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A graphical method for the detection of the occurrence of thermal processes in mixed systems by means of derivatography

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Abstract

Thermal reactions between the different solid constituents in mixtures can be detected by graphical treatment of the derivatographic curves of the components in the isolated state and of the multi-component system. To solve this problem, the introduction of relative thermal curves (RTA), i.e. relative DTA (RDTA), relative DTG (RDTG) and relative TG (RTG), is proposed. Their construction and use are presented using the example of the thermal decomposition of mixtures of the crystallohydrates of copper nitrate (CNT) and chromium nitrate (CNN).

INTRODUCTION

Thermal analyses of two- and multi-component solid systems predominantly complicated thermal curves for several possible reasons including the formation of new compounds. Conventional classical interpretation of these curves and the detection of the temperature regions of new thermal effects often present difficult problems. For their solution in some oxide systems, the use of the derived derivative thermogravimetric curve (DDTG) has been suggested [1]. This curve was constructed from the TG measurements of the isolated components and their mixtures. The authors of this method have applied it again on several occasions [2–4].

The introduction of the DDTG curve for mixed systems is undoubtedly correct and is a novelty, but further comparison of this curve with the experimental DTA and DTG curves of the mixture is inconsistent, giving only an incomplete solution.

To eliminate these inconsistencies and limitations, the present author suggests the introduction of relative thermal analysis (RTA) for thermal research of mixed systems. Experimental analyses by this method are troublesome in practice, require the standard apparatus to be modified. The remedy is a simple graphical method employing standard derivatograms.

The proposed method consists of the detection of the ranges and directions of the deviations from the additivities of the thermal behaviour between the sum of the separate constituents and the behaviour of their mixture during an increase in the heating temperature.

Principle of the construction of the RTA curves

From the derivatographic measurements of the general mono- and 2-component system $(A + B)$, the following data are given

$$DTA_A = f_1(t) \qquad DTA_B = f_2(t) \qquad DTA_{AB} = f_3(t)$$

$$DTG_A = f_4(t) \qquad DTG_B = f_5(t) \qquad DTG_{AB} = f_6(t)$$

$$TG_A = f_7(t) \qquad TG_B = f_8(t) \qquad TG_{AB} = f_9(t)$$

Plotting the RTA curves of a mixture of a binary $(A + B)$ system requires graphical addition of the functions $(f_1 + f_2)$, $(f_4 + f_5)$ and $(f_7 + f_8)$ and, subsequently, a graphical subtracting of these summary curves from the experimental derivatographic curves for the mixture of $(A + B)$

$$RDTA_{AB} = DTA_{AB} - (DTA_A + DTA_B) = f_3(t) - [f_1(t) + f_2(t)] = f_{10}(t)$$

$$RDTG_{AB} = DTG_{AB} - (DTG_A + DTG_B) = f_6(t) - [f_4(t) + f_5(t)] = f_{11}(t)$$

$$RTG_{AB} = TG_{AB} - (TG_A + TG_B) = f_9(t) - [f_7(t) + f_8(t)] = f_{12}(t)$$

For these resulting thermal curves, the designations RDTA, RDTG and RTG are proposed, where R indicates relative. The RTG is evidently equivalent to DDTG, as proposed previously [1].

The graphical procedure for the construction of the RTA curves includes copying the relevant thermal curves from derivatograms of individual constituents, as well as that of their mixture, e.g. the DTA curves, onto separate scale tracing papers with exact maintenance of the same position of the T curve (in slope and in scale), and then measuring the distances of all the points on these curves from the arbitrarily accepted horizontal reference lines. Later, these distances are added (or subtracted) graphically using compasses in order to obtain the resulting summary or difference curves.

General characteristics of the proposed RTA

When the values of the functions f_{10}, f_{11} and f_{12} are equal to zero, in these temperature ranges their plot gives a horizontal line. In these cases, the composite behaves as a simple mixture of the components and the decomposition of either of these is not affected by the presence of the other.

The presence of positive or negative peaks on the plot of the RTA curves indicates additional thermal activities or the absence of the expected activity and may be related to different physical or chemical conversions. Hence, the

RDTA curve indicates the nature, magnitude and temperature range of the thermal processes which occur during contact between the components (and also under influence of the atmosphere) during the thermal treatment. The type of phases formed may be identified by means of additional analytical techniques (XRD, IR spectrometry, etc.).

To verify the conclusions drawn from the RDTA curves, application of the RDTG technique is certainly helpful. The RDTG curve will also identify processes of disintegration (as mass losses) or of interaction with the surrounding atmosphere (as mass gains). The absence of peaks on the RDTG curves in the presence of thermal effects on the RDTA curves indicates the existence of physical processes, such as phase (e.g. melting) or polymorphic conversion of the intercomponent compounds formed in the system. Hence, direct comparison of the RDTA and RDTG curves of the given system is most informative.

The practical application of the proposed RTA method is quite simple but requires high precision in the control of the temperature rise to maintain a valid comparison of all the curves, because all deviations from linearity in temperature rise may cause the appearance of apparent effects during addition or subtraction of the compared curves.

Examples of applications

Detailed presentation of the construction of the RTA curves and the possibilities of their interpretation are discussed using the example of a mixed system of the crystallohydrates of $Cu(NO_3)_2 \cdot 3H_2O$ (CNT) and $Cr(NO_3)_3 \cdot 9H_2O$ (CNN) in molar ratios of (1:2) and (1:1). These mixtures were chosen to demonstrate the applicability of the proposed method because of the low melting point of the nitrates used and the resulting homogeneous mixtures of components obtained before the start of the decomposition.

EXPERIMENTAL

Samples and their thermal analysis

The following samples were investigated: CNT Analar grade (POCh, Gliwice, Poland), CNN Analar grade (POCh, Gliwice, Poland), equimolar mixture of CNT and CNN, and a mixture of CNT and CNN in the molar ratio (1:2).

The thermal behaviour of the samples was studied with an automatic Paulik–Paulik–Erdey derivatograph, manufactured by MOM (Budapest, Hungary). The following conditions were used: sample size, 0.1–0.5 g; reference material, α-Al_2O_3 (calcined at 1500°C); sample holder, Pt crucible placed on a thermocouple rod; thermocouple, Pt/Pt–Rh; linear heating rate, 10°C min^{-1}; temperature range, 20–900°C; atmosphere, static air.

Weighed portions of CNT and CNN in the case of the single systems were the same as the quantities of the components in each mixture, which enabled verification of the additivity without additional calculations. The experimental measurements were limited to 3 derivatograms for each run. Two programmed runs enabled the influence of the quantitative composition of the mixture on the course of the RTA of the system studied to be deduced.

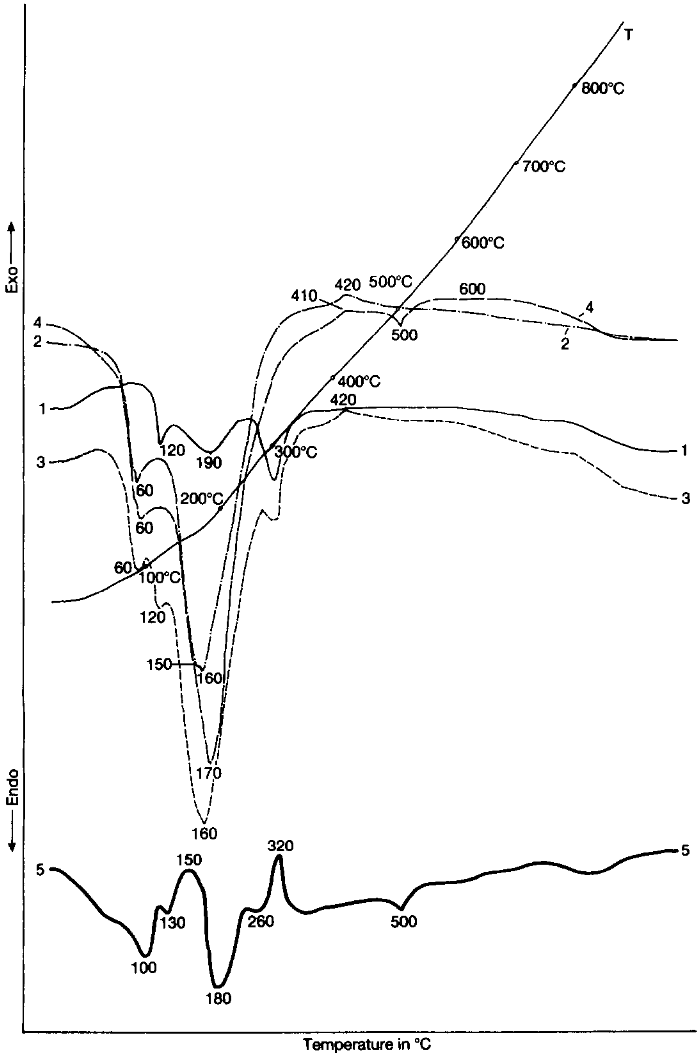

Fig. 1. Construction of the RDTA curve for CNT–CNN mixture (molar ratio 1:2). Description of the curves: 1, DTA curve of CNT; 2, DTG curve of CNN; 3, graphical sum of curves 1 and 2; 4, DTA curve of (1:2) molar CNT–CNN mixture; 5, RDTA curve, as the graphical difference between curves 4 and 3.

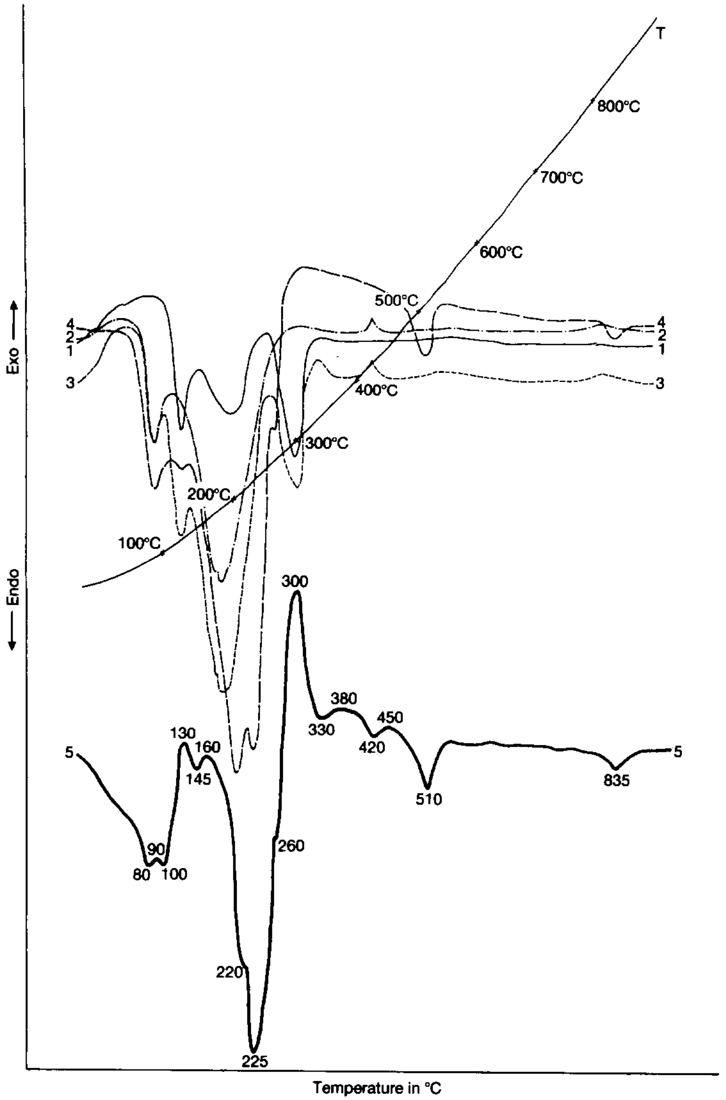

Fig. 2. Construction of the RDTA curve for CNT–CNN mixture (molar ratio 1:1). The curves are analogous to those in Fig. 1.

RESULTS

DTA curves obtained from derivatograms of single components and from their mixtures in different ratios are presented in Figs. 1 and 2, and the corresponding DTG curves are shown in Figs. 3 and 4. For both compositions in question, the DTA and DTG curves of single components are summed graphically, thus yielding two theoretical curves presenting the additivity in thermal behaviour of each component (curves 3 on Figs. 1–4).

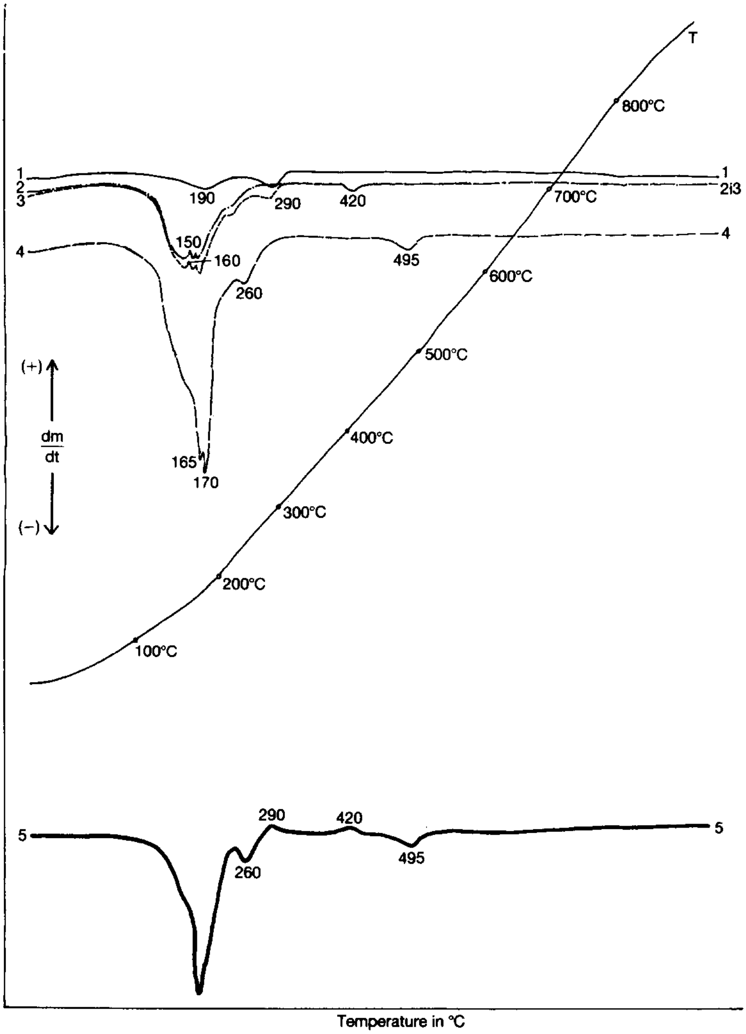

Fig. 3. Construction of the RDTG curve for CNT–CNN mixture (molar ratio 1:2). Description of the curves: 1, DTG curve of CNT; 2, DTG curve of CNN; 3, graphical sum of curves 1 and 2; 4, DTG curve of (1:2) molar CNT–CNN mixture; 5, RDTG curve, as the graphical difference between curves 4 and 3.

Subsequently, these summary curves are subtracted graphically from the experimental DTA and DTG curves for the particular mixtures of the components (curves 4 on Figs. 1–4). In this way we obtain the relative thermal curves RDTA and RDTG for both compositions investigated (curves 5 on the Figs. 1–4).

The RTG curves were obtained in a similar way. Because the RTG curves are not as clear as those described here for RDTG, they have not been shown on the figures and have not been considered in the discussion.

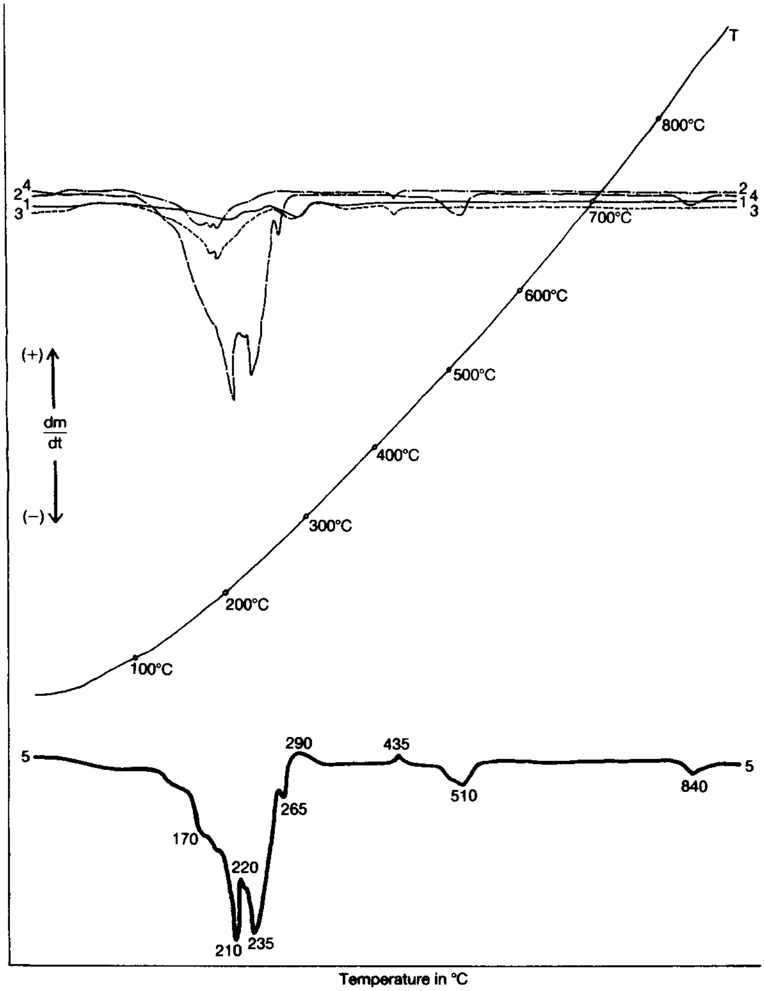

Fig. 4. Construction of the RDTG curve for CNT–CNN mixture (molar ratio 1:1). The curves are analogous to those in Fig. 3.

A direct comparison of the RDTA and RDTG curves for CNT–CNN systems investigated are presented in Figs. 5 and 6.

Conclusions from the results of RTA in CNT–CNN systems

From the shape of the RTA curves obtained, it is apparent that additional endothermic effects in the mixtures studied in the range 80–100°C are not connected with mass losses. They can probably be associated with the melting process of the new phases arising in the mixtures from the components at lower temperatures and referred to as "parent phases" [5, 6]. Such a melt may subsequently decompose with evolution of gaseous products at

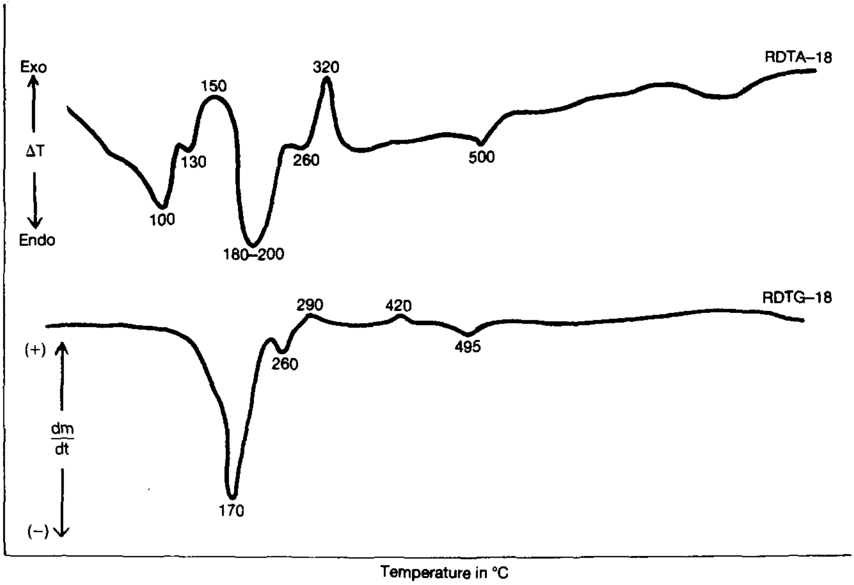

Fig. 5. Comparison of the RDTA and RDTG curves for (1:2) molar CNT-CNN mixture.

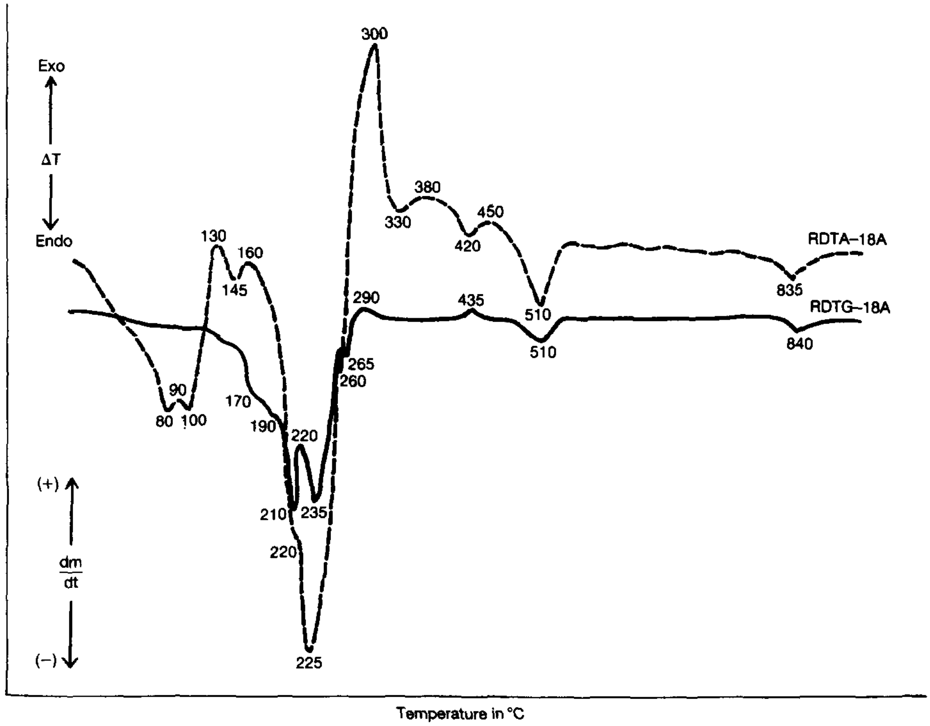

Fig. 6. Comparison of the RDTA and RDTG curves for (1:1) molar CNT-CNN mixture.

the temperatures 130, 145 and 170–235°C. The other endothermic effects registered on the RDTA curves at higher temperatures are, as a rule, accompanied by negative peaks on the RDTG curves, confirming the decomposition of the intermediate products created during the temperature increase (in ranges 260–265, 495–510 and 835–840°C).

The maxima on the RDTA curves at 300–320 and 450°C are accompanied by small positive peaks on the RDTG curves at 290 and 435°C, which suggest the participation of atmospheric oxygen in the processes occurring in these temperature ranges.

Exceptional cases are the two endothermic peaks at 330 and 420°C and the two exothermic effects at 380 and 450°C, as well as the broad exothermic hump between 560 and 800°C, all without weight changes on the RDTG curves. These cases may be due to phase transitions or other transformations.

Finally, comparison of the RTA curves in Figs. 5 and 6 indicates that the mixture of 1:2 molar composition is thermally more stable than that derived from the 1:1 system. In the latter, there is an additional endothermic process between 835 and 840°C, connected with the evolution of gaseous decomposition products (mass loss at 840°C).

However, it is clear that a detailed interpretation of the conversion which nitrate mixtures undergo during rising temperature conditions, requires, in addition to RTA, the application of further analytical techniques for identification of the particular decomposition products. This will be the subject of a future publication in the framework of the present investigation.

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