THE EFFECT OF PROCEDURAL VARIABLES ON TG, DTG AND DTA CURVES OF CALCIUM CARBONATE

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The effect of procedural variables, including sample mass, heating rate, particle size and partial pressure of carbon dioxide, on TG, DTG and DTA curves for the decomposition of A. R. calcium carbonate and limestone has been studied. Such variables have 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 and has been called the bed-depth effect. This effect is most pronounced in nitrogen but is much reduced in carbon dioxide. Inert diluents have little effect on the TG curves but changing the composition of the inert carrier gas causes variations which are correlated with the thermal conductivity of the gas. Water vapour causes a lowering of the DTG and DTA peak temperatures.

Introduction

Although the effect of procedural variables on the appearance of DTA curves has been much discussed (e.g. [1–4]), most of the observations have been qualitative, leading to vague statements such as 'a heating rate of 10 deg/min is generally satisfactory'. More recently several papers have been published on the influence of sample mass and heating rate on the form of phase transition peaks studied using differential scanning calorimetry [5–10]. Rather less attention has been devoted to such influences on TG and DTG curves, which give information only about reactions involving gaseous reactants or products, although similar effects can be predicted [11–16]. Since DTG and DTA are often used together in comparative studies, it is important to know the magnitude of these effects and how they differ from one technique to the other. Furthermore, if the kinetic mechanism is known, calculations can be made to demonstrate quantitatively the effect of procedural variables, such as sample mass and heating rate, on the appearance of an experimental thermal analysis curve. Such calculations are to be reported

in a later paper, but it is essential to have reliable experimental data to use as a yardstick to check the reliability of the calculated data.

The objective of this paper is, therefore, to present detailed experimental data for the decomposition of calcium carbonate obtained by means of TG and DTA. The effects of several important procedural variables, including sample mass, presence of an inert diluent, heating rate, crucible geometry and atmosphere (both inert and that involved in the reaction), are reported and explained.

Experimental

Two samples of calcium carbonate were used, one A.R. material, the other a natural limestone from Matlock, Derbyshire. Both samples were shown by X-ray diffraction to be composed of the mineral calcite, with only one additional peak being observed at d = 3.345 Å. This peak was very weak and indicated the presence of a very small amount of quartz. The A.R. calcium carbonate was a high purity synthetic chemical with a minimum assay of 99.5% and all impurities <0.1% (but SiO_2 was not listed). The limestone had a chemical analysis of CaO, 55.7%; SiO_2, 0.4%; MgO, 0.1%; and Fe_2O_3, 200 ppm; it was ground to <200 mesh British Standard sieve (<75 μm).

TG curves were obtained on 50–400 mg samples using heating rates of 1 deg·min^{-1} or 7 deg·min^{-1} on a Stanton HT–SF thermobalance. DTA curves were taken on 50–300 mg samples at a heating rate of 10 deg·min^{-1} using a slightly modified form of the DTA cell designed by Wilburn [17]. In each apparatus the atmosphere was controlled by a flow of 300 ml·min^{-1} of dry, CO_2–free nitrogen. This could be replaced by or mixed quantitatively with carbon dioxide or other gases. The total pressure was always 1 atmosphere.

Since preliminary studies had shown the importance of sample mass as discussed below, straight sided cylindrical crucibles were used to ensure that the depth of the sample bed was directly proportional to the sample mass. The diameter of the crucibles used for TG was 10 mm whilst that for DTA was 7 mm.

T_x is defined as that temperature at which the fraction reacted is x. Values for T_x between 0.1 and 0.9 obtained from the TG curves were always reproducible to within ±5° and DTA peak temperatures to within ±2°.

Results

Effect of sample mass in an atmosphere of nitrogen

The DTG and DTA peak temperatures obtained using different sample masses of A.R. calcium carbonate and limestone in a flowing nitrogen atmosphere above the sample are given in Table 1. Variation in sample mass has a marked effect, which is at least as great for DTG as for DTA. Thus when the sample mass was increased from 50 to 300 mg the DTG peak temperature of limestone increased by 95° and the DTA peak temperature by 80°. For A.R. calcium carbonate the increase observed using DTG was 85°.

Table 1 Effect of sample mass on the peak temperatures for the decomposition of calcite and A.R. calcium carbonate in nitrogen

Heating rate:	DTG 7 deg·min^{-1}		DTA 10 deg·min^{-1}	
Sample mass,	A.R. CaCO$_3$		Limestone	
	DTG,	DTA,	DTG,	DTA,
mg	°C	°C	°C	°C
50	805	852	810	862
100	845	880	–	895
200	880	–	898	928
300	890	–	905	942
400	895	–	–	–
200 (pellet)	895	937	895	940

To quantify the lowering of the decomposition temperature as sample size is reduced, it is useful to define certain temperatures which can be obtained easily and reproducibly from the TG curves. The temperatures, $T_{0.1}$, $T_{0.5}$ and $T_{0.9}$, are those at which 10%, 50% and 90% of the available carbon dioxide has been evolved respectively. These temperatures are listed in Table 2 for A.R. calcium carbonate decomposed under two different atmospheres and at two heating rates. As the sample mass was increased so also the magnitude of the area under the peaks observed for both DTG and DTA increased.. It can be seen from the DTG curves for A.R. calcium carbonate (Fig. 1) that the rate of mass loss during the early part of the reaction in nitrogen (up to ca. 790°) was similar for all sample masses, but continued to progressively higher temperatures as the sample mass was increased. This led to T_x values which increased progressively with sample mass (Table 2). The difference $T_{0.9}-T_{0.1}$, denoted by

ΔT, which approximates to the temperature range of the reaction, but involves parameters that can be determined more precisely than the initial and final temperatures, increased as the sample mass was increased.

Table 2 The effect of sample mass on the TG curve for A.R. calcium carbonate under various conditions

Sample mass, mg		$T_{0.1}$	$T_{0.5}$	$T_{0.9}$	ΔT^*
A. Heated at 1 deg·min^{-1} in nitrogen					
50		634	689	712	78
100		655	712	740	85
250		672	739	773	101
250	(pellet)	694	759	796	102
B. Heated at 7 deg·min^{-1} in nitrogen					
50		716	788	818	102
100		742	818	855	113
200		768	845	890	122
300		775	853	902	127
400		775	865	915	140
C. Heated at 7 deg·min^{-1} in carbon dioxide					
50		941	952	967	26
100		943	954	977	34
200		948	970	997	49
300		957	981	1012	55

$\Delta T = T_{0.9} - T_{0.1}$

It can also be seen from Table 1 that the thermal analysis peak temperatures for samples of limestone were about 10° higher than those for samples of an equal mass of A.R. calcium carbonate, both materials being in powdered form. In contrast, the peak temperatures for these samples in pelletised form were, within experimental error, the same (Table 1). The bulk densities of the A.R. calcium carbonate and limestone powders were 0.8 and 1.6 g·cm^{-3}, respectively, whereas the bulk densities of the pellets of both materials were 2.0 g·cm^{-3}. It can be concluded that the DTG and DTA peak temperatures are dependent on the sample volumes.
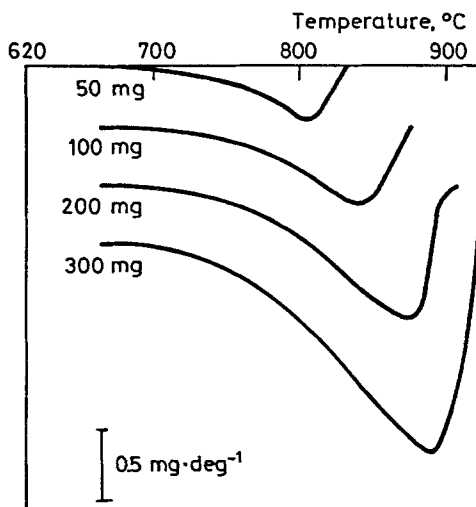
Fig. 1 The effect of sample mass on the DTG curves of A.R. calcium carbonate heated at
7 deg·min^{-1} in flowing nitrogen

The sample depth is related to the diameter of the straight-sided crucibles
used in both the TG and DTA experiments by the simple relationship:

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

where h is the depth of a sample of mass m and density p in a crucible of
diameter d. The suffixes 1 and 2 refer to the larger and smaller crucible
respectively. If the true density of the material is the same in both crucibles
then Eq. (1) reduces to:

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

Therefore, the bed-depth for a 100 mg sample in the 7 mm diameter DTA
crucible used in this investigation should be almost the same as that for a
200 mg sample in the 10 mm diameter TG crucible:

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

The importance of the bed-depth of the sample can be confirmed by com-
paring the peak temperatures listed in Table 1 for DTA (100 mg samples)

with those for DTG (200 mg), which are similar, as also are those for DTA (50 mg) and DTG (100 mg).

To test this hypothesis further the crucible used in the TG experiments was replaced by another of larger diameter (12.5 mm instead of 10 mm), but still with vertical sides. The DTG peak temperature for a 300 mg sample of limestone was reduced by 15° to 890° in the larger crucible, similar in magnitude, as predicted by Eq. (2), to the DTG peak temperature (898°) observed for a 200 mg sample in the 10 mm diameter crucible and to the DTA peak temperature (895°) for a 100 mg sample in a 7 mm diameter crucible.

Examination of the data listed in Table 1 indicates that for a given sample mass of a powdered sample, the DTA peak temperature was always observed at a higher temperature than the corresponding DTG peak temperature. These higher values are attributed mainly to the change in the diameter of the crucibles, although the use of different heating rates (discussed below) and the effects of heat transfer [18] are also significant.

Effect of heating rate

The data listed in Table 2 also show that TG curves obtained under identical experimental conditions, except heating rate, are displaced to higher temperatures as the heating rate is increased. Thus an increase in the heating rate from 1 deg·min^{-1} to 7 deg·min^{-1} for 100 mg of A.R. calcium carbonate heated in nitrogen resulted in an increase of 87° in the value of $T_{0.1}$, 106° in $T_{0.5}$, and 115° in $T_{0.9}$.

These differences increased slightly with increasing sample mass and increased with increasing extent of reaction (Table 3). The values shown for 250 mg samples in Table 3 are based on interpolation of the 200 mg and 300 mg results shown in Table 2 for samples heated at 7 deg·min^{-1}. The effect of variation in heating rate is large; the shift in temperature is of the order of 100°. Similar effects are observed when DTA runs are carried out at different heating rates.

Table 3 The effect of heating rate on the TG curve for A.R. calcium carbonate in nitrogen

Sample mass, mg	$\Delta T_{0.1}$	$\Delta T_{0.5}$	$\Delta T_{0.9}$
50	82	99	106
100	87	106	115
250	100	110	123

ΔT_x = the difference in temperature between a TG curve obtained at 7 deg·min^{-1} and one at 1 deg·min^{-1} when the fraction reacted is x

Although such shifts in the peak temperature of DTA curves with increase in the heating rate are mentioned by Mackenzie [3] and have been the subject of recent papers concerning DSC [5–10], the magnitude of the effect for TG curves does not seem previously to have been defined quantitatively. These very appreciable displacements in the temperature of TG curves with increase in heating rate or sample mass make comparison of TG and DTG curves from different studies difficult, unless they have been carried out under similar experimental conditions.

The displacement of the TG curve with change in the heating rate can be demonstrated theoretically from calculations based on specific reaction equations [19]. The calculated temperature shift of the TG curve for calcium carbonate for an increase in heating rate from 1 $deg \cdot min^{-1}$ to 7 $deg \cdot min^{-1}$ is of the order of 100°, which agrees closely with the data presented in Table 3.

Effect of an inert diluent in a nitrogen atmosphere

The effect of sample dilution on TG curves in nitrogen was studied by adding fired magnesium oxide or South African quartz (SiO_2) to A.R. calcium carbonate. Previous studies [20] had shown that there was no appreciable reaction between silica and either of the carbonates used for this study prior to decomposition in nitrogen or carbon dioxide atmospheres.

Preliminary experiments were carried out using 50 mg of A.R. calcium carbonate diluted with 250 mg of (a) magnesia and (b) silica heated at a rate of 7 $deg \cdot min^{-1}$ in flowing nitrogen. The DTG peak temperatures were observed at 815° and 825°, respectively, compared with 805° for 50 mg and 890° for 300 mg of calcite heated alone.

Table 4 The effect of dilution with magnesia on the TG curves of A.R. calcium carbonate heated at 1 $deg \cdot min^{-1}$ in nitrogen

Sample,		$T_{0.1}$	$T_{0.5}$	$T_{0.9}$
$CaCO_3$	MgO	°C	°C	°C
mg	mg			
50	—	634	689	712
50	50	632	688	714
50	100	638	690	714
50	150	630	686	712
100	—	655	712	740
250	—	672	739	773

TG data obtained when A.R. calcium carbonate was diluted with magnesia and heated at 1 deg·min^{-1} are shown in Table 4. The values of T_x are unchanged within experimental error, even when the mass of diluent was three times that of the calcite. It can be seen that the effect of an inert diluent is small, since TG, DTG and DTA curves obtained on diluted samples are similar to those for the equivalent mass of carbonate heated alone, rather than that for the mass of carbonate equal to the total mass of the diluted sample.

The relationship of these results to those already published concerning the effect of dilution [21, 22] will be discussed later, but it can be concluded now that it is the bed-depth of *active* reactant that is the important factor in affecting the temperature range of the decomposition observed by thermal methods.

Effect of particle size

As the particle size of the limestone was reduced, the DTG and DTA peak temperatures also decreased by about 10°. However, the effect was small compared with those produced by sample mass, partial pressure of carbon dioxide and heating rate and, therefore, is not considered in greater detail.

Effect of carbon dioxide atmosphere

TG curves for the decomposition of A.R. calcium carbonate heated at 1 deg·min^{-1} in various partial pressures of carbon dioxide are shown in Fig. 2 and the data are summarized in Table 5. The TG curves obtained in partial pressure of carbon dioxide were steeper than those in nitrogen (Fig. 2). The data listed in Table 5 show a dramatic increase in the values of $T_{0.1}$, $T_{0.5}$ and $T_{0.9}$ even when a low partial pressure of carbon dioxide was used. The value of ΔT, $T_{0.9}-T_{0.1}$, was very much greater in a nitrogen atmosphere than in any of those containing carbon dioxide. Furthermore, as the carbon dioxide partial pressure was increased the magnitude of ΔT approached a constant value of 16 ± 3.

DTG curves for the same material heated at 7 deg·min^{-1} in various atmospheres are shown in Fig. 3. An increase in the partial pressure of carbon dioxide over the sample caused a marked increase in the DTG and DTA peak temperatures, which again was similar in magnitude for both DTG and DTA (Table 6) and for both limestone and A.R. calcium carbonate. The value of x at the DTG peak temperature in nitrogen is ca. 0.8, but in carbon dioxide it is

0.3–0.4. The TG curves are, therefore, more widely separated than the DTG and DTA peak temperatures would suggest.
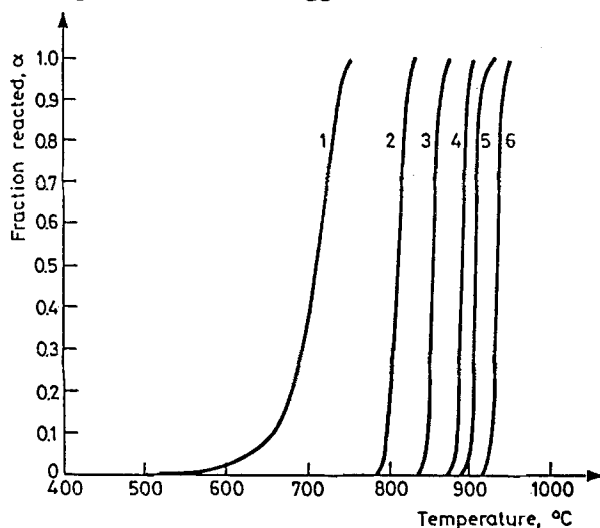

Fig. 2 The effect of partial pressure of carbon dioxide on the TG curves of A.R. calcium carbonate (100 mg) heated at 1 deg·min^{-1} in 1.0 atmos. N_2; 2. in 0.1 atmos. CO_2; 3. in 0.3 atmos. CO_2; 4. in 0.5 atmos. CO_2; 5. in 0.7 atmos. CO_2; 6. in 1.0 atmos. CO_2. In runs 2–5, N_2 was mixed with CO_2 to give a total pressure of 1 atmos.

Table 5 Effect of partial pressure of carbon dioxide on the TG curve for A.R. calcium carbonate heated at 1 deg·min^{-1}

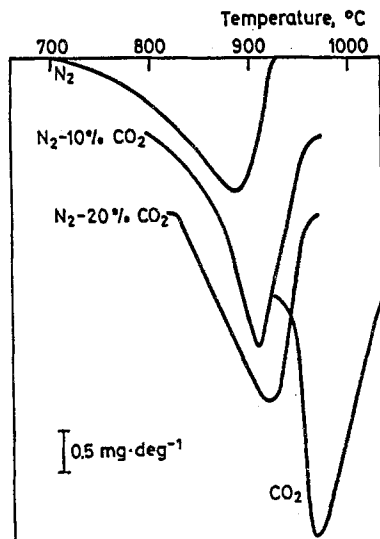| CO_2	N_2	$T_{0.1}$	$T_{0.5}$	$T_{0.9}$	ΔT*
	A. 100 mg samples				
—	1.0 atmos	655	712	740	85
0.1	0.9 atmos	798	814	826	28
0.3	0.7 atmos	850	859	869	19
0.5	0.5 atmos	887	896	904	17
0.7	0.3 atmos	905	911	918	13
1.0	— atmos	930	937	946	16
	B. 250 mg samples				
—	1.0 atmos	672	739	773	101
0.1	0.9 atmos	803	824	840	37
0.5	0.5 atmos	886	901	912	26
1.0	— atmos	930	937	948	18

$\Delta T = T_{0.9} - T_{0.1}$

Fig. 3 The effect of partial pressure of carbon dioxide on the DTG curves of A.R. calcium
carbonate (300 mg) heated at 7 deg·min^{-1}

The sharpening of the peak allows the determination of more reliable
onset decomposition temperatures, i.e. temperatures at which loss in mass
was first observed, in atmospheres containing carbon dioxide. In Table 7
these onset temperatures and values for $T_{0.1}$ (for runs involving 100 mg
samples heated at 1 deg·min^{-1}) are compared with the thermodynamic
decomposition temperatures, determined from the relationship:

$$\Delta G^{\circ} = - R \cdot T \ln p_{CO_2} = \Delta H^{\circ} - T \cdot \Delta S^{\circ} = 40250 - 34.4 T \qquad (3)$$

The values shown in Table 7 for $T_{0.1}$ are $34 \pm 5^{\circ}$ higher than the ther-
modynamic decomposition temperatures and $20 \pm 2^{\circ}$ higher than the onset
temperatures, which may be regarded as procedural decomposition tempera-
tures. Therefore, conditions are sufficiently close to equilibrium in the
presence of CO_2 for the increase in these early decomposition temperatures
to be explained by thermodynamic considerations.

With the assumption that the temperature $T_{0.1}$ is 34° higher than the ther-
modynamic decomposition temperature, Eq. (3) can be used to calculate the
partial pressure of carbon dioxide in the nitrogen atmosphere. For the 100 mg
sample heated at 1 deg·min^{-1} this pressure is determined as $4.9 \cdot 10^{-3}$ atmos.

The increase in the decomposition temperatures at higher values of x does
not reflect the increase in thermodynamic decomposition temperatures. Thus
the difference in $T_{0.1}$ between runs in nitrogen and in 0.1 atmos. of carbon

ioxide is 143°, between 0.1 and 0.5 atmos. of carbon dioxide is 89°, and between 0.5 and 1 atmos. of carbon dioxide is 43°, whereas the corresponding differences in $T_{0.9}$ are only 86°, 78° and 42°, while differences in T_m, the peak temperature, are still less. It should be noted that the comparison of T_m values is not as meaningful as the comparison of T_x values, since the fraction reacted at the peak temperature, x_m, varies with atmosphere (Table 6). Both these observations indicate that the shape of the TG curve in carbon dioxide is different from that in nitrogen, which can be confirmed by inspection of the curves in Fig. 2. This indicates that a different kinetic mechanism must be operating in carbon dioxide atmospheres from that in nitrogen.

Table 6 Effect of partial pressure of carbon dioxide on the peak temperature ($^\circ C$) for limestone and A.R. calcium carbonate

Atmosphere		A.R. CaCO₃			Limestone		
		DTG		DTA	DTG		DTA
CO_2	N_2	T_m	x_m	T_m	T_m	x_m	T_m
—	1.0	890	0.80	880	905	0.80	895
0.1	0.9	910	0.64	895	925	0.70	907
0.2	0.8	920	0.66	902	945	—	915
1.0	—	970	0.31	950	970	0.40	957
ΔT		80		70	65		62

ΔT is the difference in temperature between T_m for carbon dioxide and T_m for nitrogen.
DTG obtained on 300 mg samples heated at 7 deg·min^{-1}
DTA obtained on 100 mg samples heated at 10 deg·min^{-1}

Table 7 Effect of partial pressure of carbon dioxide on the decomposition of A.R. calcium carbonate

p.p. of CO_2 in atmosphere	Decomposition Temperature, $^\circ C$			
	Th.D.	onset T	$T_{0.1}$	ΔT
0.1 atmos	759	700	798	39
0.3 atmos	821	830	850	29
0.5 atmos	852	865	887	35
0.7 atmos	873	885	905	32
1.0 atmos	897	910	930	33

ΔT is the difference in temperature between $T_{0.1}$ and the thermodynamic decomposition temperature
The results are based on data obtained from TG using a 100 mg sample heated at 1 deg·min^{-1} at a total pressure of 1 atmos. made up from N_2–CO_2 mixtures
Th. D. = thermodynamic decomposition temperature

The effect of sample mass on the TG curves for the decomposition of calcium carbonate conducted in atmospheres containing carbon dioxide is shown in Tables 2 and 5. In contrast to the results obtained in nitrogen, variation in the sample mass (bed-depth) has only a small and decreasing effect on the decomposition temperature as the partial pressure of carbon dioxide increases. It can be seen from the data for 100 mg and 250 mg samples given in Table 5 that $T_{0.5}$ increased by $27°$ in N_2, but only by $10°$ in 0.1 atmos. of CO_2, by $5°$ in 0.5 atmos. CO_2, and by zero in 1 atmos. of CO_2. The bed-depth effect is expected to disappear in an atmosphere of 100% CO_2, because the atmosphere within the sample bed should remain constant.

The effect of heating rate in carbon dioxide atmospheres is similar to that observed in nitrogen, but much smaller in magnitude. Thus for 100 mg of A.R. calcium carbonate heated in 1 atmosphere of carbon dioxide, an increase in the heating rate from $1 \deg \cdot \min^{-1}$ to $7 \deg \cdot \min^{-1}$ resulted in an increase in $T_{0.1}$ of $13°$ (cf. $87°$ in nitrogen), in $T_{0.9}$ of $31°$ (cf. $115°$) and in ΔT of $18°$ (cf. $28°$). These observations are also in accordance with a much reduced bed-depth effect in CO_2.

Effect of inert atmospheres

The decomposition of the two samples of calcium carbonate was studied in various inert carrier gases of different thermal conductivities. For these experiments a standard sample of mass 300 mg was used for TG and either 100 mg or 200 mg for DTA.

The use of argon rather than nitrogen as the inert carrier gas led to increased peak temperatures (Table 8), whereas the presence of hydrogen or water vapour in the nitrogen led to lower peak temperatures, but these effects were much smaller than those due to the variation in partial pressure of carbon dioxide. The thermal conductivities are in the sequence:

$$\text{water vapour} \approx \text{argon} < \text{nitrogen} \ll \text{hydrogen}$$

which suggests that the higher the thermal conductivity of the carrier gas, then the lower is the observed decomposition temperature. This is in agreement with the work of Wilburn, Dollimore and Crighton [23], who have shown theoretically that increased conductivity of the gaseous space between the furnace and the sample, particularly when the temperature was measured at the periphery of the sample as in TG, lowered the peak temperature.

The presence of water vapour in the carrier gas clearly causes some chemical interactions. It has been shown that the rate of nucleation of the

product oxide is dependent on the partial pressure of the water vapour in the atmosphere [24]. The crystallite size of the calcium oxide, formed after heating to 1100° at 1 deg·min^{-1} in various atmospheres followed by quenching, was determined by X-ray line broadening [25]. The results shown in Table 9 confirm that the presence of carbon dioxide and especially water vapour had a large effect on the crystallite size of the product. It is possible that a similar chemical interaction involving surface OH groups occurs when hydrogen is present in the atmosphere, but its high thermal conductivity is probably sufficient to explain the lower observed temperatures.

Table 8 Effect of variation of composition of carrier gas on the peak temperature for the decomposition of calcium carbonate

Atmosphere	A.R. CaCO$_3$		Limestone		Note
	DTG	DTA	DTG	DTA	
	°C	°C	°C	°C	
nitrogen	890	920	–	–	(a)
argon	903	929	–	–	(a)
0.9 N$_2$–0.1 H$_2$	–	904	–	–	(a)
0.9 N$_2$–0.1 CO$_2$	–	935	–	–	(a)
0.9 Ar–0.1 CO$_2$	–	938	–	–	(a)
dry N$_2$	890	880	910	895	(b)
1.0 N$_2$–sat. H$_2$O vapour	890	871	895	885	(b)
carbon dioxide	–	950	–	957	(b)
CO$_2$–sat. H$_2$O vapour	–	950	–	955	(b)

(a) DTG (300 mg samples) and DTA (200 mg) heated at 10 deg·min^{-1}
(b) DTG (300 mg samples) heated at 7 deg·min^{-1} and DTA (200 mg) heated at
    10 deg·min^{-1}

Table 9 Variation of crystallite size of calcium oxide with atmosphere

Atmosphere	Dry	Wet
N$_2$ (1 atmos)	610 Å	1080 Å
CO$_2$ (0.5 atmos)–N$_2$ (0.5 atmos)	3770 Å	98000 Å

Discussion

It is clear from the results presented in the previous section that the TG, DTG and DTA curves of calcium carbonate are dependent on all of the pro-

cedural variables investigated, but especially on variation in sample mass, heating rate and partial pressure of carbon dioxide. It is also established that the magnitude of these effects is very similar for DTG and DTA, as can be seen from the variation in the peak temperatures listed in Tables 1 and 6.

These results may all be explained in terms of the bed-depth effect, which arises because carbon dioxide is evolved during the reaction at a rate faster than it can escape from the sample, causing a local increase in the partial pressure of carbon dioxide within the powder bed. The deeper the bed, i.e. the greater the mass of undiluted sample in a given diameter crucible, the greater is the build-up of partial pressure of carbon dioxide under the same experimental conditions. Thus there is a retardation in the rate of reaction, since the decomposition reaction of calcite is a reversible one and is therefore dependent on the partial pressure of carbon dioxide according to Eq. (3).

The increase in partial pressure of carbon dioxide within the powder bed may be brought about by any of the three major variables. Thus the greater the mass of the sample, the more CO_2 is evolved, causing a build-up in partial pressure of carbon dioxide. Similarly the faster the heating rate, the greater the rate of reaction, also leading to a temporary build-up in partial pressure of carbon dioxide. Additionally, variation in the heating rate affects the peak temperature because the heating rate appears in the basic equation of the TG curve [16, 26]. Hence the effect of increasing sample mass or heating rate is essentially that of increasing the partial pressure of carbon dioxide and therefore all three procedural variables are closely inter-related.

The effect of these procedural variables (the bed-depth effect) should in theory disappear in 1 atmosphere of carbon dioxide. The results shown in Table 2 show that variation in the sample mass has a much smaller effect on the DTG peak temperatures in CO_2 than it did on those obtained in an atmosphere of nitrogen. The slight increase in the DTG peak temperatures for the larger samples in carbon dioxide is because heat transfer becomes significant, and self-cooling of these samples occurs, retarding the rate of reaction.

The DTG and DTA peak temperatures (Table 6) for limestone in an atmosphere of nitrogen and the lower partial pressures of carbon dioxide were about 15° higher than the corresponding temperatures for A.R. calcium carbonate, whereas the peak temperatures were similar in 1 atmosphere of carbon dioxide. This is in accordance with the increased bed-depth effect for the denser limestone, but disappears in 1 atmos. of CO_2 since the composition of the atmosphere within the powder bed remains constant throughout the decomposition. These results for calcite are in agreement with those of

Rowland and Lewis [27] who reported that the use of a carbon dioxide atmosphere raised the peak temperature by 60° and sharpened the peak, an effect also observed by Stone [28].

The effects of dilution by incorporation of an inert diluent such as MgO or SiO_2 (Table 4) are also in accordance with the bed-depth effect postulated above, since there is no build-up of partial pressure of carbon dioxide when an inert diluent is added. This conclusion is similar to that of Warne and Mackenzie [22]; their results and those of Gokhale and Rao [21] are discussed further in another paper on the thermal decomposition of magnesite and dolomite [29].

Conclusions

1. TG curves for the decomposition of limestone and A.R. calcium carbonate are dependent on procedural variables, particularly on sample mass, heating rate and the partial pressure of carbon dioxide, in a similar way to DTA curves. The magnitudes of all three effects are very similar for DTA and for DTG.

2. As discussed by Coats and Redfern [13] for TG:

$$(T_{0.1})_a > (T_{0.1})_b \text{ and } (T_{0.9})_a > (T_{0.9})_b \text{ and } (T_{0.9} - T_{0.1})_a > (T_{0.9} - T_{0.1})_b$$

where a and b are heating rates and $a > b$.

3. Variation in the partial pressure of carbon dioxide has a large effect on the decomposition of calcium carbonate.

4. Variation of the sample mass when the carbonates are decomposed in nitrogen has a similar effect to that of the partial pressure of carbon dioxide because of the build-up of carbon dioxide pressure within the sample (the bed-depth effect). This effect is similar in magnitude for both DTG and DTA. Using larger diameter crucibles for samples of equal mass causes the DTA curve to be displaced to lower temperatures, since it is the sample depth rather than its mass that affects the curve.

5. Variation of sample mass in 1 atmosphere of carbon dioxide has only a slight effect on the position of the TG curve for the decomposition of calcite, since the composition of the atmosphere within the sample bed does not change during the decomposition. The small variation observed is attributed to self-cooling of the sample due to the large endothermic effect associated with the decomposition.

6. The peak temperature for the calcium carbonate decomposition in nitrogen (but not in carbon dioxide) depends on the bulk density of the sample; thus a pellet decomposes at a higher temperature than the less dense A.R. calcium carbonate powder. These observations can be explained in terms of the bed-depth effect.

7. An inert diluent has little effect on the decomposition temperature, since it causes no increase in the partial pressure of carbon dioxide within the powder bed.

8. The DTG peak temperature varies according to the thermal conductivity of the inert carrier gas; thus it increases in the sequence $H_2 < N_2 < Ar$.

9. The presence of water vapour in the inert carrier gas lowers the decomposition temperature for calcite.

References

1 T. D. Daniels, Thermal Analysis, Kogan Page, 1973.
2 M. I. Pope and M. D. Judd, Differential Thermal Analysis, Heyden & Son Ltd., London 1977.
3 R. C. Mackenzie, Differential Thermal Analysis, Vol.1, Academic Press, London 1970.
4 J. W. Dodd and K. H. Tonge, Thermal Methods, John Wiley & Sons, Chichester 1987.
5 P. Navard and J. M. Haudin, J. Thermal Anal., 29 (1984) 405.
6 R. Courchinoux, N. B. Chanh, Y. Haget, E. Tauler and M. Cuevas-Diarte, Thermochim. Acta, 128 (1988) 45.
7 S. Sarge, S. Bauerecker and H. K. Cammenga, Thermochim. Acta, 129 (1988) 129.
8 C. Sandu and R. K. Singh, Thermochim. Acta, 132 (1988) 89.
9 H. Utschick, B. Gobrecht, C. Fleischhauer, A. Treffurt and H. Müller, J. Thermal Anal., 33 (1988) 297.
10 J. C. Van Miltenburg and M. A. Cuevas-Diarte, Thermochim. Acta, 156 (1989) 291.
11 C. J. Keattch and D. Dollimore, An Introduction to Thermogravimetry, 2nd Ed., Heyden & Son Ltd., London 1975.
12 A. E. Newkirk, Analyt. Chem., 32 (1960) 1558.
13 A. W. Coats and J. P. Redfern, The Analyst, 88 (1963) 906.
14 P. K. Gallagher and D. W. Johnson, Thermochim. Acta, 6 (1973) 67.
15 H. R. Oswald and H. G. Wiedemann, J. Thermal Anal., 12 (1977) 147.
16 K. N. Ninan, J. Thermal Anal., 35 (1989) 1267.
17 F. W. Wilburn, Ph. D. Thesis, University of Salford, 1972.
18 R. Melling, F. W. Wilburn and R. M. McIntosh, Analyt. Chem., 41 (1969) 1275.
19 F. W. Wilburn and J. H. Sharp, unpublished results.
20 F. W. Wilburn and C. V. Thomasson, Phys. Chem. Glasses, 2 (1961) 126.
21 K. V. G. K. Gokhale and T. C. Rao, J. Thermal Anal., 2 (1970) 83.
22 S. St. J. Warne and R. C. Mackenzie, J. Thermal Anal., 3 (1971) 49.
23 F. W. Wilburn, D. Dollimore and J. Crighton,Thermochim Acta, 181 (1991) 191.
24 I. F. Guilliatt and N. H. Brett, J. Mat. Sci., 5 (1970) 615.
25 I. F. Guilliatt and N. H. Brett, J. Brit. Ceram. Soc., 6 (1969) 56.
26 J. H. Sharp, Reaction Kinetics, Chap. 28, Differential Thermal Analysis, Vol. 2, Ed. R. C. Mackenzie, 1972, p. 63.
27 R. A. Rowland and D. R. Lewis, Am. Miner., 36 (1951) 80.
28 R. L. Stone, J. Amer. Ceram. Soc., 37 (1954) 46.

29 J H. Sharp, F. W. Wilburn and R. M. McIntosh, J. Thermal Anal., 37 (1991) 2021.

Zusammenfassung — Bei der Zersetzung von A.R. Calciumcarbonat bzw. Kalkstein wurde der Einfluß der Versuchsparameter, einschließlich Probenmasse, Aufheizgeschwindigkeit, Partikelgröße und Partialdruck von CO_2 auf den Verlauf der TG-, DTG- und DTA-Kurven untersucht. Diese Parameter haben einen deutlichen Einfluß auf DTG und DTA, der sich in beiden Fällen im gleichen Ausmaß bemerkbar macht. Der Einfluß der Masse bzw. Tiefe einer unverdünnten Probe äußert sich in einem Ansteigen des Partialdruckes von Kohlendioxid innerhalb des reagierenden Pulvers und wird als Bett-Tiefen-Effekt bezeichnet. Dieser Effekt kommt in Stickstoff besonders zur Geltung und tritt in Kohlendioxid in den Hintergrund. Inerte Verdünnungsmittel haben einen nur geringen Effekt auf die TG-Kurve aber eine Änderung der Zusammensetzung des inerten Trägergases verursacht Veränderungen, die auf der Wärmeleitfähigkeit des Gases begründet sind. Wasserdampf verursacht, daß DTG- und DTA-Signale bei niedrigeren Temperaturen auftreten.