

## INFLUENCE OF CO<sub>2</sub> PRESSURE ON THE KINETICS OF THERMAL DECOMPOSITION OF PbCO<sub>3</sub>

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### ABSTRACT

Kinetic analysis has been performed on TG and DTG diagrams for the reaction  $\text{PbCO}_3 \rightarrow \text{PbO} + \text{CO}_2$  recorded at different pressures of CO<sub>2</sub> up to 20 kPa. The results obtained show that the thermal decomposition of PbCO<sub>3</sub> at pressures of CO<sub>2</sub> lower than 20 kPa takes place via the following two steps:  $\text{PbCO}_3 \rightarrow \text{PbCO}_3 \cdot 2\text{PbO} \rightarrow \text{PbO}$ . The lack of reliable data on the equilibrium pressures for these two consecutive reactions does not allow a kinetic analysis on the TG and DTG data to be performed. The fact that there are literature reports of other by-products from the thermal decomposition of PbCO<sub>3</sub> under open atmosphere, in addition to that found here, has been interpreted by considering the mass transfer phenomena of CO<sub>2</sub> through the sample.

### INTRODUCTION

A number of authors [1–5] have paid attention to the study of the thermal decomposition of carbonates having calcite–aragonite structure, because of

TABLE 1

Kinetic data on the thermal decomposition of PbCO<sub>3</sub> selected from the literature

Reaction	Atmosphere	Mechanism	<i>E</i> (kJ mol <sup>-1</sup> )	Ref.
PbCO <sub>3</sub> → PbO	Vacuum	R <sub>3</sub>	168	6
PbCO <sub>3</sub> → PbO	Air	R <sub>3</sub>	173	7
PbCO <sub>3</sub> → PbCO <sub>3</sub> · 2PbO	Air	Zero order	71	8
PbCO <sub>3</sub> · 2PbO → PbO	Air	Zero order	92	8
PbCO <sub>3</sub> → PbCO <sub>3</sub> · 2PbO	Air	F <sub>1</sub> (α)	118	9
PbCO <sub>3</sub> · 2PbO → PbO	Air	F <sub>1</sub> (α)	234	9
PbCO <sub>3</sub> → PbO	N <sub>2</sub>	R <sub>3</sub>	267	10
PbCO <sub>3</sub> → PbCO <sub>3</sub> · PbO	CO <sub>2</sub> –N <sub>2</sub>	D <sub>1</sub>	360–473	11
PbCO <sub>3</sub> · PbO → PbCO <sub>3</sub> · 2PbO	CO <sub>2</sub> –N <sub>2</sub>	D <sub>1</sub>	339–699	11
PbCO <sub>3</sub> · 2PbO → PbO	CO <sub>2</sub> –N <sub>2</sub>	D <sub>1</sub>	406–980	11

the interest of these materials both in ceramic reactions and as starting materials for the preparation of oxides. There are a number of papers [6–11] on  $\text{PbCO}_3$ , the results of which are summarized in Table 1. This Table completes and updates the data reported by Brown et al. [12].

Table 1 shows the lack of agreement among the kinetic parameters obtained by different authors. This behaviour could be explained by considering the influence of the  $\text{CO}_2$  generated during the salt decomposition which is strongly dependent on the experimental conditions [13,14].

The scope of the present paper is to study the influence of the  $\text{CO}_2$  pressure on the thermal decomposition of  $\text{PbCO}_3$  in order to achieve a better understanding of the reaction mechanism.

## EXPERIMENTAL

$\text{PbCO}_3$  (Merck a.r.) was used as received. DTG curves were obtained by using a Cahn electrobalance, model RG, equipped with a derivation adapter Mark II. This system permits work in both high vacuum and under a gas atmosphere. TG and constant rate thermal analysis (CRTA) diagrams were recorded using a Mettler thermoanalyser which allows a vacuum better than  $2.6 \times 10^{-7}$  kPa, and permits a constant decomposition rate to be maintained.

## RESULTS AND DISCUSSION

### *Kinetics of the thermal decomposition of $\text{PbCO}_3$ under vacuum*

Figure 1 shows the CRTA curve obtained for  $\text{PbCO}_3$ . A cyclic CRTA curve was also recorded in order to obtain additional kinetic information; by way of example, Fig. 2 shows one of the cycles. The total weight loss recorded has shown that the thermal decomposition of  $\text{PbCO}_3$  takes place in a single step yielding  $\text{PbO}$  as the final product, in agreement with the X-ray diffraction analysis.

The CRTA data have been analysed by means of the following kinetic equation developed elsewhere [15]:

$$\ln(1/f(\alpha)) = \ln(A/C) - E/(RT) \quad (1)$$

where  $\alpha$  is the reacted fraction at the time  $t$ ;  $f(\alpha)$  is a function depending on the reaction mechanism;  $C$  is the constant decomposition rate previously selected;  $A$  is the Arrhenius pre-exponential factor;  $E$  is the activation energy;  $R$  is the gas constant and  $T$  the absolute temperature.

In the case of the cyclic CRTA experiment carried out under the conditions described above, the two states of the sample to be compared in a

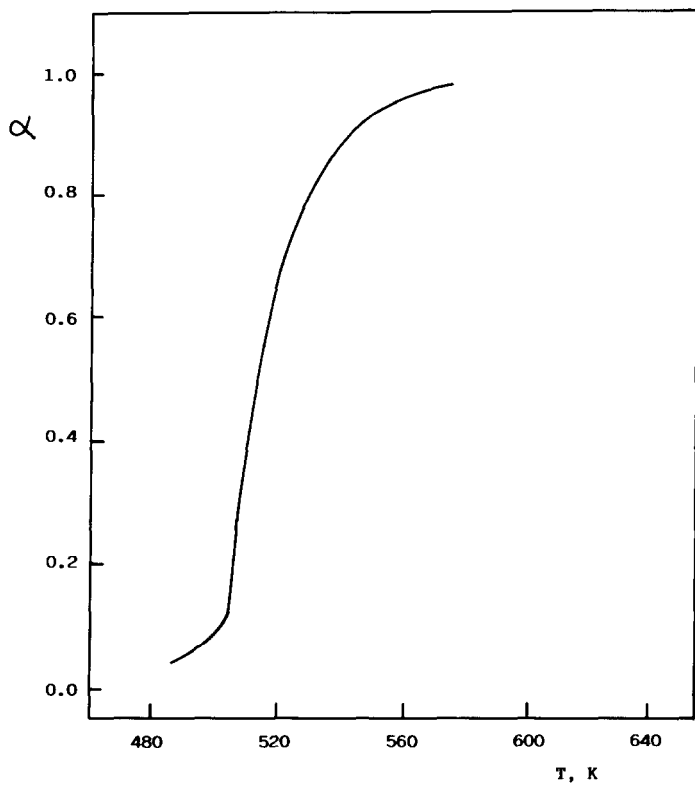


Fig. 1. CRTA curve for  $\text{PbCO}_3$ .

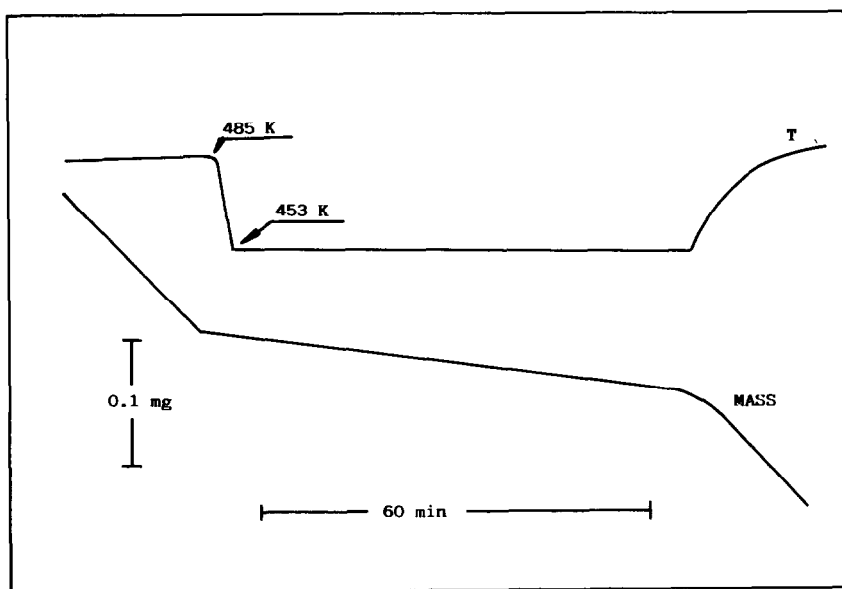


Fig. 2. Cyclic CRTA curve for  $\text{PbCO}_3$ .

particular cycle have almost the same reacted fraction. Thus, the activation energy can be calculated without prior knowledge of the actual reaction mechanism [16] by means of the following expression, which can easily be derived from eqn. (1):

$$\ln(C_1/C_2) = -E/R(1/T_1 - 1/T_2) \quad (2)$$

where  $C_1$  and  $C_2$  are the two rates in the cycle which correspond to the temperatures  $T_1$  and  $T_2$ , respectively.

The kinetic analysis of the cyclic CRTA diagram of  $\text{PbCO}_3$  has pointed out that the activation energy is independent of the reacted fraction over the whole range investigated. An activation energy,  $E = 121 \text{ kJ mol}^{-1}$ , has been obtained from the mean value of fifteen determinations carried out in the range  $0.1 \leq \alpha \leq 0.9$ . This value of the activation energy only agrees with the one determined from the kinetic analysis of the corresponding CRTA curve included in Fig. 1 if it is assumed that the thermal decomposition of  $\text{PbCO}_3$  fits first-order kinetics (decay law) (i.e.,  $f(\alpha) = 1 - \alpha$ ).

The above results show that the activation energy and the Arrhenius pre-exponential factor of the thermal decomposition of  $\text{PbCO}_3$ , calculated from CRTA data, are independent of both the starting sample weight,  $W_i$ , and the constant rate selected,  $C$ , over all the range investigated ( $W_i \leq 100 \text{ mg}$  and  $10^{-4} \text{ min}^{-1} \leq C \leq 10^{-3} \text{ min}^{-1}$ ). This fact points out that the kinetic parameters obtained do not seem to be influenced by heat and/or mass transfer phenomena, which is in good agreement with previous works [17] which stated that the CRTA technique leads to a more effective control of these phenomena than conventional TG.

In order to check the above statement, it was considered of interest to perform the kinetic analysis of the series of TG and DTG curves shown in Figs. 3 and 4 which were recorded in a wide range of sample weights and/or heating rates,  $\beta$ . The kinetic analysis of these curves has been carried out by the method of Coats and Redfern [18]:

$$\ln[g(\alpha)/T^2] = \ln[AR/(E\beta)] - E/(RT) \quad (3)$$

where  $g(\alpha) = \int_0^\alpha [d\alpha/f(\alpha)]$  is a function depending on the reaction mechanism. Taking into account the previous results from CRTA experiments, a first order kinetic law was assumed to hold [i.e.,  $g(\alpha) = -\ln(1 - \alpha)$ ] for determining the kinetic parameters of the thermal decomposition of  $\text{PbCO}_3$  from TG and DTG curves. The results obtained are included in Table 2. These data point out that the activation energy and the Arrhenius pre-exponential factor are strongly dependent on the sample size and the heating rate. It is noteworthy that it has not been possible to obtain from TG data an activation energy which is independent of these two experimental parameters, even by using the lower values of sample weight and heating rate allowed by the experimental equipment used in the present work.

In summary, we can conclude from the above results that the CRTA technique leads to more reliable kinetic data than the conventional TG or

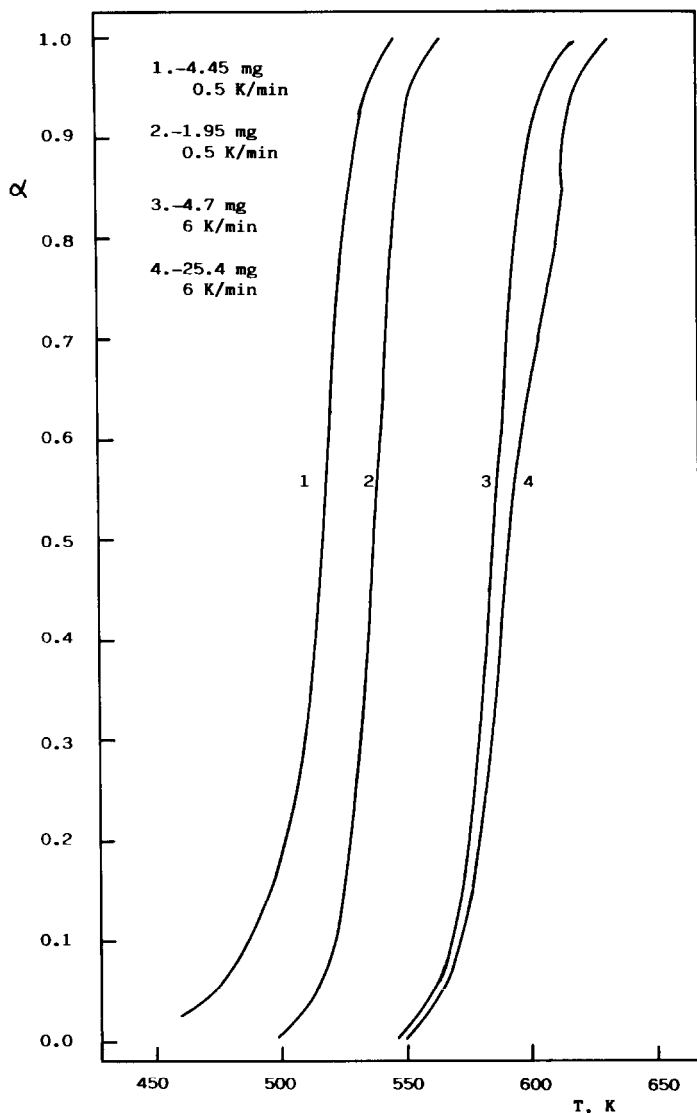


Fig. 3. TG curves of the thermal decomposition of  $\text{PbCO}_3$  in vacuum.

DTG methods. In other words, these two techniques do not allow the influence of the  $\text{CO}_2$  generated in the reaction to be avoided, even for small samples, while the CRTA method leads to kinetic parameters independent of the sample weight for a range of more than 100 mg. The TG and DTG data in Figs. 3 and 4 probably do not correspond to the single step represented by the equation  $\text{PbCO}_3 \rightarrow \text{PbO} + \text{CO}_2$ , but are more likely the result of the overlapping of two processes giving  $\text{PbO}$  as the final product. The fact that a shoulder is observed in Fig. 3, when the TG of  $\text{PbCO}_3$  is

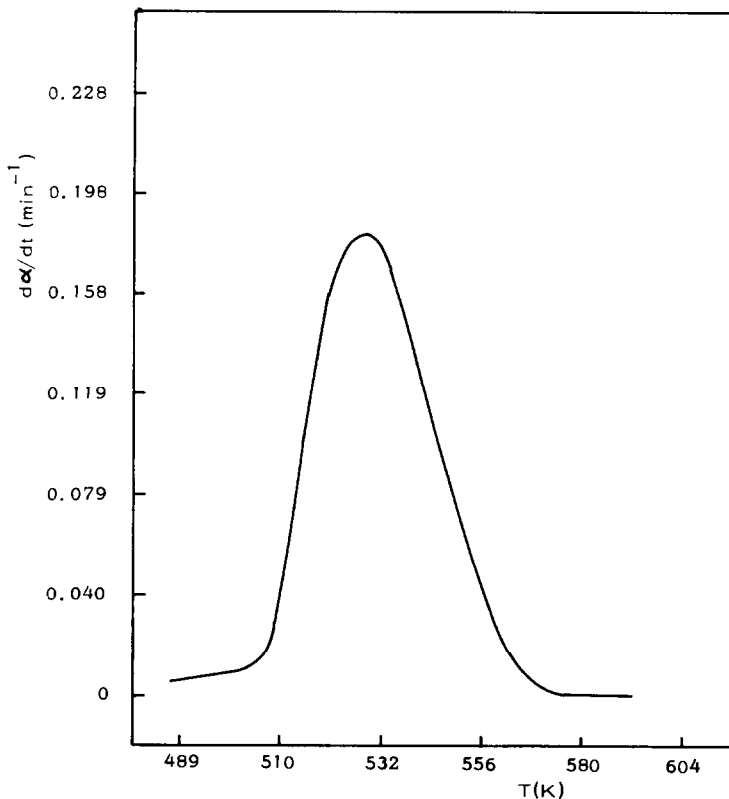


Fig. 4. DTG curve of the thermal decomposition of  $\text{PbCO}_3$  in vacuum.

recorded by using both relatively high sample weight and heating rate, seems to support the above statement. The study of the thermal decomposition of  $\text{PbCO}_3$  under a  $\text{CO}_2$  atmosphere would be interesting in order to clarify the mechanism of this reaction.

TABLE 2

Kinetic parameters of the thermal decomposition of  $\text{PbCO}_3$  calculated from TG and DTG data (integral method) obtained in vacuum using different sample weights and/or experimental equipment and heating rate by assuming a first-order kinetic law

Equipment	Sample weight (mg)	Heating rate ( $\text{K min}^{-1}$ )	$E$ ( $\text{kJ mol}^{-1}$ )	$A$ ( $\text{min}^{-1}$ )	Regress. coeff.
Mettler thermobalance	1.95	0.5	238	$5 \times 10^{21}$	-0.9971
Mettler thermobalance	4.45	0.5	163	$8 \times 10^{14}$	-0.9974
Mettler thermobalance	4.70	6	259	$5 \times 10^{22}$	-0.9974
Mettler thermobalance	25.42	6	162	$4 \times 10^{13}$	-0.9896
Cahn electrobalance	23	6	211	$1 \times 10^{20}$	-0.9937

*Kinetics of the thermal decomposition of PbCO<sub>3</sub> under CO<sub>2</sub> pressure*

The results shown in Figs. 5 and 6 point out that the stoichiometry of the thermal decomposition of PbCO<sub>3</sub>, at pressures of CO<sub>2</sub> up to 20 kPa, is consistent with the following steps:



These results are supported by the X-ray diffraction analysis of the samples, quenched from temperatures at which the first step of the DTG traces, in Figs. 5 and 6, is complete. These results are in close agreement with those reported by Yamaguchi et al. [19] who concluded that cerussite decomposes to PbO through PbCO<sub>3</sub> · 2PbO as the only intermediate at pressures lower than 1 atm, while at pressures close to 1 atm, the by products are PbCO<sub>3</sub> · PbO and PbCO<sub>3</sub> · 2PbO. These data disagree with those reported by Ball and Casson [20] who have concluded that these two intermediates are formed at a CO<sub>2</sub> pressure of 10 kPa. However, it is noteworthy to point out that the CO<sub>2</sub> pressure to which Ball and Casson refer is the partial one in CO<sub>2</sub>/N<sub>2</sub> mixtures at 1 atm of total pressure. It would be expected that, in such

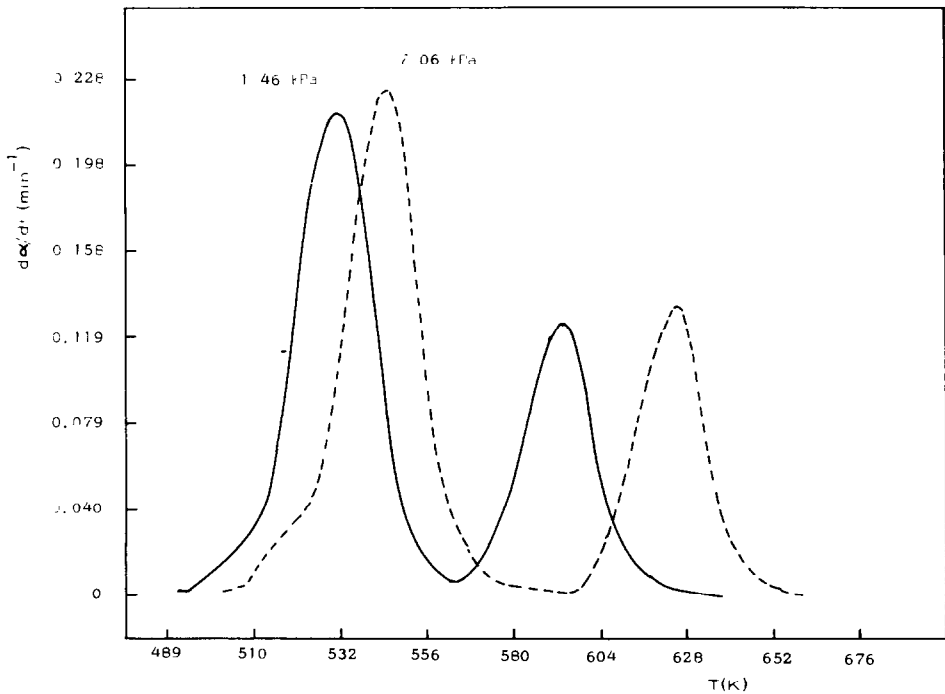


Fig. 5. DTG curves of the thermal decomposition of PbCO<sub>3</sub> under CO<sub>2</sub> pressure.

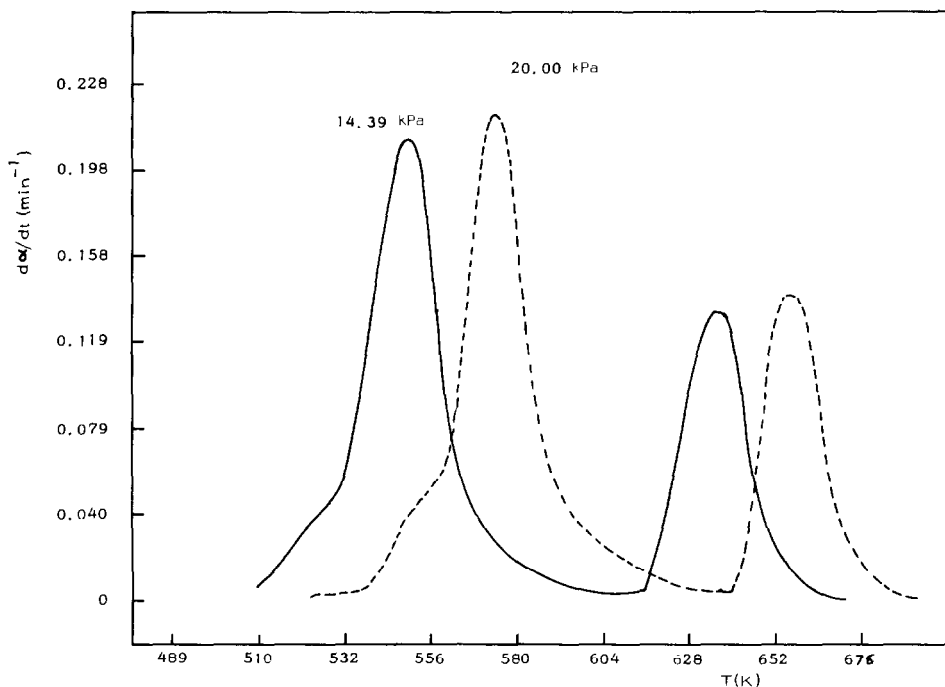
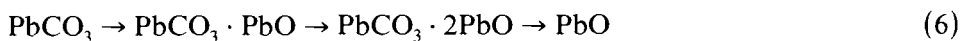


Fig. 6. DTG curves of the thermal decomposition of  $\text{PbCO}_3$  under  $\text{CO}_2$  pressure.

conditions, the  $\text{CO}_2$  self generated in the reaction would raise the pressure of  $\text{CO}_2$  in the close vicinity of the sample towards values much higher than the initial partial pressure. It has been shown in a previous paper [21] that the  $\text{CO}_2$  generated during the thermal decomposition of carbonates, under nitrogen or helium atmosphere, would raise the partial pressure of  $\text{CO}_2$  surrounding the sample to values similar to the total external pressure.

The above considerations explain the fact that some workers [22] have found the thermal decomposition of  $\text{PbCO}_3$  under air or nitrogen atmosphere to take place according to eqns. (4) and (5), while others [20] have concluded that their results must be interpreted in terms of the following reaction scheme:



In fact these two different results can be easily interpreted by considering that the pressure exerted around the sample by the  $\text{CO}_2$  self generated in the reaction is strongly dependent on the experimental conditions.

It is noteworthy to point out that Maciejewski and Leyko [23] have studied the thermal decomposition of cerussite under  $\text{CO}_2$  pressure and reported the following intermediates:  $5\text{PbCO}_3 \cdot \text{PbO}$ ,  $2\text{PbCO}_3 \cdot \text{PbO}$ ,  $7\text{PbCO}_3 \cdot 5\text{PbO}$ ,  $\text{PbCO}_3 \cdot \text{PbO}$  and  $\text{PbCO}_3 \cdot 2\text{PbO}$ . None of these intermediates have been supported by X-ray evidence. Grisafe and White [24]



give only four intermediates at pressures of  $\text{CO}_2$  in the range 15–1400 bars:  $2\text{PbCO}_3 \cdot \text{PbO}$ ,  $\text{PbCO}_3 \cdot \text{PbO}$ ,  $4\text{PbCO}_3 \cdot 3\text{PbO}$  and  $\text{PbCO}_3 \cdot 2\text{PbO}$ . According to Ball and Casson [20] some of the intermediates postulated by Maciejewski and Leyko [23] could be explained in terms of the effect of the  $\text{CO}_2$  pressure on the decomposition rate of  $\text{PbCO}_3 \cdot \text{PbO}$ .

On the other hand it is noteworthy to point out that there is a strong disagreement between the values reported by Peretti [25], Grisaffe and White [24], Ball and Casson [20] and Yamaguchi et al. [19] for the dissociation pressures of  $\text{CO}_2$  of the reactions represented by eqns. (4) and (5).

As far as there is no reliable data available on the dissociation pressure for intermediates of the thermal decomposition of  $\text{PbCO}_3$ , it has not been possible to carry out, in a proper way, the kinetic analysis of data in Figs. 5 and 6 taking into account the microreversibility principle.

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