THE SEPARATION OF ADDITIVELY OVERLAPPING TG STEPS BY NON-LINEAR OPTIMIZATION

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ABSTRACT

A method for the kinetic analysis of overlapping reactions is
described. Typical reactions of dehydration are used to demon-
strate the procedure.

INDRODUCTION

The experiences hitherto aquired in the kinetic analysis of non-
isothermal experiments show that the kinetic parameters obtained
by the known procedures in general do not describe the experimen-
tal curve in an optimum manner. In particular, this ist true of
overlapping reactions. The reasons for this are discussed and in-
vestigations have shown that the sources of errors can ɪartly be
eliminated /1/. By applying a non- linear optimization method to
TG and DTG data a better fit of .the theoretical conversion curve
to the experimental one could be abtained.

RESALTS AND DISCUSSION

Typical dehydration reactions characterized by a single reaction
step were studied to demonstrate this method with specially pre-
pared $Mg(OH)_2$ /3/, natural halloysite and chlorite, a four-sheet
silicate, having been used for the studies. These experiments were
carried out by the use of the Mettler thermoanalyzer TA 1. The re-
sults of the kinetic analysis in the evelution intervals cited are
shown in Table 1. The relative error of E ist found to be $\pm$ 5 %.
It can be seen that, indepently of the selected interval of the
conversion curve, constant parameters are obtained. This fact pro-
ves the reaction to be a single-step one. If overlapping occurs,
the parameters change by describing the conversion curve by inter-
vals. This is demonstrated, for example, with china clay (Table 2).

Table 1. Kinetic parameters for single-step reactions

Substance	Range (K)	Parameters		
		E (kJ/mol)	n	WL (%)
Mg(OH)$_2$	620 - 730	192,2	0,8	29,6
	640 - 730	191,8	0,8	29,6
	660 - 730	202,4	0,8	29,0
	680 - 730	202,6	0,8	29,7
	640 - 710	187,7	0,7	29,6
	660 - 710	199,9	0,8	29,0
Halloysite	700 - 860	146,3	0,6	11,7
	700 - 850	144,1	0,6	11,8
	720 - 850	145,6	0,6	11,8
	740 - 850	145,1	0,6	11,8
	760 - 850	148,3	0,6	11,8
Chlorite	800 - 1010	187,2	1,0	9,9
	850 - 990	178,7	1,0	9,8
	820 - 1010	185,5	1,1	9,9

Table 2. Kinetic parameters for various intervals of china clay

Range (K)	Parameters		
	E(kJ/mol)	n	WL (%)
750 - 835	176,2	1,2	10,6
750 - 845	179,1	1,4	10,5
760 - 845	176,4	1,3	10,6
770 - 845	171,3	1,2	10,8
750 - 855	178,8	1,4	10,7
750 - 865	179,7	1,4	10,5
750 - 870	181,8	1,4	10,4
750 - 890	193,9	1,7	11,3
750 - 900	198,2	1,8	11,5
750 - 910	204,5	2,0	12,6
750 - 920	216,9	2,2	12,7

The procedure as represented ist the prerequisite to the descrip-
tion of additively overlapping reactions. With carbon-containing
clay, as an example, two reaction steps are revealed by deter-
mining the kinetic parameters in intervals (Fig. 1). The step ob-
tained with the clay investigated in the range of 700 to 760 K
corresponds to the step of dehydroxylation of the kaolinite. The
content of double-sheet silicate in the clay can be determined
from the separated weight step with high accuracy. The reaction
step located in front of the dehydroxylation can be described in
an optimum manner by the use of the parameters cited, having to be
ascribed to the oxidation of the carbon contained in the clay
(humic acids). The reaction step in the final range corresponding
to the difference curve between the two calculated weight steps

and the experimental curve is caused by the dehydroxylation of non-distinguishable three-sheet clay minerals. Their content can be determined from the difference between the total weight loss and the calculated weight steps.
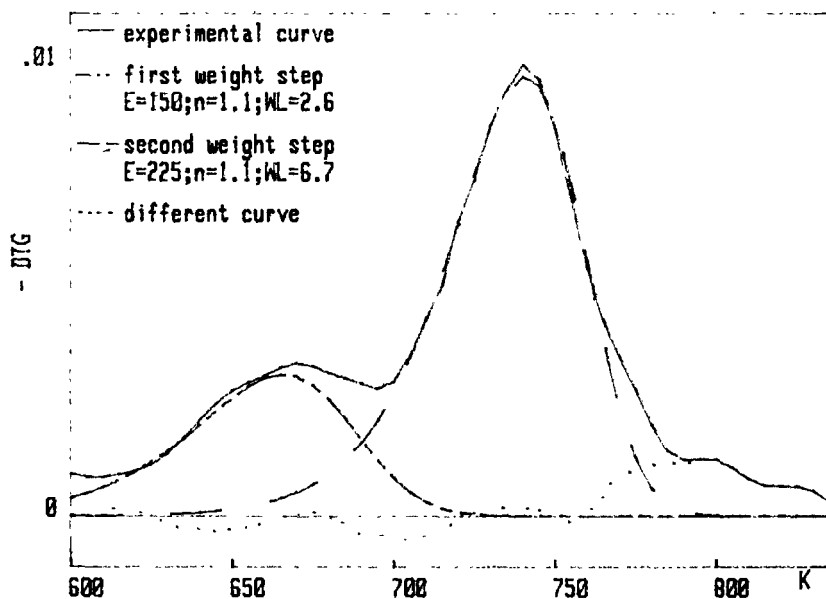

Fig.1. Model curve as calculated for carbon-containing clay

The investigation into the thermal decomposition of mixed carbo-nate $(CaCO_3 + SrCO_3)$ shows that two overlapping decomposition steps occur. The kinetic analysis gives the following result (Table 3).

For the first reaction step from 940 to 1050 K the kinetic para-meters remain constant as the evaluation interval varies. When the interval is extended up to higher temperatures, the effect of overlapping becomes evident from the variation of the parame-ters. By subtraction of the model curve (calculated with E = 205,7; n = 0,8) we obtain an overlapping-free second reaction step which, in turn, can be optimized similarly to a single-step reaction.

Table 3. Kinetic parameters of the decomposition of mixed
        carbonate

Range (K)	Parameters		
	E (kJ/mol)	n	WL (%)
940 – 1050	205,9	0,8	17,2
960 – 1050	205,0	0,8	17,2
980 – 1050	205,4	0,8	17,2
960 – 1060	217,2	0,9	17,0
960 – 1070	231,4	1,0	17,0
1140 – 1260	262,1	0,35	20,3
1170 – 1260	262,1	0,35	20,3
1120 – 1260	262,1	0,35	20,3

The thermal analysis of bauxite, in general, indicates several
overlapped dehydration steps of the hydrated oxides contained.
For the exemple studied we were able to describe two reaction
steps by kinetic analysis. The first (E = 286,2; n = 1,3; WL =
34,1 %) corresponds to the dehydration of hydrargillite, the
second (E = 175,0; n = 1,4; WL = 19,2 %) to that of alumogoethi-
te. For the identification by phase analysis one has to take in-
to consideration that the dehydration temperature is highly
affected by the degree of disorder of the hydroxides.

CONCLUSIONS

The results show the kinetic analysis of overlapping reaction
steps by non-linear optimization of the TG and DTG curves to be
possible. The prerequisite to the application of this method,
however, ist the existence of an overlapping-free partial interval
in at least one reaction step. From the partial weight losses ob-
tained quantitative statements as to the phase composition of
mineral mixtures can be made.

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