Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

INVESTIGATION OF THE THERMAL DECOMPOSITION OF CALCIUM CARBONATE BY SIMULTANEOUS EMANATION THERMAL ANALYSIS, DIFFERENTIAL THERMAL ANALYSIS AND EVOLVED GAS DETECTION

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(Received February 1st, 1972)

ABSTRACT

An apparatus allowing simultaneous emanation thermal analysis (ETA), differential thermal analysis (DTA) and evolved gas detection (EGD) is described and its use is demonstrated on the study of the thermal decomposition of calcium carbonate.

INTRODUCTION

Together with the still spreading use of the common methods of thermal analysis (as DTA and TG), a trend towards simultaneous analysis of one sample in a single apparatus by several thermoanalytical methods has appeared, in order to allow a more unambiguous interpretation of the results. For our purpose a commercially available DTA apparatus was adapted for the simultaneous performance of ETA, DTA, and EGD. As the detectors for both ETA and EGD are not in direct contact with the sample in the furnace, but only with the gas stream coming out from the apparatus, a combination of these methods with DTA is easily performed.

The emanation thermal analysis (ETA), based on the measurement of the release of radioactive emanation, formed from radioactive isotopes previously incorporated in solids, found an advantageous application in the study of solids[1-3]. The inert radioactive gas (emanation) formed in the substance studied as a result of the radioactive disintegration of the parent isotopes of the emanation (^{228}Th or ^{224}Ra) does not react with the substance. The emanation is released from the crystal lattice as a result of physico-chemical processes only, which take place in the substance. The ETA* indicates continuously various types of processes related to changes of the magnitude of the sample surface or of conditions for diffusion of the inert gas in the solid.

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*We suggest the use of the abbreviation ETA for the method in question, in spite of the fact that this abbreviation has already been used for "electrothermal analysis". In our opinion the latter should be more precisely called "electroconductivity thermal analysis" (ECTA).

Gases envolved from the sample during its thermal treatment may be the object of both qualitative and quantitative analysis (EGA); as in our case a single parameter (thermal conductivity) characterizing the composition of the effluent gas stream was recorded without an analytical calibration, we speak about evolved gas detection (EGD).

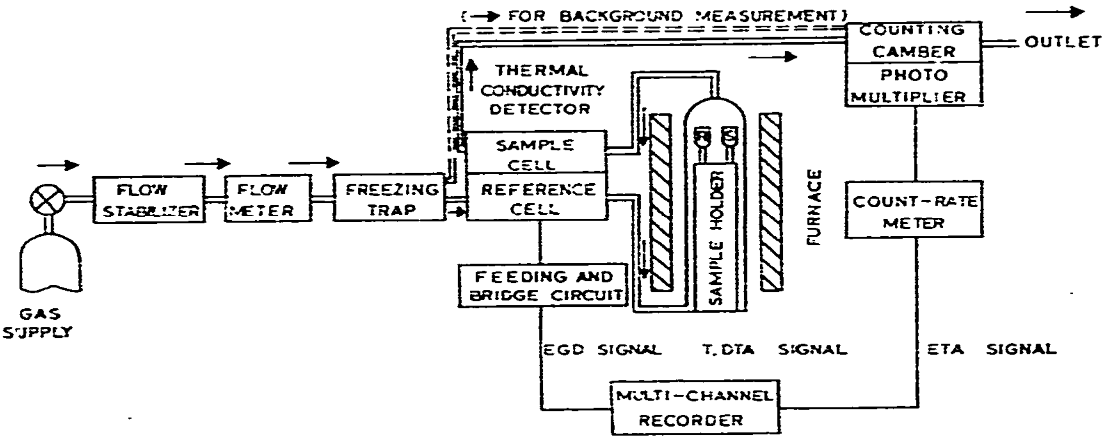

Fig. 1. Schematic diagram of the equipment for simultaneous ETA, DTA and EGD.

EXPERIMENTAL

The equipment was constructed by adapting a commercial DTA apparatus (the high-temperature model of Netzsch–Gerätebau) with a gas flow sample holder (model DDK). The schematic diagram of the equipment is given in Fig. 1.

The thermal analysis of the sample is performed in a gas stream, which serves as a gaseous medium and as carrier gas for the emanation and other gaseous products released from the sample during its thermal treatment. The flow rate of the gas is controlled by a flow stabilizer and measured. After passing a freezing trap with solid CO_2 and the reference cell of the thermal conductivity detector, the gas enters the tube of the sample holder at its bottom and passes in an ascendant flow in the proximity of the platinum crucibles with the sample (S in Fig. 1) and the reference substance (R) (silicium carbide). The gaseous products and the emanation released from the sample are carried by the gas stream first into the sample cell of the thermal conductivity detector, then into the α-counting chamber, which is connected with a photomultiplier (Tesla) and a count-rate meter (Vakutronik), and finally to the outlet. For measurements of the radioactive background before and after each analysis the equipment is provided with a by-pass leading the carrier gas directly into the α-counting chamber.

The signals from the bridge circuit of the thermal conductivity detector, the DTA apparatus ($T,\Delta T$) and the ETA device are simultaneously registered by the adapted multi-channel recorder of the DTA apparatus.

The following experimental conditions were used:
sample weight, 100 mg; carrier gas, air; gas flow rate, 60 ml/min; heating rate, 5°/min.

The ETA curves express the relative emanation power, E, in counts per min as a function of the temperature, t (see Fig. 2).

The DTA curves were presented in the following way: ΔT was given as the thermoelectric force (in μV) of the Pt–PtRh differential thermocouple, the maxima and minima on the curve corresponding to the exo- and endothermic effects, respectively.

The EGD curves indicate the difference between the thermal conductivities of the entering carrier gas and the effluent gas stream (carrier gas + evolved gases) as the recorder response (in μV) as a function of the temperature. Maxima and minima on the curve correspond to the evolution of gases with higher and lower thermal conductivity, respectively.

The incorporation of a source of radioactive emanation ^{220}Rn was performed by the impregnation of the sample with an alcoholic solution of ^{228}Th (as the chloride); the specific activity of the labelled sample was 0.1 mCi/g. This method is convenient for minerals, commercial reagents and other samples which cannot be labelled during their preparation.

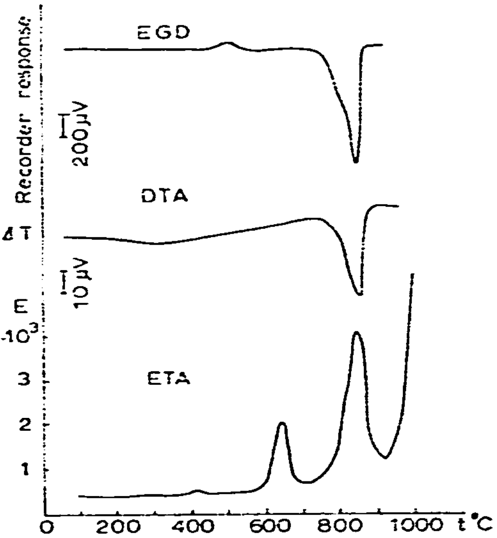

Fig. 2. ETA, DTA and EGD heating curves of $CaCO_3$.

RESULTS AND DISCUSSION

The ETA, DTA and EGD heating curves of $CaCO_3$ (calcite) in air are given in Fig. 2. The small effect on the ETA curve at about 400 °C is caused by the dehydration of $Ca(OH)_2$ formed on the surface of the sample[4]. The corresponding effect on the EGD curve is delayed and broadened because of water condensation in the apparatus.

No dehydration effect was observed in samples previously decomposed to CaO by heating at 1000°C, and cooled in a stream of dry nitrogen. When such samples of CaO were left in air for 24 h, the same effect could be observed again. This shows the applicability of the method for the detection of traces of humidity in CaO.

The sharp maximum at 640°C on the ETA curve indicates a thermochemically irreversible process; this maximum is not observed on the ETA curve of a $CaCO_3$ sample previously heated to 700°C. The effect may be caused, for example, by sintering of the originally extremely-dispersed powder (grains of 10 μ in diameter).

The dissociation of $CaCO_3$ is distinctly indicated on all three curves. The temperature of the dissociation of calcite varies, according to the literature, between 800 and 915°C, being largely dependent on the heating rate[5,6]. The rise of the ETA curve above 900°C is caused by Rn diffusion in the sample.

CONCLUSIONS

It has been shown that it is useful to combine various experimental techniques of thermal analysis in one equipment; the simultaneous performance of ETA, DTA and EGD on one sample gives more-complete information about the processes taking place in the sample during its thermal treatment.

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