Laboratory and computing methods

MODIFIED STA-409/3/6 THERMOBALANCE FOR DIGITAL PROCESSING OF T, DTA AND TG CURVES

ŠTEFAN SVETÍK, PETER KOTTÁŠ

Faculty of Chemical Technology, Slovak Technical University, Radlinského 9, 812 37 Bratislava

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The authors modified the STA-409/3/6 thermobalance by replacing the sample carrier for thermogravimetric analysis (TG) by that for combined thermogravimetric and differential thermal analysis (DTA), containing PtRh10-Pt thermocouples (commercial product). The PMD-85 microcomputer, which is currently available on the market, was used in experimental data acquisition curve data was written in the Basic language, together with programs for computing the activation energy E, the frequency factor Z and the reaction order n, which consider the various formal mechanisms of thermal decomposition of solids by the non-isothermic method on the basis of the thermogravimetric curves.

INTRODUCTION

In view of the fact that e.g. conversions of polymorphous modifications or melting of substances do not involve any changes in weight but on the other hand the TG records of heterogeneous reactions involving liberation or absorption of gaseous substances can be evaluated efficiently and precisely providing quantitative data, it is very advantageous to record DTA, TG and possibly also DTG curves at the same time, thus simplifying the problems connected with the interpretation of thermal transformations of the substances being investigated [1].

Together with the other thermoanalytical methods, thermogravimetry and differential thermal analysis belong to a group of methods allowing the basic kinetic constants of reactions to be derived, namely the rate constant, the activation energy, the order of the reaction and its frequency factor [2, 3].

Concluded thermal analysis usually yields its results in the form of a diagram; however, the mathematical description of the relationship is unknown, as is a detailed interpretation of the results from the physical point of view. The experimentator's experience is satisfactory for an orientation assessment of the measurement. Computer processing of the measuring results represents a significant improvement of the evaluation process. Recently, a great deal of attention has been paid to on-line linking of thermoanalytical instruments with computers. The linking being described below is of the passive type, the computer carrying out data acquisition and processing.

CHARACTERISTICS OF THE APPARATUS AND THEIR INTERCONNECTING

The thyristor temperature controller (type 411, Netzsch) is essentially a proportional controller regulated by the input voltage signal provided by a thermoelectric cell attached to the outer side of the furnace winding.

The thermobalance (type STA-409, Netzsch) allows the measurements to be carried out over the temperature range of 0 to 1000 °C. The modification of the thermobalance consisted of replacing the TG sample carrier by that intended for TG and DTA measurements, fitted with PtRh10-Pt thermocouples measuring the temperature and the temperature difference between the sample and the inert standard material. The thermobalance produces analog signals of T, DTA and TG, all within the range of ± 15 mV.

The channel switch (of original design) contains four relay switches which, on command from the microcomputer, connects the T, DTA, TG and 0 mV signals (the last ones for voltmeter calibration) to the input of the digital voltmeter.

The digital voltmeter (type MT-100, Metra Blansko) operates as a ± 14-bit A/D converter. The measuring range chosen, 15 mV, provides a sensitivity of about 1 μV.

The microcomputer (type PMD-85, Tesla Bratislava) is a standard 8-bit microcomputer. It is used to acquisit, process and evaluate the measuring data. Its peripheries include a printer (type K-6314, Robotron), as a recording output device, and a floppy disk unit as a data storage medium. Fig. 1. shows a block diagram of functional interconnection between the devices employed.

Fig. 1. Block diagram of the instrument configuration

SOFTWARE

Two program modules were worked out, one for data acquisition from the measuring apparatus and the processing of T, DTA and TG curves, and the other for the evaluation of kinetic constants of the processes involved in thermal decomposition of the respective solids.

The program for data acquisition and processing of T, DTA and TG curves was written in the BASIC/G language, the periphery control subprograms are in the instruction code. The program consists of individual moduli allowing further expansion and makes use of the window technique for the selection of commands and setting of parameters. In its present form, the program controls the following operations:

— the setting of measuring parameters (name of sample, its weight, room temperature, heating rate, measuring temperature interval, DTA scale, TG scale, time of sampling);
— the measurement proper. According to the parameters set in advance, the individual points on the *T*, DTA and TG curves are alternately scanned. Following their measurement, the experimental points are stored and plotted on the display;
— processing of the experimental curves. The curves can be redrawn in any required scales for T, DTA and TG. The graphic cursor can be shifted along the entire curve while displaying the actual values of T, DTA and TG. The graphic plot of the experimental data is supplemented with informative texts specifying the position and deviation of the curves from the zero line;
— the plotted curves are transmitted to the printer as a hard copy of the display screen;
— the data from the curves are entered onto the floppy disk and reread for storage.

The program for the determination of kinetic parameters by means of non-isothermal thermogravimetry is written in the BASIC/G language. It is again in modular form and at present is capable of performing the following functions:

— reading of experimental data from the floppy disk;
— selection of the kinetic equation according to which the experimental data is to be processed; the choice comprises ten equations [4];
— calculation of the activation energy, frequency factor, the order of the reaction, the correlation coefficient of Arrhenius relationship;
— graphic representation of the calculated relationships;
— alphanumerical and graphic printing of the results.

RESULTS AND DISCUSSION

To verify the function of the experimental configuration, analyses were made of calcium oxalate and magnesium hydroxide. The experimental measurements were carried out at heating rates of 5, 10 and 20 °C min^{-1} in air atmosphere; the sample weight did not exceed 40 mg. The various heating rates were used to establish their effect on the course of thermal decomposition and to determine the order of the reaction by Kissinger's method [5]. Figs. 2 and 3. show the courses of thermal analysis of $Mg(OH)_2$ and $CaC_2O_4 . H_2O$ as an example of the output obtained from the modified STA-409 apparatus.

The values of the order of the reactions obtained from the DTA curves, and those of activation energy and the frequency factor from the TG curve for the thermal decomposition of $CaC_2O_4 . H_2O$ and $Mg(OH)_2$ (Fig. 4 and Table I) are in a very satisfactory agreement with the literary data (Table II).

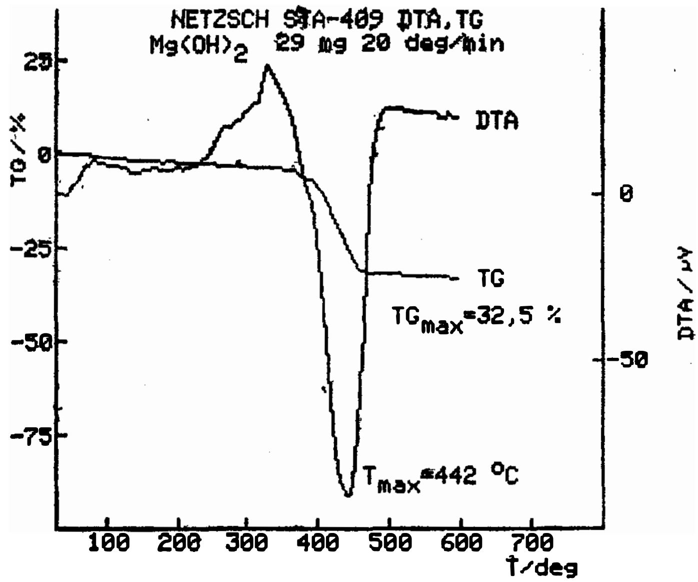

Fig. 2. The results of thermal analysis of $Mg(OH)_2$ *as an output of the STA-409 instrument configuration*

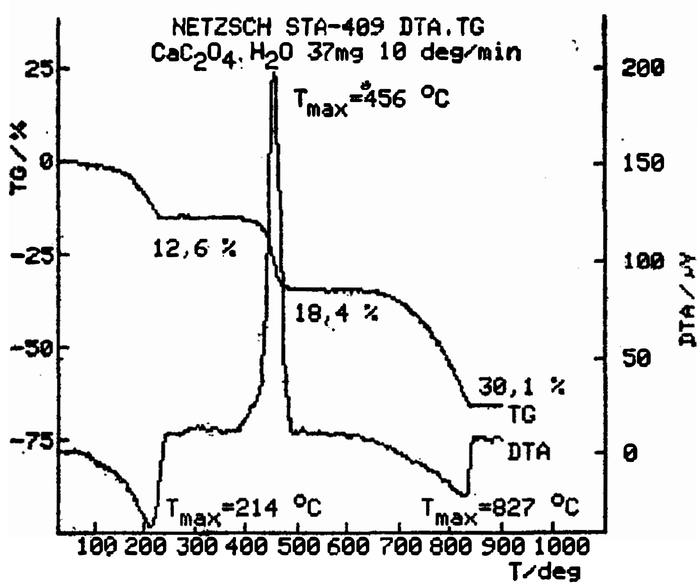

Fig. 3. The results of thermal analysis of $CaC_2O_4 . H_2O$ *as an output of the STA-409 instrument configuration.*

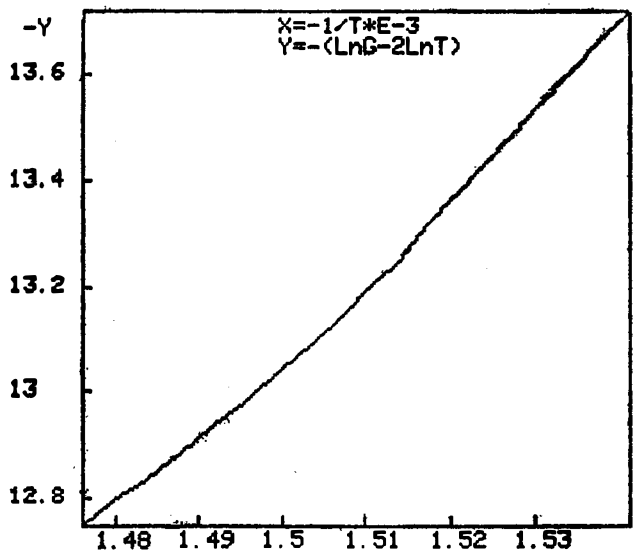

Fig. 4. The results of thermogravimetric analysis of $Mg(OH)_2$ *under non-isothermal conditions of heating at a rate of 5 °C min⁻¹ calculated by means of Kröger—Ziegler's equation for the 30 to 80 % conversion interval.*

Table I

An example of of the values determined for the reaction order, the activation energy and the frequency factor of thermal decomposition of $CaC_2O_4 . H_2O$ and $Mg(OH)_2$

Thermal decomposition process	Temperature interval [°C]	*n*	*E* [kJ mol⁻¹]	ln *A*
$CaC_2O_4 . H_2O = CaC_2O_4 + H_2O$	164—205	0.35	71	16.29
$CaC_2O_4 = CaCO_3 + CO$	435—443	0.60	215	33.63
$CaCO_3 = CaO + CO_2$	733—772	0.61	231	25.59
$Mg(OH)_2 = MgO + H_2O$	385—394	0.63	117	20.29

Table II

Thermal decomposition of $Mg(OH)_2$ and $CaC_2O_4 . H_2O$ — literary data

Sample	Method	Author	Determined			ref.
			n	*E* [kJ mol⁻¹]	ln *A*	
$Mg(OH)_2$	DTA	Kissinger	0.44	131	15.18	[6]
$Mg(OH)_2$	TG	Gregg	0.66	114	13.26	[7]
$Mg(OH)_2$	DTA	Koishi	0.99	105	15.84	[7]
I. $CaC_2O_4 . H_2O$	DSC	Balek	0.34	82	17.64	[8]
II. $CaC_2O_4 . H_2O$	DSC	Balek	0.58	206	27.11	[8]
III. $CaC_2O_4 . H_2O$	DSC	Balek	0.59	239	23.36	[8]

The dispersion of the published values of activation energy established by the TG method as compared to those calculated from the DTA curves of the experimental samples can be associated with experimental arrangement, the sample weight, the heating rate, the choice of static or dynamic furnace atmosphere and its composition.

It may be concluded that the modified configuration of instruments allows the results of TG and DTA, obtained simultaneously under identical conditions, to be evaluated in a complex manner. Its use is recommended primarily for orientation assessment of the processes involved in thermal decomposition of solids and materials, as well as for approximate calculation of the kinetic parameters of these processes.

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UPRAVENÉ TERMOVÁHY STA-409/3/6 PRE DIGITÁLNE SPRACOVANIE T, DTA A TG KRIVIEK

Štefan Svetík, Peter Kottáš

Chemickotechnologická fakulta SVŠT, Radlinského 9, 812 37 Bratislava

Na termováhach STA-409/3/6 firmy Netzsch sme vykonali úpravu, ktorá spočívala vo výmene nosiča vzorky pre termogravimetrickú analýzu (TG) za nosič vzorky pre kombináciu termogravimetrickej a diferenčnej termickej analýzy (DTA) s termoelektrickými článkami PtRh10-Pt (firemný výrobok). Na zber a spracovanie údajov z experimentu sa využil bežne dostupný mikropočítač PMD-85.

Upravená prístrojová zostava umožňuje komplexné spracovanie výsledkov TG a DTA, získaných simultánne za rovnakých podmienok. Doporučuje sa predovšetkým pre orientačné hodnotenie mechanizmov procesov tepelného rozkladu tuhých látok a materiálov, ale aj k orientačnému výpočtu kinetických parametrov týchto procesov.

V jazyku Basic sme vypracovali výpočtové programy na určenie aktivačnej energie E, frekvenčného faktora Z a poriadku reakcie n, uvažujúce rôzne teoretické formálne mechanizmy tepelného rozkladu tuhých látok.

Na overenie funkcie prístrojovej zostavy a programov na výpočet kinetickych konštánt sme použili $CaC_2O_4 . H_2O$ a $Mg(OH)_2$.

Obr. 1. Bloková schéma prístrojovej zostavy.

Obr. 2. Výsledky termickej analýzy $Mg(OH)_2$ *ako výstupu z upravenej prístrojovej zostavy STA-409.*

Obr. 3. Výsledky termickej analýzy $CaC_2O_4 . H_2O$ *ako výstup z upravenej prístrojovej zostavy STA-409.*

Obr. 4. Výsledky termogravimetrickej analýzy termického rozkladu $Mg(OH)_2$ *v neizotermických podmienkach ohrevu 5 °C . min*$^{-1}$ *počítané pomocou rovnice Krögerovej—Zieglerovej pre interval konverzie 30—80 %.*

Modified STA-409/3/6 Thermobalance for Digital Processing of T, DTA and TG Curves

ТЕРМОВЕСЫ STA-409/3/6, ПРИСПОСОБЛЕННЫЕ ДЛЯ ОБРАБОТКИ T, DTA И TG КРИВЫХ

Штефан Светик, Петер Котташ

Словацкий политехнический институт, химико-технологический факультет, Радлинского 9, 812 37 Братислава

На термовесах STA-409/3/6 фирмы Netzsch провели приспособление, заключающееся в замене иосителя пробы для термогравиметрического анализа (TG) носителем для комбинации термогравиметрического и дифференциального термического анализа (DTA) с термоэлектрическими парами PtRh 10-Pt (изделие фирмы). Для отбора и обработки экспериментальных данных использовали доступный в продаже микровычислитель PMD-85.

Приспособленный прибор дает возможъость комплексной обработки результатов TG и DTA, нолученных одновременно при одинаковых условиях. Рекомендуется его использование прежде всего для ориентационной оценки механизмов процессов термического разложения твердых веществ и материалов и для ориентационного расчета кинетических параметров данных процессов.

На языке Basic разработали программы расчетов, предназначенных для определения энергии активации E, фактора частотности $З$ и порядка реакции n, учитывая разные теоретические формальные механизмы термического разпожения твердых веществ.

Для проверки работы сопряжения приборов и программ, предназначенных для расчета кинетических констант использовали $CaC_2O_4 . H_2O$ и $Mg(OH)_2$.

Рис. 1. Блок-схема сопряжения приборов.

Рис. 2. Результаты термического анализа $Mg(OH)_2$ *в виде выхода из сопряжения приборов* STA-409.

Рис. 3. Результаты термического анализа $CaC_2O_4 . H_2O$ *в виде выхода из сопряжения приборов* STA-409.

Рис. 4. Результаты термогрависметрического анализа термического разложения $Mg(OH)_2$ *при неизотермических условиях нагрева* $5°$ *C . мин .* $^{-1}$, *расчитанные с помощью уравнения Крегеровой-Зиглеровой при интервале конверсии 30—80 %.*