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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_2. The first stage of the decomposition of dolomite ($CaMg(CO_3)_2$) 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 ($MgCO_3$) and calcite ($CaCO_3$). 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.

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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 $deg\cdot min^{-1}$ were used on a Stanton HT–SF thermobalance. DTA curves were taken on similar sample masses at a heating rate of 10 $deg\cdot min^{-1}$. Crucible diameters were 10 mm for TG and 7 mm for DTA. In each apparatus the atmosphere was controlled by a flow of 300 $ml\cdot min^{-1}$ 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, in 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°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

$$\frac{h_1}{h_2}=\frac{d_2^2\cdot p_2\cdot m_1}{d_1^2\cdot p_1\cdot m_2} \tag{1}$$

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:

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

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

$$\frac{h_1}{h_2} = \frac{10^2 \times 100}{7^2 \times 200} \sim 1 .$$

Thus the DTG and DTA peak temperatures should be the same. The relevant data are shown in Table 1 of reference [1], from which the following points are worth noting:

a) For A.R. $CaCO_3$ the DTA peak temperature for a 100 mg sample was 880°C, identical with the DTG peak temperature for the 200 mg sample.

b) A 50 mg sample of $CaCO_3$ using DTA (T_m of 852°C) compared with a 100 mg sample by DTG (T_m of 845°C).

c) A 100 mg sample of limestone by DTA (T_m of 895°C) compared with a 200 mg sample by DTG (T_m of 898°C).

d) A 150 mg sample of magnesite by DTA (T_m of 649°C interpolated) compared with a 300 mg sample by DTG (T_m of 645°C).

These results illustrate the important part played by the bed-depth of the sample in the generation of DTA and DTG curves. Variation in sample mass had a marked effect on the DTG (Fig. 1) and DTA (Table 1) curves for both A.R. $CaCO_3$ and calcite. The magnitude of the effect was similar for both DTA and DTG. This was also true for magnesite [2], although it can be seen from Fig. 1 and Table 1 that the effect was much smaller for magnesite than for calcite. Whereas a change in sample mass from 50 to 300 mg displaced the DTG and DTA peak temperatures for $CaCO_3$ and calcite by about 90°C, the displacement was only about 30°C for magnesite. Another difference observed was that the variation of peak temperature with sample mass was apparently linear for $MgCO_3$ whereas it was curved for $CaCO_3$ and calcite. This may be associated with the ease of reversibility of the calcite decomposition.

Table 1 DTA peak temperature *vs.* sample mass for some carbonates heated in nitrogen

Sample	DTA peak temperature / °C			
Mass	50 mg	100 mg	200 mg	300 mg
A.R. $CaCO_3$	852	880	—	—
Calcite	862	895	928	942
Magnesite	638	642	655	663
Dolomite (1st)	798	802	800	790
Dolomite (2st)	867	882	905	920

It can be observed from the data in Table 1 that no such consistent displacement was observed for the *first peak* of the dolomite decomposition [3], but the *second peak* behaved in an analogous manner to that of calcite in that the DTA peak temperature increased by 53°C when the sample mass was increased from 50 mg to 300 mg. This difference would have been greater but for the influence of the CO_2 lost during the first stage of the decomposition which particularly affected the 50 mg sample. The first stage of the decomposition of *dolomite* has an entirely different dependence on mass. The DTA peak temperatures listed in Table 1 were remarkably constant and showed no significant variation with sample mass. Similar results were obtained by DTG, ranging from 785° to 807°C for samples of 200–500 mg. It is shown elsewhere [3], and references therein that the peak temperature varies in a complex manner with increasing partial pressure of carbon dioxide, reaching a minimum value when between 10 and 20% CO_2 is present in the atmosphere.

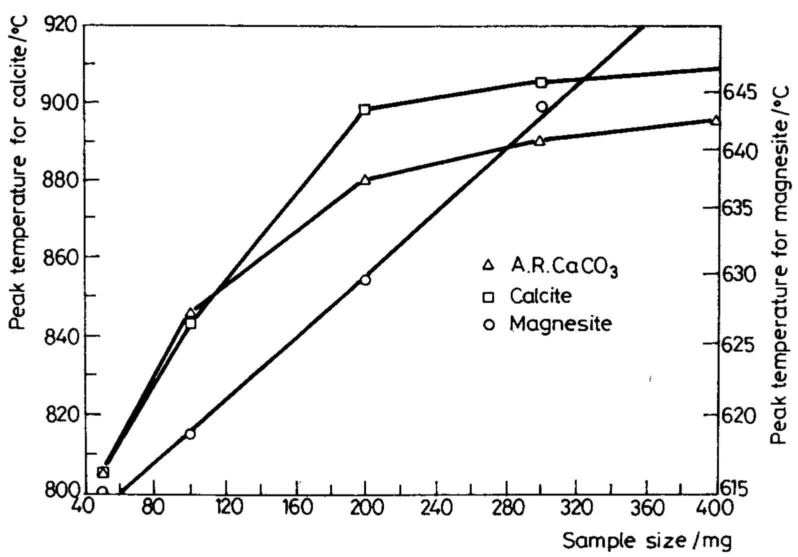

Fig. 1 Effect of sample mass on DTG peak temperatures for calcite, A.R. calcium carbonate and magnesite (heating rate 7 deg·min^{-1} in nitrogen)

Some data for a 1:1 molar mixture of magnesite and calcite are given in Table 3 of reference 2 for comparison with those for dolomite, which has the same chemical composition. This mixture behaves in the manner predicted from the data for magnesite and calcite heated alone.

The effect of an inert diluent

This effect was studied by adding MgO to calcite (Fig. 2) and also by adding quartz to magnesite. The results shown in Table 4 of Ref.[1] and Table 4 of Ref.[2] show that the influence of the inert diluent is negligible, as the peak temperatures observed in the presence of the diluent were similar to that for an equivalent mass of active material heated alone, rather than that for a mass equal to the total mass of the sample. Thus it is the bed-depth of the active reactant that is the important factor which affects the temperature range of the decomposition. This aspect has been thoroughly investigated by Warne and Mackenzie [4].

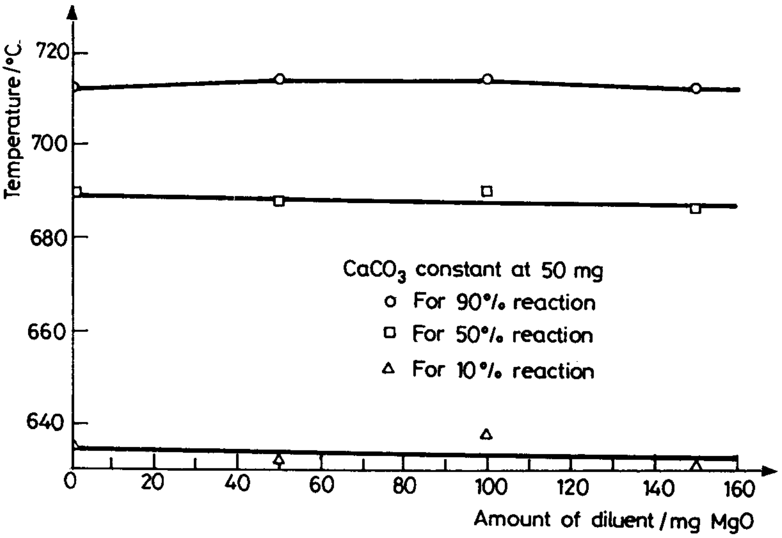

Fig. 2 Effect of dilution on TG curve for A.R. calcium carbonate (heating rate 1 deg·min^{-1} in nitrogen)

Although the depth of the sample normally determines the overall position of the DTA or DTG curve for carbonate decompositions, the behaviour of dolomite is different [3]. Indeed, had very small samples been used for this investigation the anomalous effect observed for the first stage of the dolomite decomposition would never have been observed because the two peaks would have merged into a single peak. When investigating industrial processes using thermal methods, larger samples will often yield more representative data [5].

Effect of heating rate

A change in heating rate produces a large effect. Increase in heating rate from 1 to 7 deg·min^{-1} for the decomposition of calcite resulted in an increase of 87°C in $T_{0.1}$, the temperature at which the fraction reacted reached 0.1, 106°C in $T_{0.5}$ and 115°C in $T_{0.9}$, for a 100 mg sample heated in flowing N_2. These increments increased slightly as the mass was increased. The displacement of the TG curve with change in heating rate has been demonstrated theoretically [6] from calculations based on specific reaction mechanisms. The calculated temperature shift of the TG curve for this increase is of the order of 100°C, in close agreement with the data given above. The behaviour of both peaks of dolomite (Table 6 of

Ref. [2]) was similar to that of calcite, the peak temperature shifts being about 60°–70°C for a heating rate change from 1 to 7 deg·min^{-1}. Although shifts of DTA and DSC curves with heating rate have been reported by other authors, the magnitude of the effect for TG curves does not appear to have been quantified previously. These very appreciable shifts with heating rate make comparison of DTG and TG curves from different studies difficult, unless they have been carried out under strictly similar conditions.

The effect of carbon dioxide atmosphere

TG curves for the decomposition of A.R. $CaCO_3$ in various partial pressures of CO_2 are shown in Fig. 3. These TG curves are steeper than those in N_2, with dramatic increases in the values of $T_{0.1}$, $T_{0.5}$ and $T_{0.9}$ even when low partial pressures of CO_2 were used. The increase in temperature for a 100 mg sample, on changing from 1 atmosphere N_2 to 1 atmosphere CO_2, was in excess of 200°C. The steepness of the curves is in part due to the greater influence of CO_2 on the initial part of the curve rather than on the final part, as illustrated in Fig. 4 which shows the variation in peak width (as indicated by $T_{0.9}$-$T_{0.1}$) *vs.* the partial pressure of CO_2. Even the lowest partial pressure of CO_2 used led to a dramatic change in the peak width, which decreased to a steady state at higher partial pres-

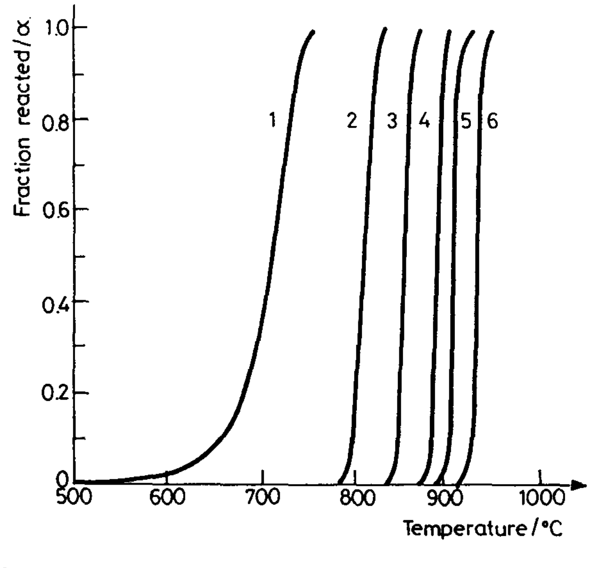

Fig. 3 Effect of carbon dioxide partial pressure on TG curves of A.R. calcium carbonate (100 mg) heated at 1°C min^{-1} in (1) 1.0 atm N_2, (2) 0.1 atm CO_2, (3) 0.3 atm CO_2, (4) 0.5 atm CO_2, (5) 0.7 atm CO_2, (6) 1.0 atm CO_2. In runs (2)-(5), N_2 was mixed with CO_2 to give a total pressure of 1 atmosphere

sures. It is also noteworthy that the fraction decomposed at the DTG peak temperature in N_2 was about 0.8 whereas in CO_2 it was only 0.3, suggesting a change in the kinetic reaction mechanism.

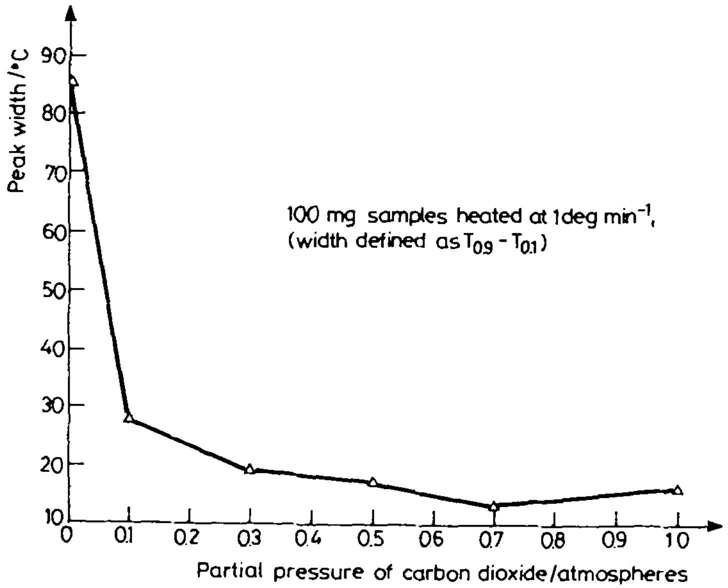

Fig. 4 Effect of partial pressure of carbon dioxide on width of DTG curves for A.R. calcium carbonate

In contrast to the results obtained in N_2, the bed-depth (i.e. the sample mass) had only a small and decreasing effect on the decomposition temperature as the partial pressure of CO_2 was increased. In 100% CO_2 the bed-depth effect disappeared, which can be explained because the atmosphere within the sample remained constant.

Results obtained for the decomposition of $MgCO_3$ in CO_2-containing atmospheres are shown in Table 5 of Ref. [2]. Increasing partial pressure of CO_2 over the sample caused the peak temperatures to increase, similar in magnitude for DTA and DTG, but the increase was much less than that observed for $CaCO_3$; the maximum increase for complete replacement of N_2 by CO_2 was of the order of 20°C. The peak temperature of the *first stage* of dolomite decomposition decreased when CO_2 was introduced into the atmosphere (Table 5 of Ref. [2] and Table 1 of Ref. [3]). This decrease varied with sample mass and heating rate but it was observed that the peak was about 30°C lower in 0.1–0.2 atmospheres CO_2 than in N_2, and was still significantly lower in 1 atmosphere of CO_2 than in nitrogen! On the other hand, the second stage of the decomposition of dolomite followed very closely the expected dependence on partial pressure of CO_2 in a similar manner to that of calcite. Thus it can be concluded that the first stage has an anomalous dependence on partial pressure of CO_2. This effect has been fully discussed elsewhere [3].

Conclusions

These results clearly indicate the great dependence of the position and shape of DTA and DTG curves on sample mass, heating rate and atmosphere. Increase in the sample mass or the heating rate brings about a temporary increase in the partial pressure of CO_2 within the powder bed of the decomposing sample. Therefore, all three procedural variables are inter-related and influenced by the depth of the sample bed. This evidence emphasizes the necessity of strict control of procedural variables when using thermal methods to evaluate gaseous decompositions and to the accurate recording of such variables when reporting results.

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Zusammenfassung — Es wurde der Einfluß von Probenmasse, Aufheizgeschwindigkeit und Partialdruck von Kohlendioxid auf die TG-, DTG- und DTA-Kurven der Zersetzung einiger gewöhnlicher Carbonate untersucht. Diese Variablen haben einen eindeutigen Einfluß, der sich bei DTG und DTA in gleicher Größenordnung bemerkbar macht. Der Einfluß der Probenmasse oder der Höhe ungelöster Proben hängt mit dem Ansteigen des Partialdruckes von Kohlendioxid im pulverisierten Reaktionsgemisch zusammen. Dieser Effekt tritt in Stickstoff am meisten hervor und wird in Kohlendioxid sehr abgeschwächt. Inerte Streckungsmittel haben einen geringen Einfluß auf den Kurvenverlauf, da sie den Partialdruck von CO_2 nicht verändern. Der erste Schritt der Zersetzung von Dolomit ($CaMg(CO_3)_2$) ändert sich mit steigendem Partialdruck von Kohlendioxid auf eine anomale Weise und folglich gleicht der Einfluß dieser Verfahrensvariablen (mit Ausnahme der Aufheizgeschwindigkeit) nicht dem, der für Magnesit ($MgCO_3$) und Calzit ($CaCO_3$) beobachtet wurde. Der zweite Schritt ist in jedem Falle stark von diesen Variablen abhängig und verläuft in einer Weise, wie sie für eine mit Magnesit verdünnte Calzitprobe vorhergesagt wurde.