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ROLE OF THE DTG CURVE IN THE EVALUATION OF TG CURVE BY COMPUTER IN CASE OF OVERLAPPING REACTIONS

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The authors justified in a computer controlled way the application of the DTG curve to the evaluation of TG curves of overlapping reactions.

It is well known that the quantitative evaluation of TG curves is rather difficult if two or more transformation processes overlap. So e.g. it would be difficult to state on the basis of the TG curve (Fig. 1) alone the extent of the individual weight changes caused by the first resp. the second of the overlapping reactions. Moreover, if neither the DTG nor the DTA curve were known, then one could not even decide as to whether the TG curve is the result of only one or of two overlapping reactions.

The introduction of the first simultaneous TG, DTG and DTA technique (derivatograph) in the fifties [1, 2] brought along among others also from the point of view of quantitative analysis new possibilities. It turned out namely that the DTG curve offers a possibility to find the inflexion point in the TG curve, to separate the overlapping weight changes and define their probable extent, respectively. Earlier, this was made by visual estimation and even nowadays this is the only alternative with respect to the DTG evaluation method to be described as follows.

In the case of Fig. 2 the second (B) of the overlapping reactions starts far before the end of the first one (A). Accordingly, when the minimum of the resultant DTG curve is projected on the resultant TG curve (C) one can accept by tacit understanding that the point indicated divides the TG curve in two parts in such a way that the amount missing in the weight change (m_a) of

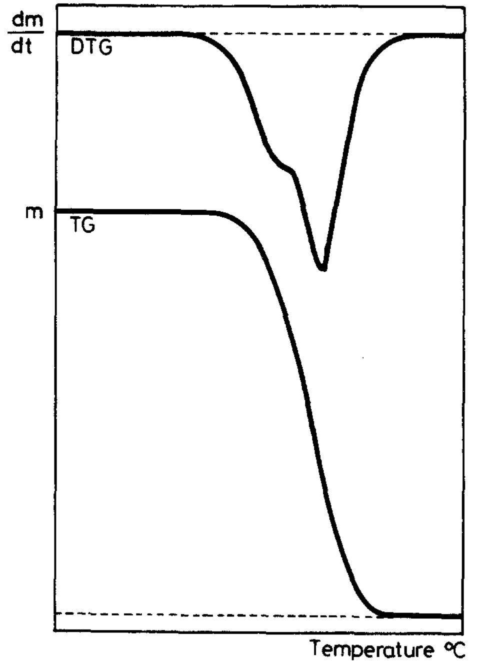


Fig. 1 TG and DTG curves of two overlapping reactions

the first reaction will be nearly identical with the excess in the weight change (m_b) caused by the second reaction. After the minimum the same is valid but in the reverse sense.

This figure shows a border-line case, which may be regarded as idealistic. Visually the two overlapping reactions (A, B) have identical, congruent courses, therefore the positive and negative errors (m_a, m_b) perfectly compensate each other.

However, in every other case the occurrence of more or less significant errors is inevitable. But what will the magnitude of this error. The authors wanted to get an answer to this question with the help of a speculative experiment carried out by means of a computer. To this operation the Derivatograph C [3, 4] proved to be suitable.

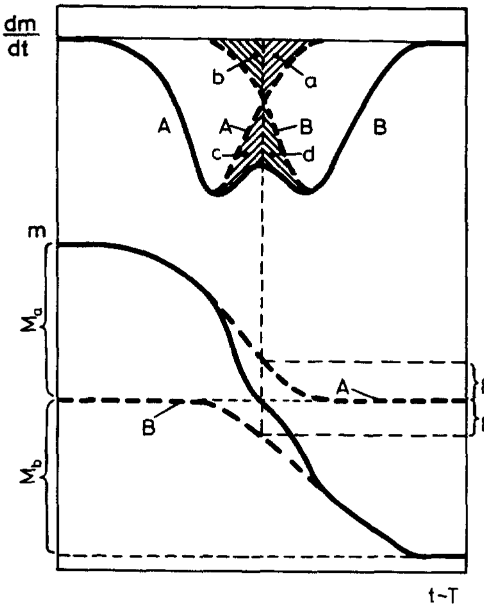


Fig. 2 Two overlapping and congruent TG and DTG curves (A, B) and their resultant (curve C). M_a and M_b: weight change caused by the two reactions; m_a and m_b: errors of the evaluation; a, b, c and d: DTG peak area formed by the overlapping

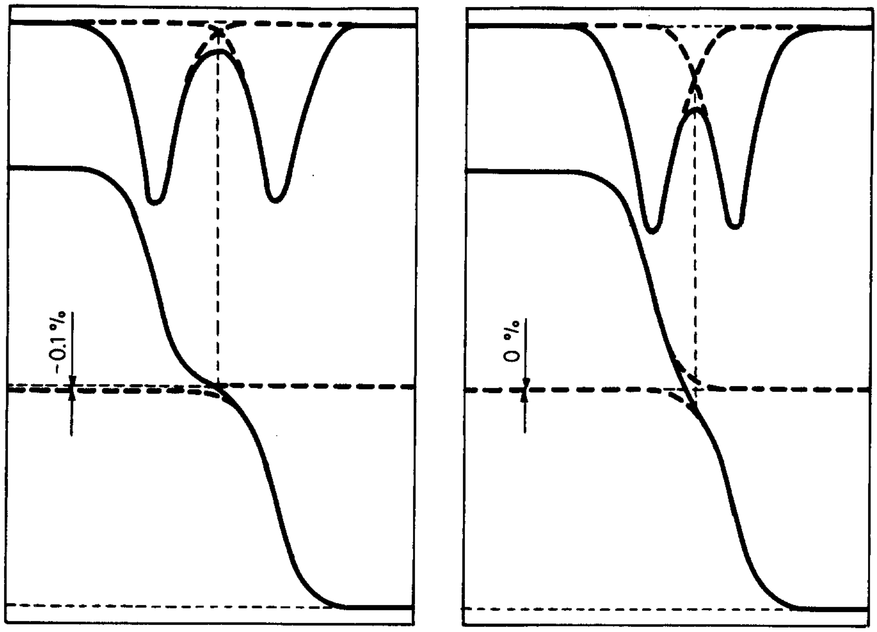
Experimental

The curves in Figs 3-6 were obtained in the following way. The algorithm of the TG curve - selected as a model - was fed into the computer of derivatograph C. From this algorithm the function pairs and their derived curves corresponding to the TG and DTG curves of the overlapping partial reactions were simulated by means of the computer. Between their course asymmetry was established (see later). Then the single members of the TG and DTG curve pairs were shifted in phase to overlap to an extent to clearly demonstrate the effects wanted. Thereafter the resultants of these curves were established.

By projecting the minimum of the resultant DTG curve on the resultant TG curve the apparent weight changes in the first and the second half of the transformation was stated. With knowledge of the original weight changes of the overlapping partial reactions the error of the evaluation can be calculated by means of the DTG curve, from case to case (Table 1).

Table 1 Error of the common evaluation of TG and DTG curves of symmetrical and assymetrical course if extent and rate of weight changes are different

Figure	Theoretical value		Calculated value												
			a			b			c			d		
			Weight change, %											
	Step		Step		Error	Step		Error	Step		Error	Step		Error
	1	2	1	2		1	2	7	1	2		1	2	
3.3.2.	50.0		49.9			50.0			50.2			50.1		
					±0.1			Ø			±0.2			±0.1
		50.0		50.1			50.0			49.8			49.8	
3.3.3.A	50.0		50.3			51.2			52.2			52.7		
					±0.3			±1.2			±2.2			±2.7
		50.0		49.7			48.8			47.8			47.3	
B	30.1		30.3			31.4			34.9			35.5		
					±0.2			±0.3						±5.4
		69.9		69.7			69.6			65.1	±4.8		74.5	
C	15.3		16.2			18.0			19.8			22.1		
					±0.9			±2.7			±4.5			±6.8
		84.7		83.8			82.0			80.2			77.9	
3.3.4.A	50.0		48.9			45.8			42.8			39.5		
					±1.1			±4.2			±7.2			±10.5
		50.0		51.1			54.2			57.2			60.5	
B	72.1		70.8			65.6			55.1			49.5		
					±1.3			±6.7			±17.0			±22.6
		27.9		29.2			34.6			44.9			50.5	
C	85.4		85.3			78.9			72.2			50.6		
					±0.1			±6.5			±13.2			±34.8
		14.6		14.7			21.1			27.8			49.4	



a) b)

Fig. 3a, b Changes of the course of the TG and DTG curves and of the error of evaluation in the case of various overlapping of two congurent TG and DTG curves if extent and rate of weight change are identical

In the case of Fig. 3 the basis of the construction of the TG curve was a reaction whose periods of acceleration and decay - similarly to the TG curves in Fig. 2 - were not only the mirror image of one another but even the whole course of the TG curves was congruent.

In order to demonstrate the sources of the error of evaluation for the case of asymmetrical overlappings, of the countless alternatives three characteristic examples were selected. In the case of Figs 4-6 the overlapping was rendered asymmetric in a way that not only the curve pair reduced in ratio 0.5 : 0.5 of the original function but also its curve pairs reduced in ratio 0.7 : 0.3 and 0.85 : 0.15 served as initial values for the calculations. In the overlapping of the curves a further asymmetry was established by changing the values of the x axis of the curve pairs, i.e. the rate of the reaction pairs in relation to one another, in speculative experiments (Figs 4-5). The course of the TG curve in Fig. 6 was originally asymmetrical. The curves in Figs 3-6 are original plots.

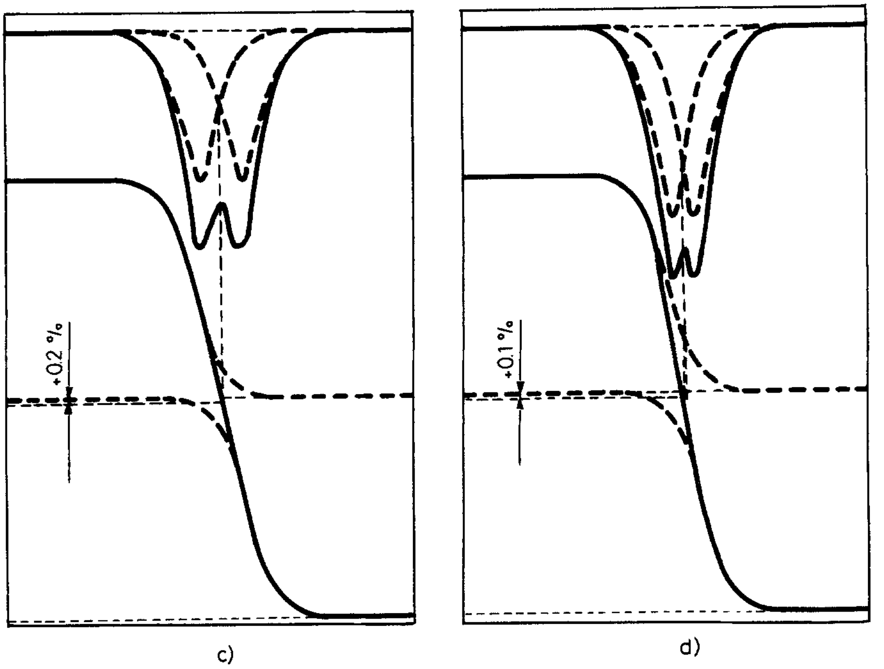


Fig. 3c, d Changes of the course of the TG and DTG curves and of the error of evaluation in the case of various overlapping of two congurent TG and DTG curves if extent and rate of weight change are identical

Discussion

From the results of the calculations shown in Figs 3-6 and Table 1 following conclusions can be drawn.

1. When the periods of acceleration and decay of the curves of two overlapping partial reactions are of symmetrical course, and these curves are also congruent, then the error of the suggested evaluation method is zero independently of the extent of overlapping (Fig. 3).

2. Even if the periods of acceleration and decay of the partial reactions are symmetrical but the two processes - due to different degree of asymmetry - are not congruent, (Figs 4 and 5) an error can be observed. The magnitude of the error increases

A./ with the extent of the overlapping (cases a, b, c, d in Figs 4-6).

B./ with the difference between the weight changes caused by the partial reactions, (cases A, B and C in Figs 4-6).

C./ with the difference between the rates of partial reactions (x axis of TG and DTG curves in Figs 4 and 5).

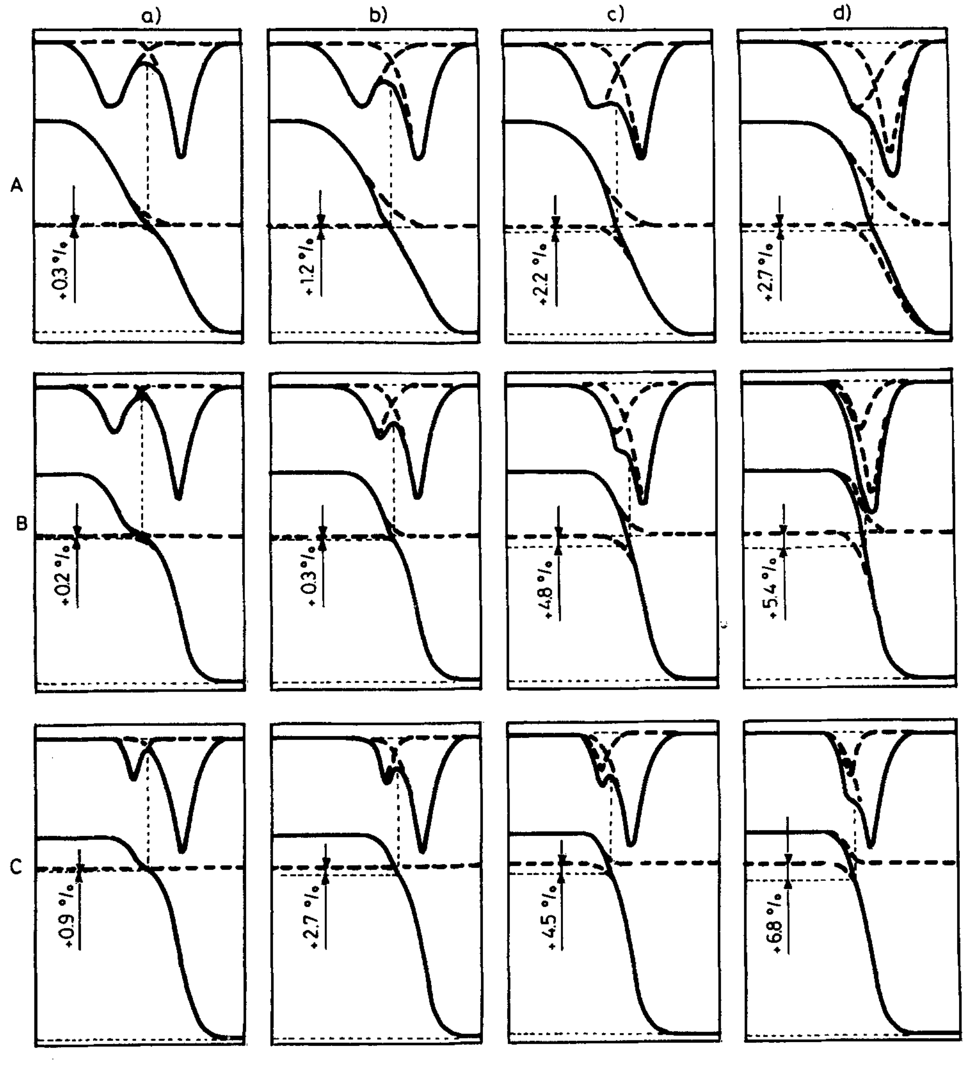


Fig. 4 Changes of the course of the TG and DTG curves and of the error of evaluation in the case of various overlapping of two TG and DTG curves of symmetrical course if extent and rate of weight change are different

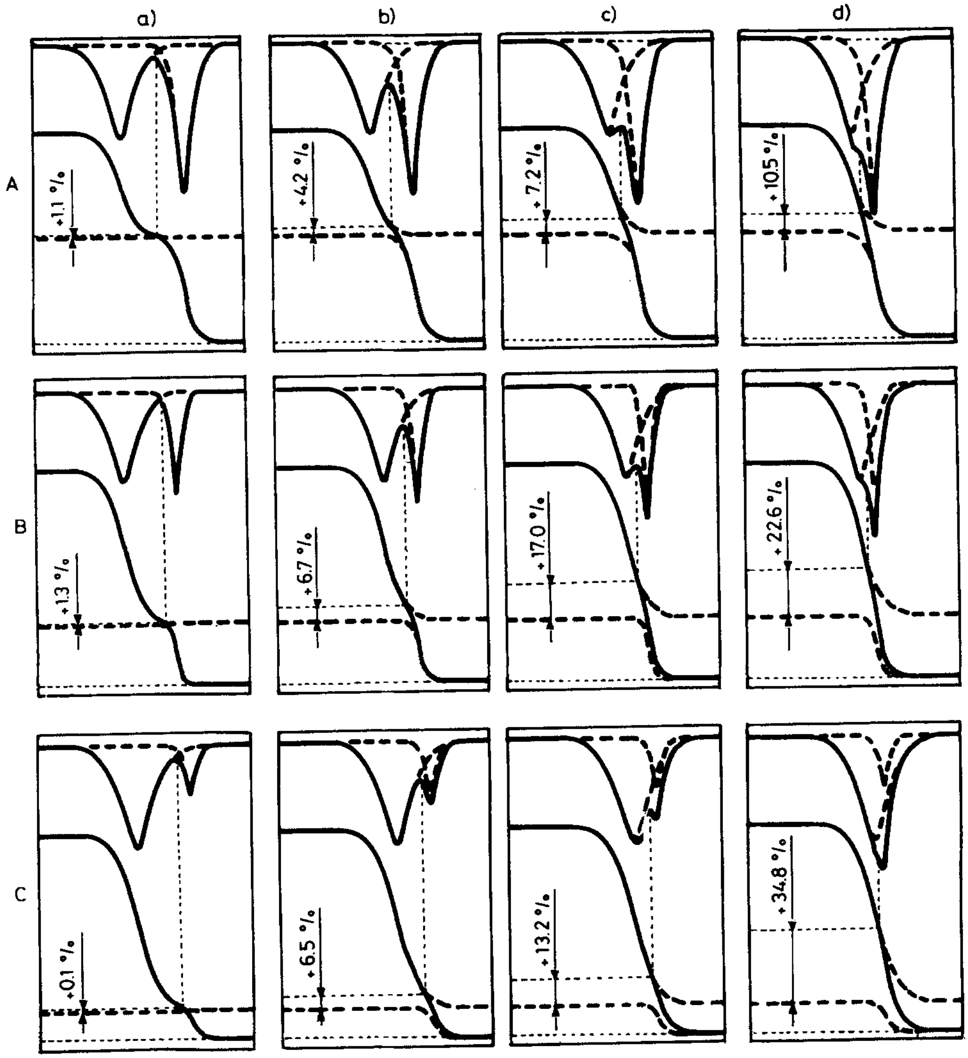


Fig. 5 Changes of the course of the TG and DTG curves and of the error of evaluation in the case of various overlapping of two TG and DTG curves of symmetrical course if extent and rate of weight change are different

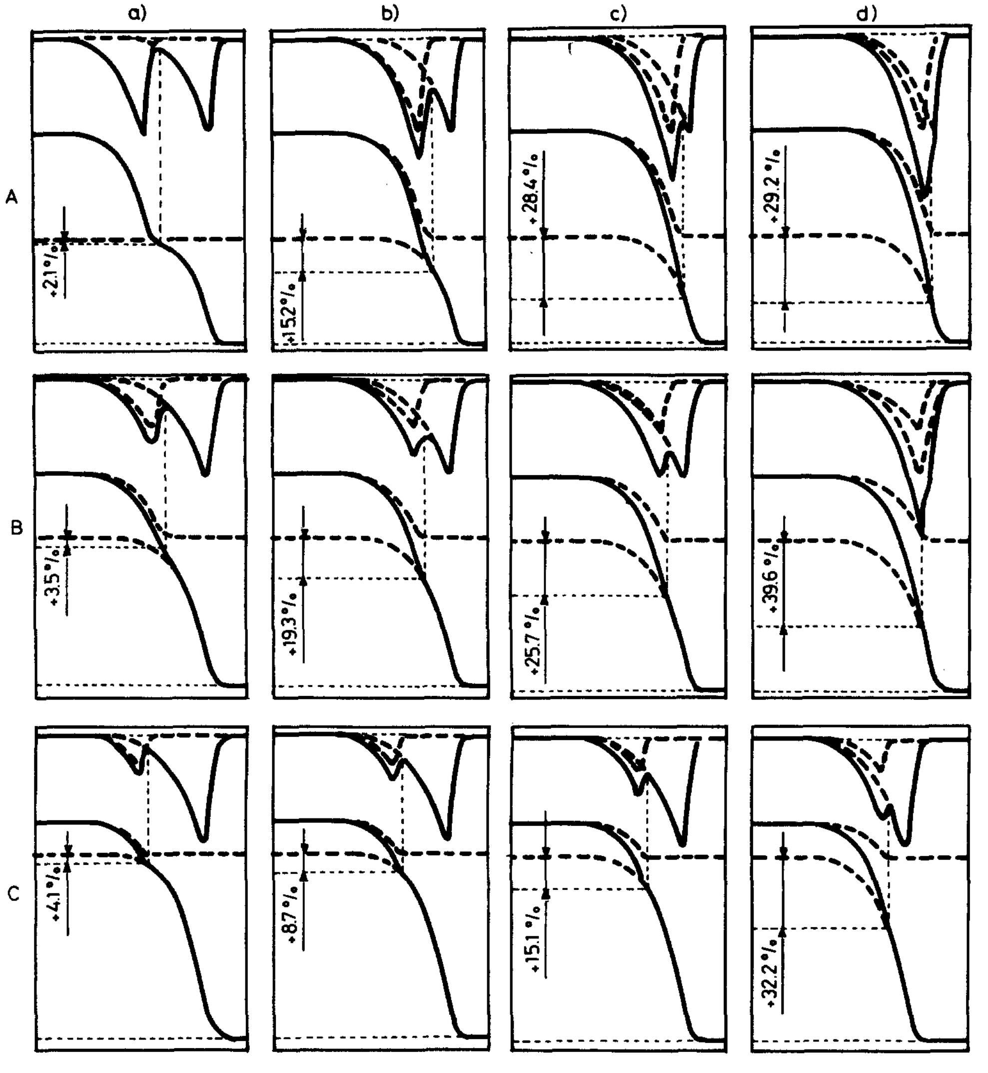


Fig. 6 Changes of the course of the TG and DTG curves and of the error of evaluation in the case of various overlapping of two TG and DTG curves of symmetrical course if extent of the weight change are different

3. The error increases significantly if the course of the partial reactions is itself asymmetrical (Fig. 6).

4. In every case the error increases the weight change of the reaction consistently accompanied originally by the smaller weight change. This circumstance offers a further possibility to decrease the error of the determination. First the magnitude of the weight change is estimated and thereafter according to the observed regularity the smaller weight change is decreased and the bigger one increased by a certain estimated value, by this correction the real value can be better approached.

5. It can be said in general that the real error of the determination is in every case smaller than it could be deduced from the shape of the resultant DTG curve. Accordingly, the appearance is less advantageous than the reality. This is proved by the TG and DTG curves in Fig. 1 since these are identical with the ones illustrated in B-a of Fig. 4 which demonstrates that the error was in the present case only ±4.8%.

Accordingly, it was proved that with the help of the suggested method the magnitude of the weight changes caused by overlapping reactions can be determined with a smaller error than with simple visual estimation which is the only alternative of the former one.

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Zusammenfassung — Auf computergestützte Art weisen die Autoren an einander überlagernden Reaktionen die Berechtigung der Anwendung der DTG-Kurven zur Erstellung von TG-Kurven nach.