured data. The use of calculated curves for studying the influence of these factors has the advantage of eliminating questions as to the validity of a uniform time law for the description of an experimental curve and allows unambiguous statements to be made as to the suitability of the mathematical optimization procedure

TABLE 1

Kinetic parameters for phase-boundary reaction ($n = 1/3$)

Range (K)	Calculated DTG values				Parameters obtained			
	E	n	G_V	S	Using erroneous TG values numerically differentiated ($S = 0.036$)			
	E	n	G_V	S	E	n	G_V	S
330–420	83.7	0.33	1.0	0.4×10^{-5}	85.4	2.03	1.1	0.7×10^{-3}
330–380	83.9	0.33	1.0	0.8×10^{-5}	83.2	0.23	1.2	0.6×10^{-3}
350–400	83.7	0.33	1.0	0.5×10^{-5}	83.1	0.27	1.0	0.7×10^{-3}
350–410	83.7	0.33	1.0	0.5×10^{-6}	85.5	0.35	1.1	0.8×10^{-3}
370–420	83.7	0.33	1.0	0.4×10^{-6}	85.1	0.35	1.1	0.7×10^{-3}

used. The studies were carried out with the following curves:

- (1) Calculated DTG curves with the accuracy $E = 12.6$.
- (2) Calculated TG curve with the random error $S = 0.036$ mV numerically differentiated. In this way, the accuracy of the data measured on the Mettler thermobalance TA1 is simulated.
- (3) Values from curve (2) cubically smoothed and differentiated each with eight points.

The calculations were carried out on the basis of the time law for phase-boundary reactions at $n = 1/3$ and $n = 2$ with the following values: $E = 83.7$ kJ mol $^{-1}$; $n = 1/3$ and 2, respectively; $T_M = 400$ K; $G_V = 1$ mV;

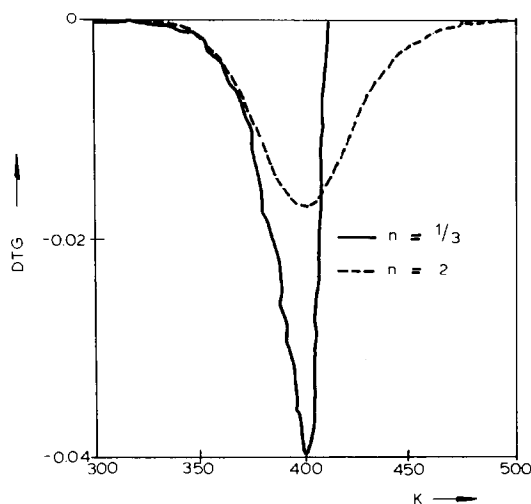


Fig. 1. Calculated DTG curves for phase boundary reaction with $E = 83.7$ kJ mol $^{-1}$; $n = 1/3$ and 2, respectively.

Using erroneous TG values cubically smoothed and numerically differentiated				Using erroneous TG values cubically smoothed and numerically differentiated (SW = 0.5 K)			
<i>E</i>	<i>n</i>	<i>G_v</i>	<i>S</i>	<i>E</i>	<i>n</i>	<i>G_v</i>	<i>S</i>
98.9	0.57	1.1	0.1×10^{-2}	84.1	0.34	1.1	0.5×10^{-3}
86.0	0.45	1.2	0.3×10^{-3}	84.1	0.35	1.1	0.2×10^{-3}
83.4	0.20	0.9	0.2×10^{-3}	83.9	0.33	1.1	0.3×10^{-3}
99.4	0.58	1.0	0.1×10^{-2}	85.6	0.35	1.1	0.2×10^{-3}
103.0	0.59	1.0	0.1×10^{-2}	86.2	0.35	1.1	0.1×10^{-3}

In $k_0 = 22.444$; SW = 2 K. The results of the calculations are given in Tables 1 and 2 for $n = 1/3$ and $n = 2$, respectively and shown in Fig. 1. The relative errors of the kinetic parameters obtained from repeated measurements were found to be $\pm 5\%$ for E and $\pm 10\%$ for n . The inspection of the results allows the following conclusions to be made:

(1) Calculated values with accuracy $E = 12.6$ in each of the partial intervals result in the data given, i.e., the total reaction step can be determined from a partial interval and, thus, can be reproduced by the latter.

(2) For erroneous values the variations of the parameters between the particular intervals increase. The differences are not systematic, but correspond to the random character of the dispersions.

(3) Cubic smoothing results in less variation of the intervals. From a comparison of the third and fourth columns in Table 1 it is evident that the step width (SW) of the data exerts a great influence on the smoothing effect, which is particularly pronounced for phase-boundary reactions with $n < 1$.

From the results obtained by calculations with erroneous theoretical values it may be deduced that the possibilities of evaluation within a partial interval of the total reaction step are dependent upon the dispersion of the measured data and upon the position and length of the interval. In general, it is to be considered that the maximum has to be involved in the evaluation. An increase in dispersion of the data can be compensated for by the evaluation of an enlarged partial interval.

The preceding calculations were carried out always on the assumption that the calculated values agree with the model equation available for the optimization. If this is not the case, then even a partial interval, when used for the evaluation, cannot be described by means of a phase-boundary reaction. To check this, theoretical values have been calculated on the basis of the time law of two-dimensional diffusion with $E = 120 \text{ kJ mol}^{-1}$, $\ln k_0 = 10$, $G_v = G_0 = 1$, $AG = 1^\circ \text{ min}^{-1}$, $T_A = 600 \text{ K}$, $T_E = 1050 \text{ K}$, SW = 3 K,

TABLE 2
Kinetic parameters for phase-boundary reaction ($n = 2$)

Range (K)	Calculated DTG values			Parameters obtained			Using erroneous TG values cubically smoothed and numerically differentiated						
	E	n	G_V	S	Using erroneous TG values numerically differentiated ($S = 0.036$)	E	n	G_V	S	Using erroneous TG values cubically smoothed and numerically differentiated	E	n	G_V
330-480	83.7	2.0	1.0	0.1×10^{-5}	85.4	2.1	1.1	0.7×10^{-3}	84.4	2.0	1.1	0.1×10^{-3}	
330-380	83.7	2.0	1.0	0.2×10^{-5}	84.0	1.9	1.1	0.6×10^{-3}	85.2	2.0	1.1	0.2×10^{-3}	
350-400	83.7	2.0	1.0	0.8×10^{-6}	86.4	2.2	1.1	0.7×10^{-3}	85.1	2.1	1.1	0.3×10^{-3}	
350-410	83.7	2.0	1.0	0.2×10^{-6}	84.0	1.9	1.1	0.8×10^{-3}	84.7	2.0	1.1	0.2×10^{-3}	
370-430	84.1	2.0	1.0	0.8×10^{-5}	82.2	2.0	1.1	0.8×10^{-3}	83.4	2.0	1.1	0.1×10^{-3}	
390-480	83.7	2.0	1.0	0.2×10^{-6}	99.8	2.4	1.0	0.7×10^{-3}	84.6	2.0	1.1	0.1×10^{-3}	

TABLE 3

Kinetic parameters for two-dimensional diffusion optimized by means of a phase-boundary reaction

Range (K)	Parameters			
	E	n	G_V	S
650–890	52.9	0.5	1.0	0.8×10^{-4}
700–850	53.4	0.6	1.0	0.2×10^{-3}
750–900	49.8	0.4	1.0	0.1×10^{-3}
800–1000	72.9	1.1	1.1	0.1×10^{-3}

and evaluated in intervals with the use of phase-boundary reactions for model equations. The results are shown in Table 3. From these results it is evident that the curve cannot be described in a uniform manner. Thus, the possibility of describing a reaction course with a time law not valid is eliminated.

APPLICATION OF THE METHOD TO CALCULATED OVERLAPPING REACTIONS

In the previous section it was demonstrated that a phase-boundary reaction can be reproduced by evaluating a corresponding partial interval. In the following this fact is utilized in the evaluation of overlapping reactions.

For that we have calculated additively overlapping TG steps by applying the following parameters to the first reaction step: $E = 83.7 \text{ kJ mol}^{-1}$, $\ln k_0 = 22.444$, $n = 1$, $G_V = TG_0 = 1$, $AG = 1^\circ \text{ min}^{-1}$, $T_A = 300 \text{ K}$, $T_E = 700 \text{ K}$,

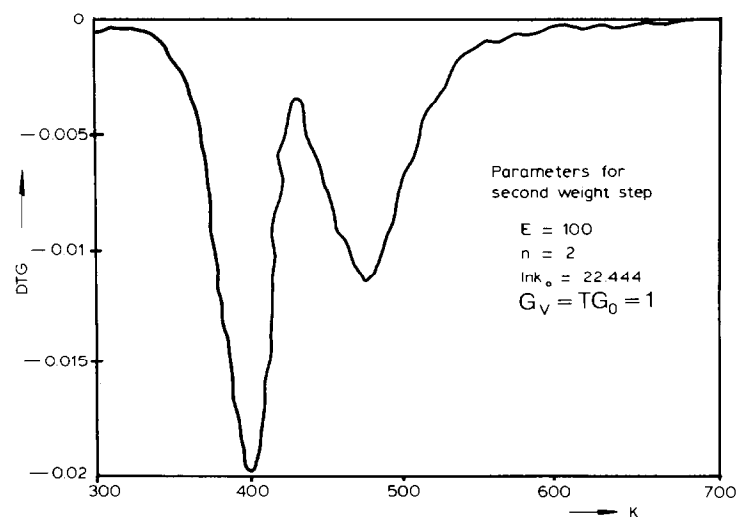


Fig. 2. Calculated additively overlapping DTG curve with $T_{M_2} - T_{M_1} = 71 \text{ K}$.

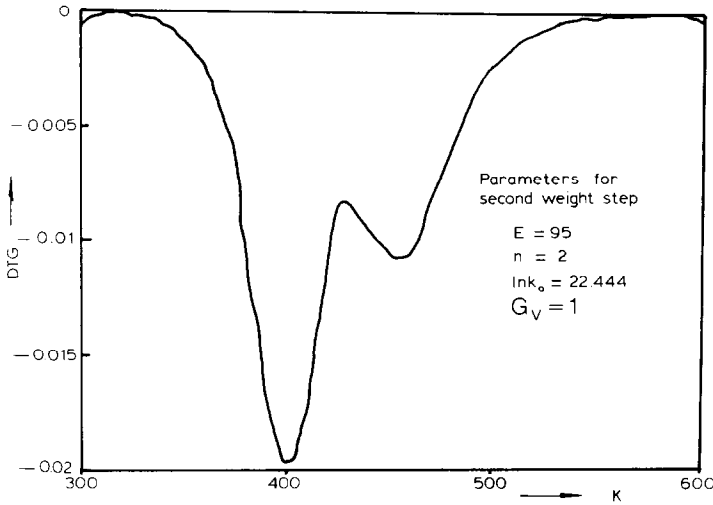


Fig. 3. Calculated additively overlapping DTG curve with $T_{M_2} - T_{M_1} = 51$ K.

SW = 2 K. The second reaction step was varied. To simulate the accuracy of experimental data ($S = 0.036$ mV), dispersions fitted with random numbers were totalled and the TG curves thus obtained were cubically smoothed and differentiated (Figs. 2-4).

For an evaluation an overlapping-free interval needs to be available; with the dispersion mentioned the interval is not sufficient. Reproducing the total reaction step from a partial interval becomes possible only when the peak maximum is involved in the evaluation.

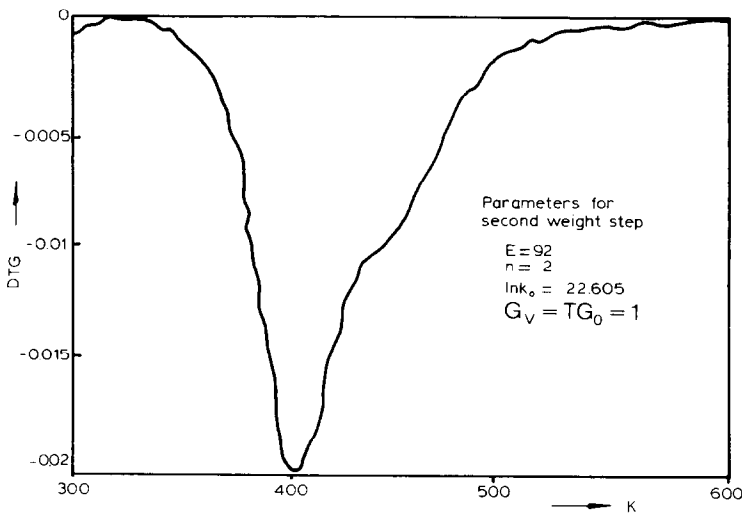


Fig. 4. Calculated additively overlapping DTG curve with $T_{M_2} - T_{M_1} = 35$ K.

The overlapping-free interval is determined by enlarging the intervals from the beginning or the end of the total reaction step with constant parameters being obtained, as stated in the previous section, until an overlapping occurs. The results obtained by applying this procedure to the curve shown in Fig. 2 are given in Table 4. By subtracting the theoretical peak calculated from the parameters valid for the second reaction step we obtain an overlapping-free partial reaction step which, when evaluated, results in the data given.

If overlapping occurs to a higher extent (cf. Fig. 3 and Table 5), the determination of constant parameters by the variation of the evaluation

TABLE 4

Kinetic parameters for overlapped DTG curve according to Fig. 2

Range (K)	Parameters			
	E	n	G_v	S
460-550	98.6	2.0	1.1	0.8×10^{-4}
450-550	100.3	2.0	1.0	0.8×10^{-4}
450-500	103.4	2.1	1.1	0.7×10^{-4}
435-500	103.4	2.1	1.1	0.7×10^{-4}
420-550	82.1	1.6	1.1	0.8×10^{-3}

TABLE 5

Kinetic parameters for overlapped DTG curve according to Fig. 3

Range (K)	Parameters			
	E	n	G_v	S
445-550	98.5	2.0	1.0	0.8×10^{-4}
445-500	97.9	2.0	1.0	0.7×10^{-4}
440-550	99.3	2.1	1.0	0.8×10^{-4}
435-500	93.2	2.0	1.1	0.8×10^{-4}
420-500	63.4	1.4	1.3	0.6×10^{-3}

TABLE 6

Kinetic parameters for overlapped DTG curve according to Fig. 4

Range (K)	Parameters			
	E	n	G_v	S
435-500	78.9	1.8	1.2	0.7×10^{-4}
430-500	54.7	1.4	1.5	0.1×10^{-3}
430-550	77.4	1.8	1.2	0.9×10^{-4}
420-550	43.8	1.3	1.9	0.3×10^{-3}

TABLE 7

Kinetic parameters for overlapped DTG curve according to Fig. 4 with $S = 0.025$ mV

Range (K)	Parameters			
	E	n	G_V	S
420–580	44.1	1.3	1.8	0.3×10^{-3}
430–550	54.4	1.4	1.5	0.1×10^{-3}
435–550	87.8	1.9	1.1	0.4×10^{-4}
440–550	85.6	1.9	1.1	0.4×10^{-4}

range is highly restricted by the diminution of the overlapping-free interval in front of the maximum (15 K).

The results obtained with the curve shown in Fig. 4 (Table 6) indicate that, when overlapping of the peak maxima occurs, a separation is no longer possible.

In general, the limits of a possible separation of peaks are defined, as stated in the previous section as to the evaluation of partial intervals of measured erroneous curves, by the density and dispersion of the data as well as by the position and length of the partial interval. Consequently, a decrease in the error of measurement down to 0.025 mV for the DTG curve shown in Fig. 4 renders the evaluation and, thus, the separation of the peaks possible (within the limits of 435–550 K; Table 7, Fig. 5).

These calculations have shown the possibility of the kinetic analysis of additively overlapping reactions. For the separation of the peaks the evaluation of non-standardized TG curves is indispensable. This, in turn, is rendered possible only by the use of non-linear optimization. Prerequisite to

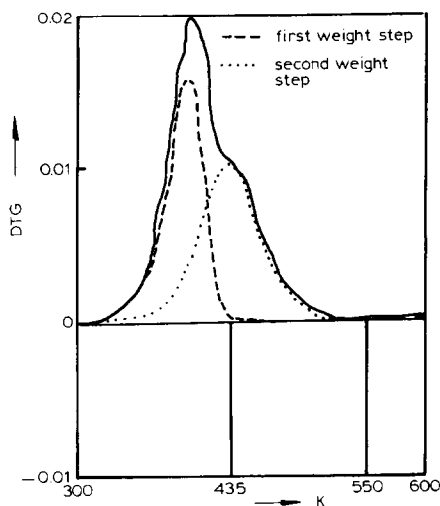


Fig. 5. Separation of the peaks for calculated additively overlapping DTG curve with $T_{M_2} - T_{M_1} = 35$ K and dispersion of the data $S = 0.025$ mV.

the evaluation is the existence of an overlapping-free interval including the maximum for only one of the overlapping partial reaction steps. Thus, these mathematical operations have opened wide applications of the method. In Part 2 of this work corresponding practical examples will be described to demonstrate the applicability of the results.

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