THE BED-DEPTH EFFECT IN THE THERMAL DECOMPOSITION OF CARBONATES

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The effect of sample mass, heating rate and partial pressure of carbon dioxide on TG, DTG and DTA curves for the decomposition of some common carbonates has been investigated. These variables gave a marked effect, similar in magnitude for both DTG and DTA. The effect of sample mass, or depth of undiluted sample, is shown to be due to an increase in the partial pressure of carbon dioxide within the reacting powder. This effect is most pronounced in nitrogen but is much reduced in carbon dioxide. Inert diluents have little effect on the curves since they do not increase the partial pressure of CO\textsubscript{2}. The first stage of the decomposition of dolomite (CaMg(CO\textsubscript{3})\textsubscript{2}) varies with increasing partial pressure of carbon dioxide in an anomalous manner and hence the effects of these procedural variables (except heating rate) are not similar to those observed for magnesite (MgCO\textsubscript{3}) and calcite (CaCO\textsubscript{3}). The second stage is, however, strongly dependent on these variables and behaves in a manner that would be predicted for a sample of calcite diluted with magnesite.

Keyword: bed-depth effect, carbonates

Introduction

The present authors have recently published papers concerned with the effect of procedural variables on the thermal decomposition of calcite [1], magnesite and dolomite [2], and the anomalous behaviour of dolomite in atmospheres containing carbon dioxide [3]. During the course of these studies it became clear that the effect of some of these experimental variables is inter-related and depends on the partial pressure of carbon dioxide within the bed of the reacting carbonate. It was also apparent that the behaviour of the three minerals, in spite of their chemical relationship and similar crystal structures, was quite different in certain respects. The aim of this paper is to use the data already published [1–3] to illustrate these points.
Experimental

TG curves were obtained on 50–400 mg samples of A.R. grade CaCO$_3$ and relatively pure mineral samples of calcite, magnesite and dolomite. Straight-sided crucibles were used to ensure that the depth of the sample bed was directly proportional to the sample mass. Heating rates of 1 or 7 deg-min$^{-1}$ were used on a Stanton HT–SF thermobalance. DTA curves were taken on similar sample masses at a heating rate of 10 deg-min$^{-1}$. Crucible diameters were 10 mm for TG and 7 mm for DTA. In each apparatus the atmosphere was controlled by a flow of 300 ml-min$^{-1}$ of dry, CO$_2$-free, N$_2$. This could be replaced by or mixed quantitatively with CO$_2$. The total pressure was always 1 atmosphere.

Results and discussion

Effect of bed-depth

While studying the decomposition of various carbonates by thermal methods, it was observed that DTA and DTG peaks for a series of equal masses of A.R. CaCO$_3$ and a mineral sample of calcite, heated under flowing nitrogen, always differed by some 10$^\circ$C although both were in powdered form. One difference was that the bulk density of calcite was twice that of the synthetic CaCO$_3$. Thus for the same mass, calcite occupied half the volume of a similar crucible compared to the CaCO$_3$.

This suggested to us that the peak temperatures of these DTA and DTG curves might be related to the depth occupied by the sample. With straight-sided crucibles, the sample depth is related directly to the diameters $d_1$ and $d_2$ of the crucibles by the formula

$$\frac{h_1}{h_2} = \frac{d_2^2 \cdot p_2 \cdot m_1}{d_1^2 \cdot p_1 \cdot m_2}$$

(1)

where $h$ is the depth of the sample of mass $m$ and density $p$, in a crucible of diameter $d$. Using the same material in different diameter crucibles, Eq. (1) reduces to:

$$\frac{h_1}{h_2} = \frac{d_2^2 \cdot m_1}{d_1^2 \cdot m_2}$$

(2)

Thus the bed-depth for a 100 mg sample in a 7 mm diameter DTA crucible should be virtually the same as that for a 200 mg sample in a 10 mm diameter TG crucible, as then