THE EFFECT OF PROCEDURAL VARIABLES ON TG, DTG AND DTA CURVES OF MAGNESITE AND DOLOMITE

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TG, DTG and DTA curves of magnesite are dependent on procedural variables, especially sample mass, heating rate and partial pressure of carbon dioxide, in a similar manner to those of calcite [1], although the magnitude of the effect is less for magnesite. The first stage of the decomposition of dolomite 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 and calcite. The second stage of the decomposition of dolomite is, however, strongly dependent on these procedural variables and behaves in a manner that would be predicted for a sample of calcite diluted with magnesia. A 1:1 molar mixture of magnesite and calcite also behaves as would be predicted from the behaviour of the single carbonates but differently from that of dolomite.

This study of the influence of procedural variables on TG, DTG and DTA curves of magnesite and dolomite follows on from that recently published concerning similar curves of calcite [1]. These three carbonates are closely related chemically and all have the same crystal structure. It has been shown, however, that the thermal decomposition of dolomite [2], and references therein is not the same as that predicted for a mixture of magnesite and calcite. Although it decomposes in two stages as follows:

\[
\text{CaMg(CO}_3\text{)}_2 = \text{CaCO}_3 + \text{MgO} + \text{CO}_2 \quad \text{(Stage 1)}
\]

\[
\text{CaCO}_3 = \text{CaO} + \text{CO}_2 \quad \text{(Stage 2)}
\]

the first stage takes place at a substantially higher temperature than that of magnesite and shows an anomalous dependence on the partial pressure of carbon dioxide in the atmosphere around the sample. The second stage, by contrast, follows closely the behaviour expected for the decomposition of calcite.
The results reported here relate to the dependence of the thermal analysis curves on the mass of the sample, the partial pressure of carbon dioxide in the atmosphere and the influence of water vapour for both carbonates, and also that of heating rate for dolomite and that of an inert diluent for magnesite.

Experimental

The sample of magnesite selected for this study was a natural mineral, which showed no X-ray diffraction peaks other than those attributed to it in the literature and was of purity greater than 99%. The dolomite was also of high purity although it did contain a trace amount of free calcite. Both minerals were ground to less than 300 mesh British Standard sieve (<55 μm).

The same TG and DTA equipment was used as in the recent paper on calcite [1] and similar experimental conditions were employed. The results of this investigation are, therefore, directly comparable with those previously reported for the decomposition of A.R. calcium carbonate and limestone.

Results

Effect of sample mass in an atmosphere of nitrogen

The effect of increasing the mass of the sample on the DTG and DTA peak temperatures of magnesite is shown in Table 1. The temperatures, \( T_{0.1} \), \( T_{0.5} \) and \( T_{0.9} \), correspond to the temperatures at which the fraction reacted, \( x \), reached 0.1, 0.5 and 0.9, respectively, (obtained from the TG curves of magnesite) are also listed in Table 1. The parameter \( x_m \) is the value of \( x \) at the DTG peak temperature.

It can be seen that variations in sample mass displaced the DTG and DTA curves of magnesite to higher temperatures and that the effect was similar in magnitude for both techniques. It was, however, a smaller effect than that observed when samples of A.R. calcium carbonate and limestone were heated under identical experimental conditions [1]. The increase was 30° for samples of magnesite (50 mg to 300 mg) studied by DTG and 25° by DTA, compared with an increase of the order of 90° for calcite.

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