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THE DIFFERENTIAL THERMAL ANALYSIS OF CERUSSITE

S. St. J. Warne and P. Bayliss, *Department of Applied Geology, University of New South Wales, Kensington, Australia.*

Abstract

The differential thermal analysis curve of cerussite ($PbCO_3$) of high purity and known chemical composition is shown to be controlled by the following independent variables; (a) dilution with inert material, (b) composition of furnace atmosphere, (c) heating rate, (d) uniformity of sizing, and (e) particle size. The six separate reactions distinguished in this work have been attributed to the following:

(1) $2PbCO_3 \rightarrow PbO \cdot PbCO_3 + CO_2\uparrow$ at 340° C.
(2) $3(PbO \cdot PbCO_3) \rightarrow 2(2PbO \cdot PbCO_3) + CO_2\uparrow$ at 390° C.
(3) $2PbO \cdot PbCO_3 \rightarrow 3PbO + CO_2\uparrow$ at 440° C.
(4) $6PbO + O_2 \rightarrow 2Pb_3O_4$ at 460° C.
(5) $2Pb_3O_4 \rightarrow 6PbO + O_2\uparrow$ at 550° C.
(6) $PbO_{(solid)} \rightarrow PbO_{(liquid)}$ at 880° C.

Introduction

A literature review by Kelley and Anderson (1935) on the thermodynamic properties of lead carbonate points out that some investigators have postulated these reactions:

(1a) $8PbCO_3 \rightarrow 3PbO \cdot 5PbCO_3 + 3CO_2\uparrow$
(1b) $3PbO \cdot 5PbCO_3 \rightarrow 4(PbO \cdot PbCO_3) + CO_2\uparrow$
(2) $3(PbO \cdot PbCO_3) \rightarrow 2(2PbO \cdot PbCO_3) + CO_2\uparrow$
(3) $2PbO \cdot PbCO_3 \rightarrow 3PbO + CO_2\uparrow$

Bruzs (quoted by Kelley and Anderson, 1935) found evidence for only two reactions:

(1) $2PbCO_3 \rightarrow PbO \cdot PbCO_3 + CO_2\uparrow$
(2) & (3) $PbO \cdot PbCO_3 \rightarrow 2PbO + CO_2\uparrow$

However the International Critical Tables (1930), Lamure (1953) and Peretti (1957) indicate the existence of three reactions:

(1) $2PbCO_3 \rightarrow PbO \cdot PbCO_3 + CO_2\uparrow$
(2) $3(PbO \cdot PbCO_3) \rightarrow 2(2PbO \cdot PbCO_3) + CO_2\uparrow$
(3) $2PbO \cdot PbCO_3 \rightarrow 3PbO + CO_2\uparrow$

Other investigators, namely Cuthbert and Rowland (1947), Kauffman and Dilling (1950), Beck (1950), Gruver (1950) and Collins and Swan (1954), leave several points in the differential thermal analysis of cerussite either unexplained or very much in doubt. These may be summarised as follows:

1. It is not clear whether the two or three endothermic peaks of the differential thermal analysis curve represent two or more reactions in

the complete dissociation of lead carbonate to lead monoxide and carbon dioxide.

2. If the three intermediate oxy-carbonates (indicated in equations above) form during the decomposition of lead carbonate, then the differential thermal analysis curve should show four endothermic peaks. The literature lists only three peaks, but no serious systematic attempt has been made to obtain a fourth peak.

3. Collins and Swan (1954) found that the three endothermic decomposition peaks are only produced if a heating rate below 6° C. per minute is used. However, Kauffman and Dilling (1950) obtained three similar peaks with a heating rate of 10 to 12° C. per minute.

4. Beck (1950) obtained one small exothermic and one small endothermic peak on the differential thermal analysis curve, after the complete decomposition of the lead carbonate had taken place, *i.e.* between approximately 505 and 580° C. These peaks were not commented upon by Beck, nor even recorded by the previous workers.

5. Beck (1950) does not show the existence of any peak in the region of 880° C., whereas Cuthbert and Rowland (1947) consider the presence of a reaction at this temperature to be due to the breakdown of the third oxy-carbonate. On the other hand, Kauffman and Dilling (1950), Gruver (1950) and Collins and Swan (1954) attribute this reaction to the melting of lead oxide.

Because of these discrepancies in the published reports of the differential thermal analysis of cerussite, it has been decided to investigate the effect of some controllable variables[1] on the curves obtained during the differential thermal analyses of samples of this mineral of known chemical composition. The variables, in order of study, are as follows:

(a) dilution with inert material
(b) composition of furnace atmosphere
(c) heating rate
(d) uniformity of sizing
(e) particle size

The results of these experiments have provided additional data concerning the nature of the decomposition reactions, which are discussed in detail below.

EXPERIMENTAL PROCEDURE

Loughnan (1960) has described fully the differential thermal analysis apparatus used throughout this study. Briefly, it consists of a Roberts

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[1] Many controllable variables are known to cause gross modifications to differential thermal analysis curves, Bayliss and Warne (1962).

and Grimshaw type furnace containing an alumina block and sample holder and a Leeds and Northrup x-y Speedomax which continuously records furnace temperature against the difference in temperature between the sample and the calcined alumina reference material. The furnace heating rate is controlled by a Leeds and Northrup type P.A.T. 50 three-element program controller. The various dynamic furnace atmospheres are maintained by a two-liter-per-minute gas flow through a finely tapered nozzle which communicates with the furnace interior by means of a hole drilled through the alumina block. The effectiveness of this method has been demonstrated by the complete suppression of the exothermic oxidation reaction of an uncovered siderite sample in a dynamic nitrogen atmosphere (Warne, 1961).

The thermogravimetric analyses are obtained from a Stanton thermobalance which heats the sample at a constant and predetermined rate, while continuously and automatically recording sample weight against temperature.

EFFECTS OF VARIABLES

The differential thermal analysis curve of cerussite was established from three chemically pure samples (Table 1 for chemical composition) at −200 mesh, with a heating rate of 15° C. per minute and a static air atmosphere. The resultant curves are almost identical (Fig. 1A). The two major peaks below 600° C., hereafter called the "340° C." peak and the "440° C." peak, agree with the curves published by Cuthbert and Rowland (1947), Beck (1950), Gruver (1950) and Collins and Swan

TABLE 1. CHEMICAL ANALYSES OF CERUSSITE SAMPLES NO. 1, 2 AND 3

	Sample No. 1[1]	Sample No. 2[2]	Sample No. 3[3]
$PbCO_3$	99.69%	98.09%	99.37%
$ZnCO_3$		0.40%	
FeO	0.20%		
SiO_2		1.46%	
Total	99.89%	99.95%	99.37%

Samples obtained respectively from: (1) The Western Australian Government Chemcal Laboratories No. S1212 (locality, Northampton, West. Australia); (2) the Australian Museum No. D2104 (locality, Broken Hill, Australia); (3) Australian Museum unregistered material (locality unknown).

Chemical analyses carried out by:

[1] The Western Australian Government Chemical Laboratories.

[2] The New South Wales Mines Department.

[3] The University of New South Wales.

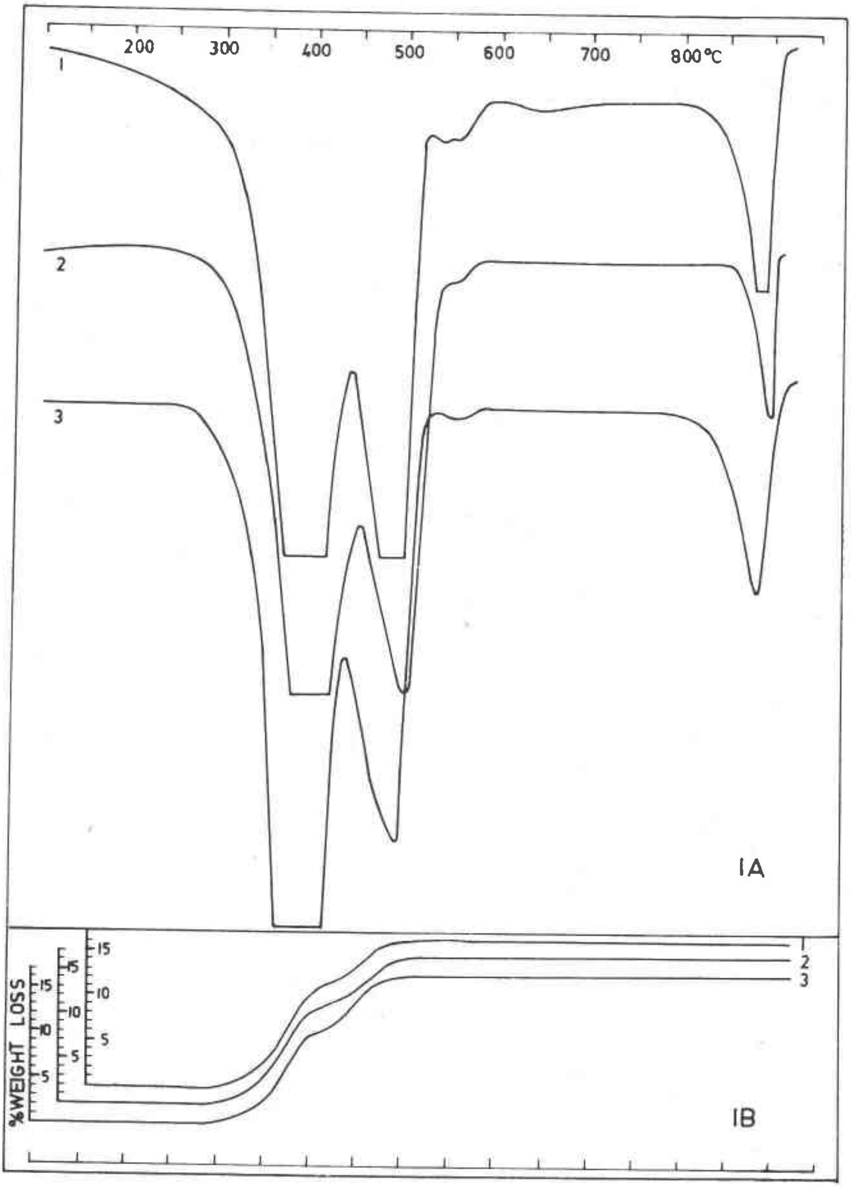


FIG. 1. 1A. Differential thermal analysis curves of different samples of cerussite, Nos. 1 to 3.

1B. Thermogravimetric analysis curves of cerussite samples, Nos. 1 to 3. In all cases at −200 mesh, heating rate 15° C. per minute, in a static furnace atmosphere of air.

(1954). A third endothermic peak, hereafter called the "390° C." peak, situated between the "340° C." and "440° C." peaks, has been recorded by Kauffman and Dilling (1950). The two minor fluctuations, one exothermic and one endothermic, hereafter called the "460° C." and "550° C." peaks, respectively, have been produced only by Beck (1950). The existence of the major endothermic peak, hereafter called the "880° C." peak, was confirmed, but since this reaction is detrimental to the thermocouples, all other differential thermal analysis curves have been taken to only 650° C.

The thermogravimetric analyses obtained in an atmosphere of air with the same heating rate of 15° C. per minute as used for the differential thermal analyses, have shown the formation of only one intermediate product $2PbO \cdot PbCO_3$ which agrees with the results of Nicol (1948) and Lamure (1953) (Fig. 1B).

Increased sample dilution with calcined alumina shows only a progressive decrease in intensity and temperature of the peaks (Fig. 2) which is in agreement with the work of Kulp *et al.* (1951) for calcite, and Rowland and Jonas (1949) for siderite.

A comparison of the differential thermal analysis curves obtained in atmospheres of oxygen and air (Fig. 3, curves 1 and 2) shows the "460° C." peak apparently truncating and significantly reducing the intensity of the "440° C." peak. In addition the "550° C." peak is greatly enlarged, while its peak temperature has moved up scale to 630° C. The only observable effect of an argon atmosphere was a greater overlap of the "340° C." and "440° C." peaks (Fig. 3, curve 3). On the other hand, carbon dioxide (Fig. 3, curve 4) has increased the separation of the "340° C." and "440° C." peaks. Also the initiation of the reaction was much later, but more vigorous, than when determined in atmospheres of air, oxygen and argon.

Because of the numerous independent variables it has been necessary to initially establish the optimum heating rate for the production of the "390° C." peak. Preliminary investigations aimed at obtaining and locating the "390° C." peak indicated that the optimum heating rate is approximately 2° C. per minute.

The conditions governing the maximum separation of the "340° C." and "440° C." peaks and the strongest development of the "390° C." peak have been independently established, thus the uniformity of sizing and particle size experiments have been carried out under these conditions, *i.e.* with a heating rate of 2° C. per minute in an atmosphere of carbon dioxide.

The effects of uniform sizing were examined by gradually decreasing the size range limits of the samples, *i.e.*, -100 mesh$+0$, $-100+200$ mesh

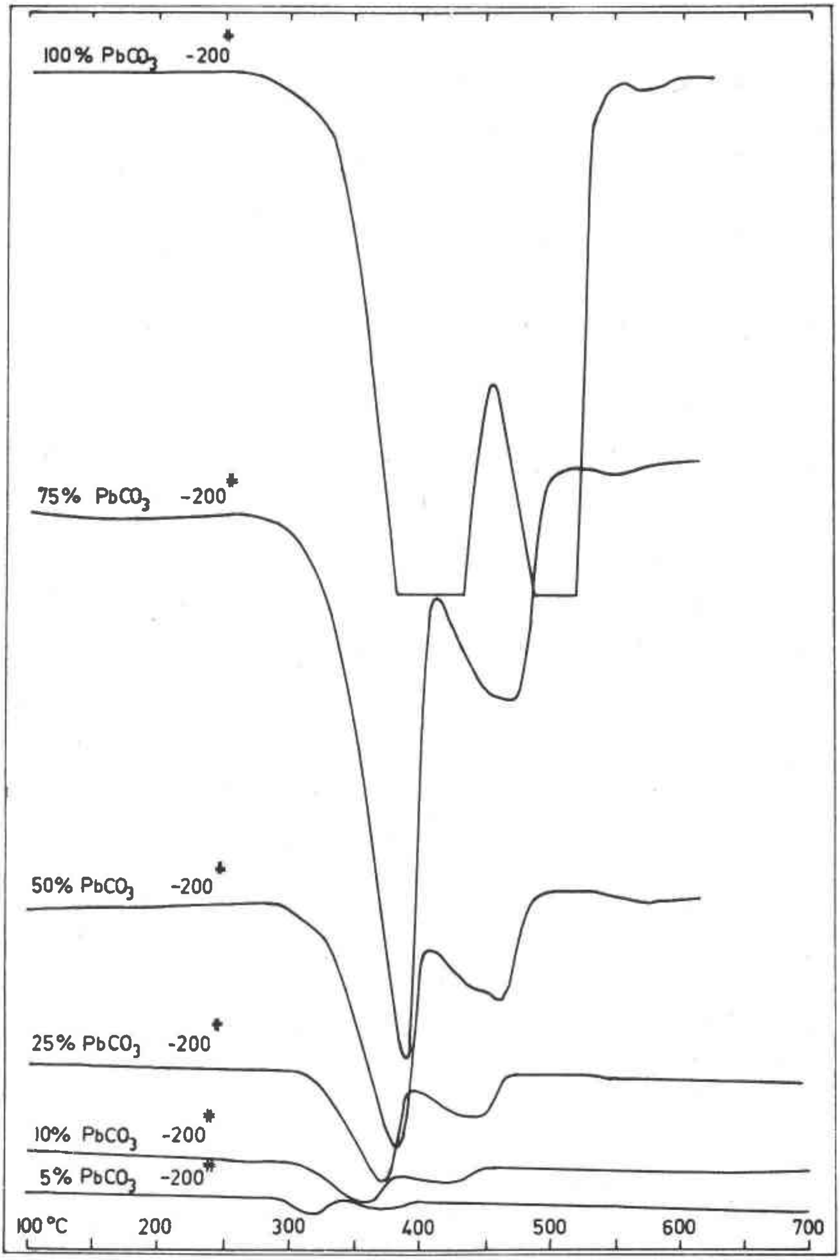
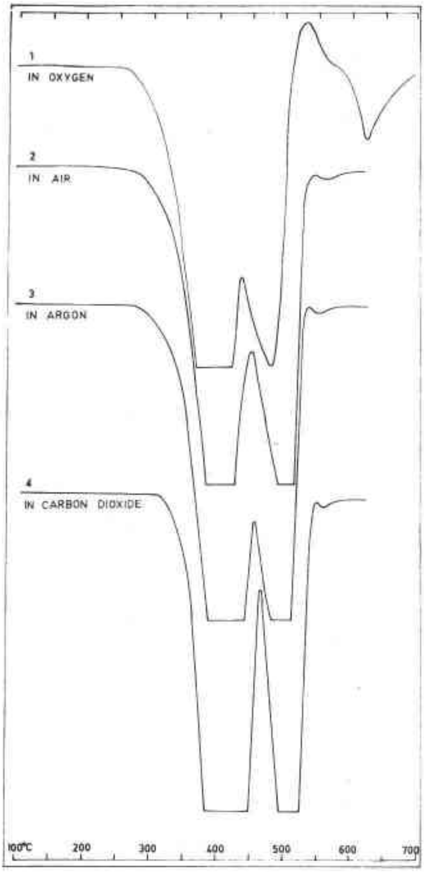


FIG. 2. The effects of progressive dilution with Al_2O_3 on the differential thermal analysis of cerussite sample No. 3 at −200 mesh, heating rate 15° C. per minute, in a dynamic furnace atmosphere of carbon dioxide gas.



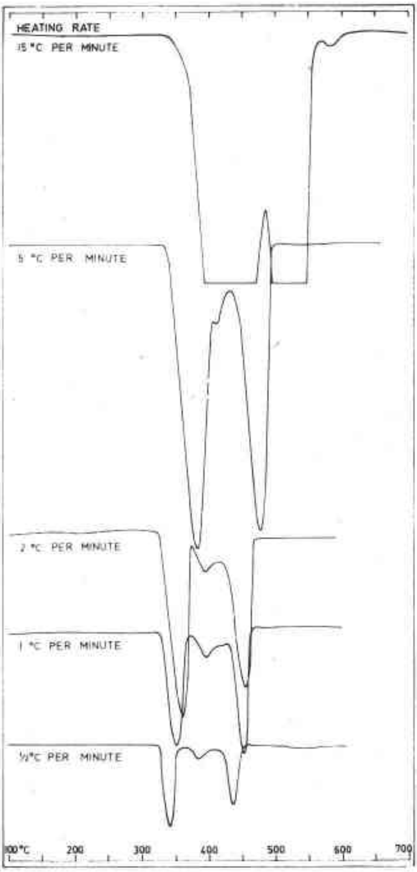


FIG. 3. (left) Effect of different dynamic furnace atmospheres on the differential thermal analysis of sample No. 3 at −200 mesh, heating rate 15° C. per minute.

FIG. 4. (right) The effect of heating rate on the differential thermal analysis of sample No. 3, on the optimum particle size fraction (−100 mesh +150 mesh) in a dynamic furnace atmosphere of carbon dioxide gas.

and −100+150 mesh B.S.S.[1] Differential thermal analyses of these samples have indicated a gradual but marked increase in the "390° C." peak with decrease in size fraction limits (Fig. 5). Inasmuch as the importance of uniform sizing of the sample is established the question of which particle size would produce the greatest enlargement of the "390° C." peak was investigated. The results obtained from −36 +50 mesh, −80 +100 mesh, −100 +150 mesh and −150 +200 mesh fractions in an atmosphere of carbon dioxide, with a heating rate of 2° C.

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[1] British Standard Sieves have been used throughout.

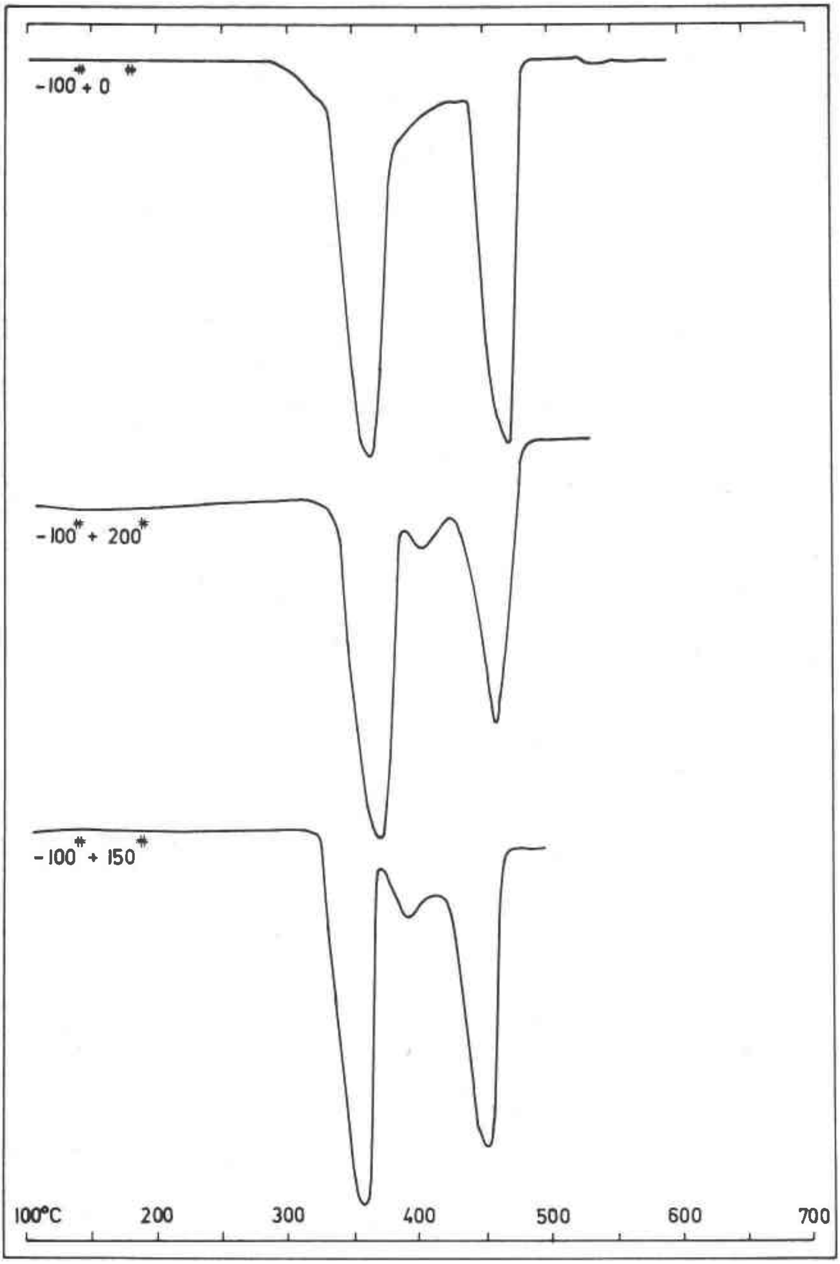

FIG. 5. The effects of increase in uniformity of sizing on the differential thermal analysis of sample No. 3 in a dynamic furnance atmosphere of carbon dioxide gas. Heating rate 2° C. per minute.

per minute, have indicated that the −100 +150 mesh fraction produces the maximum development of the "390° C." peak (Fig. 6).

The optimum heating rate required to produce the maximum development of the "390° C." peak from the −100 +150 mesh fraction, in an atmosphere of carbon dioxide, has been determined by a comparison of the curves obtained with heating rates of 15, 5, 2, 1 and $\frac{1}{2}$° C. per minute (Fig. 4). The 2° C. per minute heating rate (Fig. 4, curve 3) produces the best results and confirms the conclusion of the preliminary investigation.

Various furnace atmospheres cause significant modifications to the differential thermal analysis curve; therefore the effects of this variable have been re-evaluated under the established "optimum" conditions of heating the −100 +150 mesh fraction at 2° C. per minute. A comparison of the resultant curves (Fig. 7) shows greater modifications than those obtained under "non-optimum" conditions (Fig. 3). In air (Fig. 7, curve 1) the "440° C." peak appears appreciably foreshortened and truncated, whereas the "550° C." peak is only just noticeable. Similar truncation effects appear intensified in oxygen (Fig. 7, curve 2) as the "390° C." and "440° C." peaks are reduced by the greatly enlarged "460° C." exothermic peak. In addition the "550° C." peak is intensified and occurs at a higher temperature, *i.e.* 610° C. In an atmosphere of argon (Fig. 7, curve 4) apparently only two endothermic reactions can be differentiated.

Discussion and Conclusions

The differential thermal analysis curve of pure cerussite of known chemical composition appears to be the composite result of five endothermic and one exothermic reactions.

The three endothermic peaks at "340° C." "390° C." and "440° C." (Fig. 4, curve 5) have relative peak heights of "340° C.">"440° C.">"390° C.", which are in general agreement with the data in the International Critical Tables (1930) in respect to the number and intensity ratios of 3:2:1 respectively of the decomposition reactions.

Thermogravimetric analyses (Fig. 1B), determined under the same conditions as the differential thermal analysis curve in Fig. 1A, have shown two reactions with approximate magnitude ratios of 2:1. This indicates a combination of the "340° C." and "390° C." peaks, which is verified by curve 2, Fig. 4, where these two peaks can be seen to be superimposed.

The data in this study thus provide evidence for only two intermediate oxy-carbonates in the thermal decomposition mechanism of lead carbonate to lead monoxide and carbon dioxide. The data of Bruzs (stated by Kelley and Anderson, 1935) indicate the existence of only one inter-

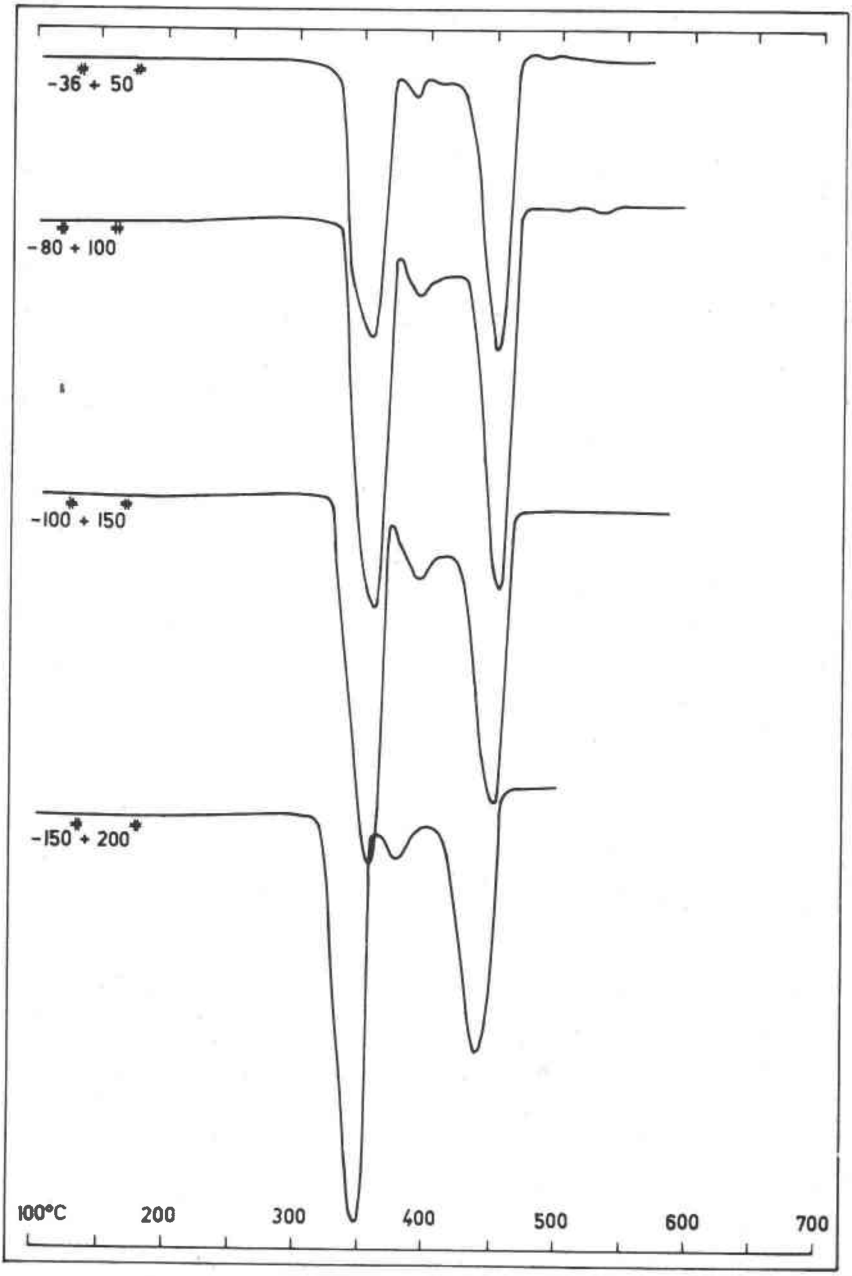

FIG. 6. The effect of particle sizes on the differential thermal analysis of sample No. 3. Heating rate of 2° C. per minute in a dynamic furnace atmosphere of carbon dioxide gas.

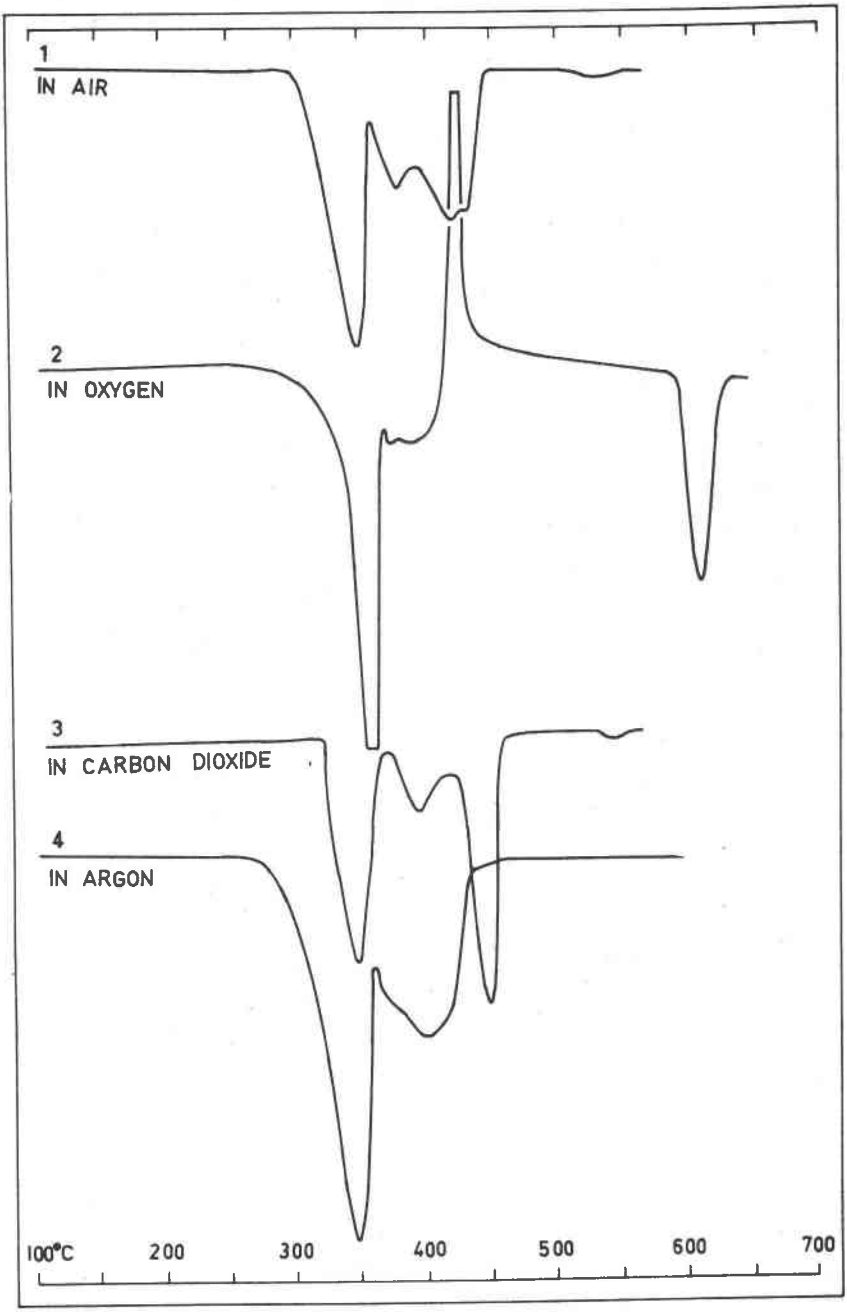

FIG. 7. The effects of different types of dynamic furnance atmospheres on the differential thermal analysis of sample No. 3, at the optimum particle size and heating rate (−100 +150 mesh, 2° C. per minute).

mediate oxy-carbonate ($PbCO_3 \cdot PbO$), which on the evidence above would be the first oxy-carbonate formed. However this decomposes to a second oxy-carbonate before a final dissociation forms lead oxide.

No evidence for the existence of the first of the three oxy-carbonates postulated by some investigators, as stated by Kelley and Anderson (1935), has been found, despite the systematic examinations of the effects of variables, using the techniques described in this study.

The configuration of this curve is not only dependent on the heating rate, but is also markedly influenced by variations in sizing, size fractions and furnace atmospheres.

The "390° C." peak is obtained by heating a −100 +150 mesh fraction at 5° C. per minute (Fig. 4, curve 2), but with the −100 mesh fraction this peak does not appear, even when a heating rate as low as 2° C. per minute is used (Fig. 5, curve 1).

These major variations which are caused by combinations of the variables are considered sufficient to account for the fact that Kauffman and Dilling (1950) obtained the "390° C." peak with a heating rate of 10 to 12° C. per minute and that Collins and Swan (1954) have only produced the peak with heating rates below 6° C. per minute.

The "460° C." and "550° C." peaks (Fig. 3, curve 1) are considered to be due to the oxidation and subsequent reduction of lead monoxide, as shown by the reversible reactions:

$$(4 \text{ and } 5) \cdots 6PbO + O_2 \rightleftharpoons 2Pb_3O_4.$$

Sherwood Taylor (1943) states that lead monoxide will oxidize slowly below 550° C., but will be reduced again above 550° C. In view of this it would be expected that under conditions of optimum oxygen availability and slow heating rate, these two peaks would become greatly enlarged on the differential thermal analysis curve. Verification of this is shown by curve 2, Fig. 7, where such enlargements can be seen to have taken place at a slow heating rate in an atmosphere of oxygen. The displacement of the "550° C." peak to 610° C. and its enlargement are attributed to the increased partial pressure of oxygen which inhibits the decomposition of Pb_3O_4 until a higher temperature has been reached, together with breakdown of the increased proportion of Pb_3O_4 resulting from optimum oxygen availability.

The Handbook of Chemistry and Physics (1960) lists the melting point of lead monoxide as 888° C., which strongly suggests that the "880° C." peak (Fig. 1A) on the differential thermal analysis curve is due to melting. The probable correctness of this view has been confirmed by visually noting the modification and melting of a cone of powdered cerussite in the furnace of the thermogravimetric balance on several occasions, by rapid removal and replacement of the furnace cap at regularly increasing temperatures in the range 800° C. to 900° C.

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