Thermochimica Acta, 9 (1974) 409–418

DISSOCIATION OF ALKALINE-EARTH TRIPLE CARBONATES IN THE PRESSURE RANGE 10^{-4}–10 TORR

J. DE KOK, J. A. W. DE KOCK AND A. BOUWKNEGT
Philips' Gloeilampenfabrieken, Light Division, Eindhoven (The Netherlands)

(Received 21 February 1974)

ABSTRACT

Alkaline-earth carbonates are used in the manufacture of electron-emissive coatings on electrodes in low-pressure gas-discharge lamps. The dissociation temperature of the carbonates, as used in the coating process, has been determined as a function of CO_2 pressure, with the evolved gas detection technique. Measurements have been made on both coprecipitated composite Ca–Sr–Ba carbonate crystals, and on mixtures of the three components, in two pressure ranges around 10^{-3} and 5 Torr*. The composite crystals generally dissociate in three steps. The experimental pressure–temperature relations of the decompositions, obtained for rates of heating between 1 and 20 K min^{-1}, are compared with the equilibrium p vs. T relations of the separate compounds, as taken from thermodynamic data in the literature. The experimental pressures found are about 1 to 2 orders of magnitude below the equilibrium pressure. In a few additional experiments it was found that the single compound $BaCO_3$ decomposed below 10^{-3} Torr in two distinct steps; the lower the pressure the more separated the dissociation temperature.

1. INTRODUCTION

The decomposition of alkaline-earth carbonates at low pressures is an important technical process in the formation of electron-emissive coatings in electron tubes and low-pressure gas-discharge lamps. Despite its technical importance, reliable data of this dissociation is scarce in the literature, especially at pressures below 1 Torr. Wolk[1] has given pressure–time curves at about 10^{-3} Torr during a fast decomposition (rate of heating 780 K min^{-1}). Judd and Pope[2–7] gave data on decomposition at about 10^{-1} Torr, and rates of heating 3–10 K min^{-1}. A review of the decomposition of single carbonate compounds has been given by Stern and Weise[8], whereas Webb and Krüger[9] gave a review of decomposition analyses of different minerals, with the differential thermal analysis (DTA) technique, at atmospheric pressure.

It is intended in this paper to provide some additional information concerning the dissociation of alkaline-earth carbonates, as used in the above-mentioned coating

---

*1 Torr = 1 mm Hg.

process, as a function of CO_2 pressure. The evolved gas detection technique (EGD) has been used in this investigation. Measurements have been performed in two pressure ranges, of about 10^{-3} and 5 Torr, with rates of heating which were of the order of 10 K min^{-1}. The dissociation of coprecipitated composite carbonates of Ca, Sr and Ba is compared with that of equivalent mixtures of the single carbonates, whereas special attention has been given to the decomposition of the single compound $BaCO_3$ at low pressures.

In the lower part of the pressure range care has been taken to make quantitative measurements of the pressure just above the dissociating species.

2. EXPERIMENTAL

a. Carbonates used in experiments

The following species have been used in the experiments:

(1) $CaCO_3$ (calcite) hexagonal, precipitated from a calcium chloride solution by the addition of an ammonium carbonate solution.

(2) $SrCO_3$ (strontianite) and $BaCO_3$ (witherite) were purchased from British Drug House.

(3) The triple carbonate A, consisting of 13% $CaCO_3$, 46% $SrCO_3$ and 41% $BaCO_3$ (mole percent). It has been made by coprecipitation from a mixed solution of the nitrates by adding a sodium carbonate solution. The crystals are shaped like needles.

(4) The triple carbonate B, with the composition 36% $CaCO_3$, 34% $SrCO_3$ and 30% $BaCO_3$ (mole percent). In this case coprecipitation from the nitrates was done by addition of ammonium carbonate. The shape of the crystals is more or less spherical.

The triple carbonates A and B are used as standard emissive coating materials. X-Ray analysis showed that the crystal lattice parameters of these carbonates differ appreciably from each other and from the single compounds.

Mean grain sizes of all these compounds were in the range 1–10 μ. According to specifications the $BaCO_3$ used contained at most 0.5% $SrCO_3$ and 0.02% $CaCO_3$ (weight percent), whereas the $SrCO_3$ contained at most 0.5% $BaCO_3$. The main impurity of $CaCO_3$ was $MgCO_3$, this level was below 0.1%. Besides, the presence of Na in all the species was possible though not more than 0.15% and the N-content did not exceed 0.2%. All other impurities were at a level below about 0.01%.

b. Measuring equipment

The experimental set-up for dissociation measurements in the 1–10 Torr pressure range is given in Fig. 1a. The essential pressure-determining part is a washing bottle, a bubbler, partly filled with silicone oil. The level of the oil determines the pressure during dissociation, because the bubbler is operated against vacuum. This pressure is measured with gauge G_1. The carbonate is contained in a nickel boat and its temperature is measured with a thermocouple. After having passed the bubbler the evolved gas expands in the vacuum vessel, the gauge G_2 indicating the pressure in the vessel. This vessel is pumped continuously by a mercury vapour pump, its volume controlling the response time of the system as a whole. Above a certain threshold, determined by the performance of the washing bottle and the response time of the vacuum system, the pressure in the vessel is a measure of the rate of development of evolved gas.

The pressure increase, necessary to develop a gas bubble in the bubbler, could not be observed on gauge G_1, and was less than 0.1 Torr. Consequently, the pressure was essentially constant in these experiments.

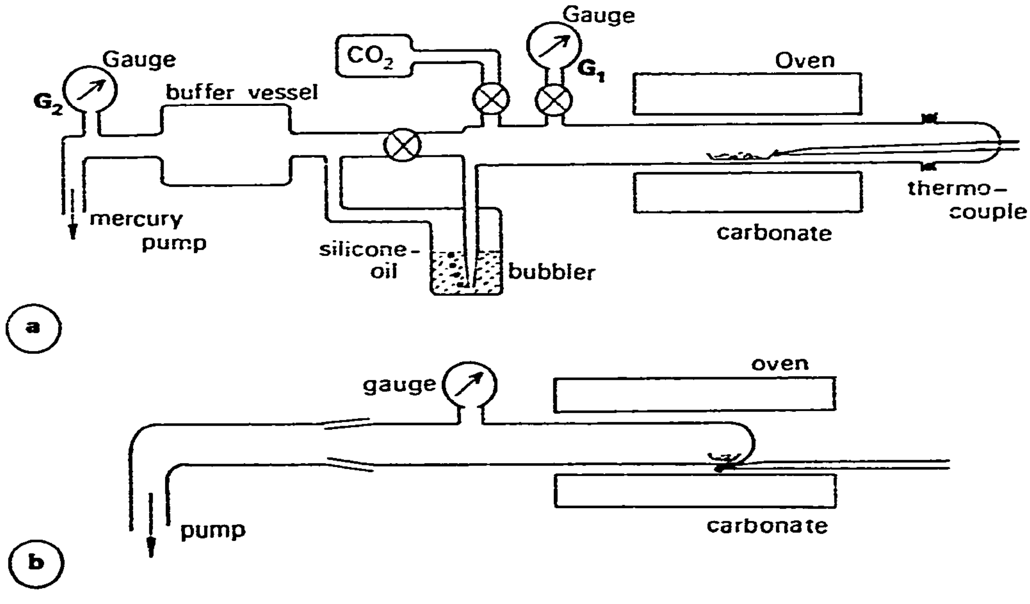

Fig. 1. (a) Apparatus for dissociation measurements in the range 1–10 Torr. (b) For measurements at 10^{-3}–10^{-5} Torr pressure.

The experimental set-up used for measurements in the range 10^{-4}–10^{-3} Torr is described in another paper[10], and schematically sketched in Fig. 1b. It should be noted that in these experiments the CO_2 pressure is essentially not constant.

c. *Experimental results*

In the low-pressure range (below 5×10^{-3} Torr) the pressure above the dissociating carbonates has been measured as a function of temperature, during dissociation of 160 mg of carbonate, at a linear rate of heating of 1.6 K min^{-1}. The pressure–temperature curves are given in Fig. 2. The two types of coprecipitated carbonates, mentioned in Section 2a. have been analysed, and compared with mixtures of carbonates with the same molecular ratio of Ca, Sr and Ba. One of the coprecipitated carbonates with 3% Zr powder added has also been examined. Zr is often used as an additive to electrode coatings used in low-pressure gas-discharge lamps. Not given in Fig. 2 are a set of experiments with the single compounds, which gave essentially the same peak temperatures as the mixtures. Consequently, interaction between the compounds during the decomposition of the mixture seems to be of minor importance.

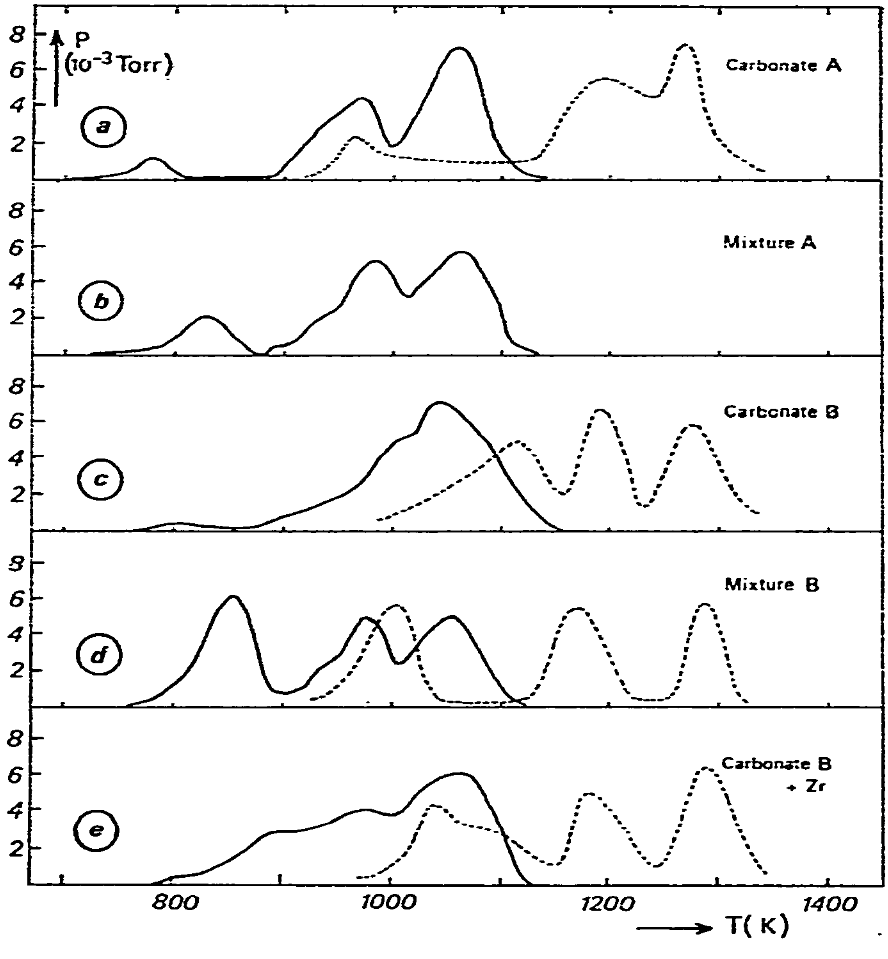

Fig. 2. Dissociation of coprecipitated alkaline-earth carbonates and equivalent mixtures. Composition indicated in text. Drawn curves, experiments at low pressure. Broken lines, experimental results at 3.5 Torr pressure with arbitrary pressure scale. Low pressure: weight 160 mg, $dT/dt = 1.6$ K min^{-1}, High pressure: weight 10 mg, $dT/dt = 20$ K min^{-1}.

An impression of the reliability of the measurements has been obtained in different ways. Firstly, it has already been shown in an earlier analysis[10] of curve d of Fig. 2 that the area under the three peaks was to a good approximation proportional to the molecular content of the three compounds of the mixture. This confirmed expectations, which were based on the approximately linear behaviour of the vacuum system, and the successive complete dissociation of the three carbonate components. Secondly, information about the reproducibility is contained in Fig. 2. The areas under the five curves shown should be equal to each other within a few percent. In fact, only deviations of about 10% around the average value are found. Finally, the rate of heating and the weight of carbonate A have been varied. A few representative examples of pressure–temperature curves are given in Fig. 3. The total area under these measured curves was approximately proportional to the product of rate of heating and carbonate mass, in conformity with the expectations. Mutual deviations from proportionality did not exceed 20%. Moreover, the peak temperature was also reproduced fairly well in this experiment. Only one of the first peaks deviates by about 20 K, mutual deviations of other peak values can be attributed to pressure differences.

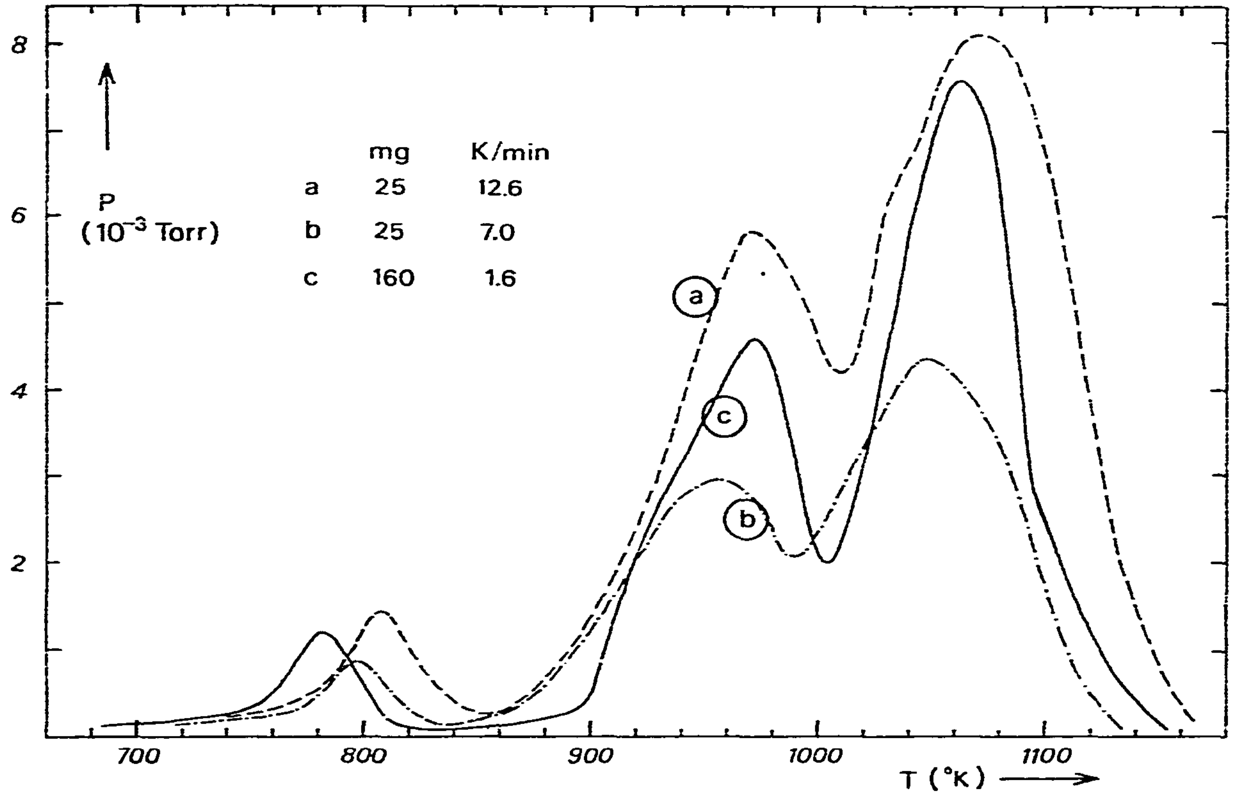

Fig. 3. Dissociation pressure versus temperature, with weight of sample and rate of heating varied. Coprecipitated carbonate A.

The same carbonates have been investigated in the 1–10 Torr pressure range, with the apparatus shown in Fig. 1a. In these measurements, 10 mg of carbonate was dissociated, with a rate of heating of 20 K min^{-1}. The dissociation rate was indicated by the pressure measured by gauge G_2 (see Fig. 1a), which was a Penning gauge. No attempt was made to measure the pressure- and gas-flow quantitatively. Consequently, the broken lines in Fig. 2, representing the curve obtained for 3.5 Torr, give only qualitative information about the dissociation behaviour of the carbonates, the pressure scale being only a relative one in this case. In most cases three well-resolved peaks are observed.

In a few experiments the carbonate contained 1% cellulose nitrate. It was found that this addition did not change the dissociation characteristics significantly in the 700–1200 K range. Only in the range below 700 K were a few smaller peaks found, caused by the decomposition of the cellulose nitrate added.

The graphs in Fig. 4 give insight into the relation between the pressure above the decomposing carbonate and the temperature. The peak pressure-values of the curves in Fig. 2 were plotted against $1/T$, where T is the temperature at which the peak is observed. A few other experimental peak values at pressures between 1 and 10 Torr, not reported in Fig. 2, were also plotted. In addition the pressure of the

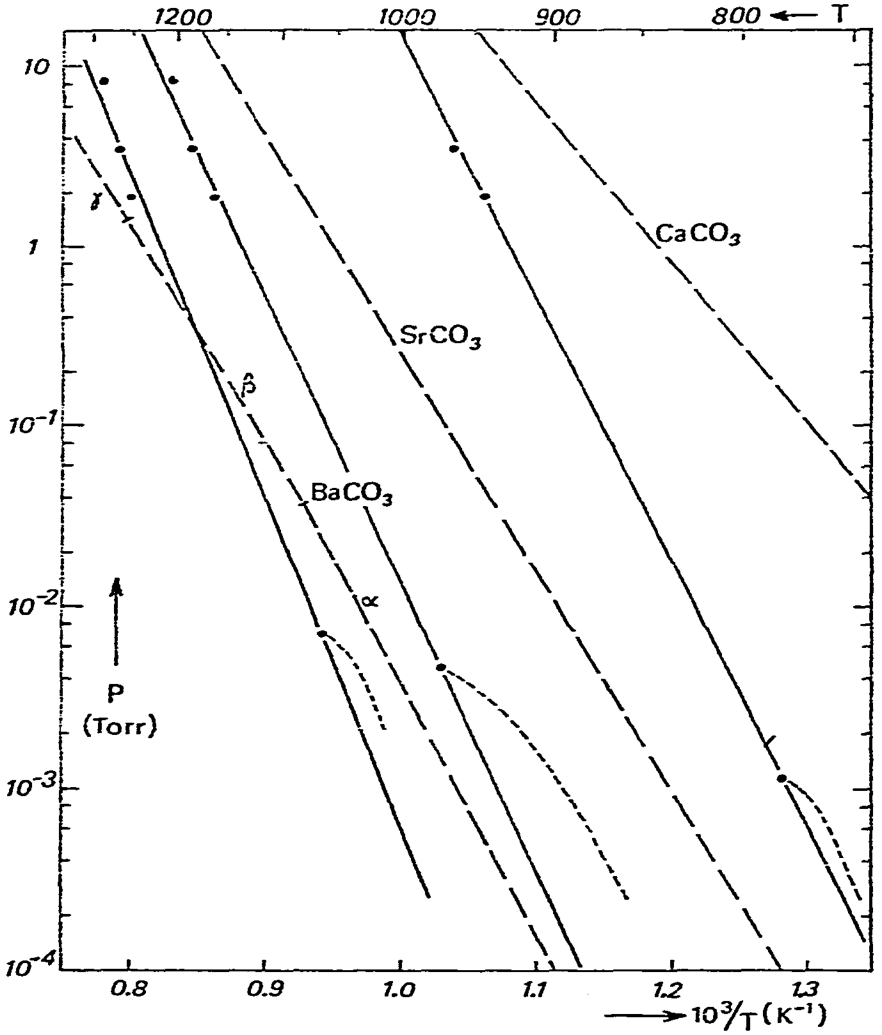

Fig. 4. Peak pressure versus temperature for carbonate A, compared with equilibrium pressure (broken lines). Dotted curves indicate experimental dissociation pressure below the peak values.

ascending parts of the curves for lower pressures are drawn in the graphs of Fig. 4. The experimental points shown are those of carbonate A.

An interesting observation has been made during the decomposition of $BaCO_3$ at low pressure. The amount of carbonate was reduced in successive experiments, keeping the rate of heating constant. Then the single decomposition peak, observed at higher pressures, was split up into two separate peaks at lower pressures. This splitting-up was greater the lower the pressure. This is illustrated in Fig. 5. It seems that a two-step reaction takes place, probably according to the formula:

$$2BaCO_3 \rightarrow BaO \cdot BaCO_3 + CO_2 \rightarrow 2BaO + 2CO_2$$

This will be discussed further in the following section.

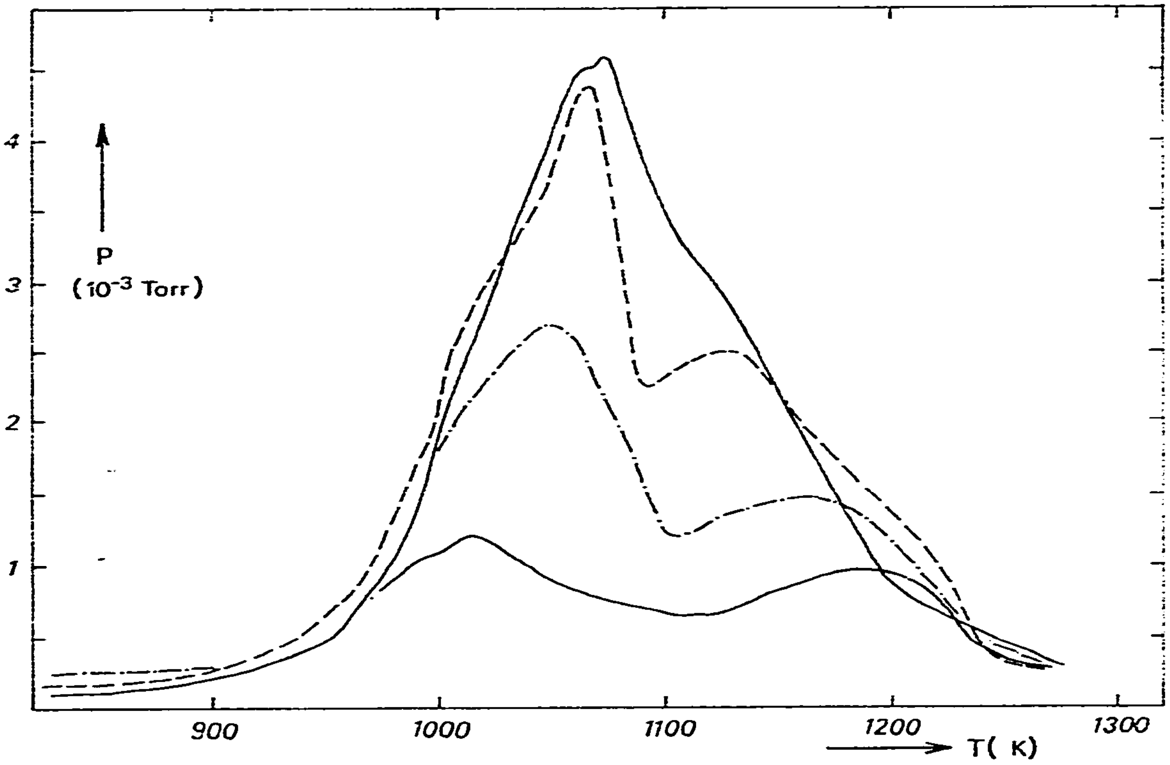

Fig. 5. Dissociation of $BaCO_3$ at low pressure, with carbonate weight varied. Top curve: 35 mg of $BaCO_3$, $dT/dt = 4.5$ K min^{-1}.

3. DISCUSSION

In the dissociation experiments at 3.5 Torr pressure, as given in Fig. 2, three fairly distinct peaks are found in all cases. In the mixtures of single alkaline-earth carbonate crystallites these peaks can be attributed to the successive dissociation of $CaCO_3$, $SrCO_3$ and $BaCO_3$; they appear at the same temperature as the single compounds. The corresponding peaks of the curves of the coprecipitated carbonates in Fig. 2 will be called the Ca-peak, etc., below.

Fig. 2 shows that the temperatures at which the Ba- and the Sr-peak appear are essentially independent of the origin of the decomposing compound, whether it is the coprecipitated carbonate A, carbonate B, or a mixture of the three alkaline-earth carbonates. This fact suggests that the influence of the chemical history or the crystal morphology on the experimental results is small. Only the temperature at which the Ca-peak appears depends a great deal on the compound dissociated. Compared with the dissociation of pure $CaCO_3$ crystals in the mixture the Ca-peak dissociation temperature is lowered for carbonate A, and much increased for carbonate B.

In the experiments at low pressure essentially the same behaviour is observed, with the complication that the three peaks merge almost completely for carbonate B, and to a lesser degree also for carbonate B with Zr added. It suggests a much stronger internal binding of the composite crystals of carbonate B, compared with carbonate A. An analogous case of peak merging at lower pressures has been reported in the literature on dolomite[11] ($CaMg(CO_3)_2$) which is also a composite crystal.

An analysis of the low-pressure p vs. T curves a and b of Fig. 2 gives evidence that carbonate A also behaves as a composite crystal, though less pronounced than carbonate B. The areas under the three peaks are proportional to the amount of CO_2 evolved. Compared with the known Ca:Sr:Ba ratio the relative area values are:

	Ca-peak (mole %)	*Sr-peak (mole %)*	*Ba-peak (mole %)*
Carbonate A	7	36	57
Corresponding mixture	13	42	45
Ratio Ca:Sr:Ba	13	46	41

There is some uncertainty in the determination of the areas, caused by the overlap of the Sr- and Ba-peaks, but the evidence of a more complicated dissociation of the composite crystals of carbonate A is clear.

The top temperatures in Fig. 2, of mixtures which dissociate at low pressures, correspond within a few percent with the 50% dissociation of one of the compounds in the mixture. This fact makes it reasonable to use these points for the description of the pressure–temperature relation of the dissociation, as given in Fig. 4. It is assumed there that the pressure is an exponential function of $1/T$, which is not in contradiction with the relatively few experimental points. It is seen in Fig. 4 that the slope of the $\log p$ vs. $1/T$ curve is steeper than the slope of the $\log p_e$ vs. $1/T$ curve[8], where p_e is the equilibrium dissociation pressure of the corresponding alkaline earth carbonate.

This fact indicates that the reaction kinetics of the decomposition limits the dissociation rate. Two possibly limiting factors are the evaporation of CO_2 from the carbonate-oxide interface, and the CO_2 flow through the oxide skin of a partly decomposed particle. The pressure difference $p_e - p$ is then the driving force of the decomposition[8]. Accordingly, the steeper slope of the experimental curve is qualitatively clear. For a quantitative interpretation of the kinetics of the dissociation process a much more detailed experimental investigation is necessary. As a consequence of these considerations the assumed exponential relationship between p and $1/T$ is quite uncertain and the deduction of an activation energy from these non-equilibrium curves is useless.

The dissociation peak values at higher pressures can be found by extrapolation of the curves of Fig. 4, if an exponential relation p vs. $1/T$ is assumed. A few atmospheric pressure values found in this way are given in Table 1. They are compared with values found in the literature for dissociation of the pure alkaline-earth carbonates at 1 atm CO_2 pressure. The rates of heating, if mentioned, were of the same order of magnitude as those in our experiments.

TABLE 1

DISSOCIATION PEAK TEMPERATURES (K) OF ALKALINE-EARTH CARBONATES AT 1 ATM CO_2 PRESSURE

Source	*Technique used*	*$CaCO_3$*	*$SrCO_3$*	*$BaCO_3$*
Duval[12]	TG	≈ 1200	—	—
Mackenzie[9]	DTA	1245	—	—
Stern and Weise (equilibrium)[8]		1150	1450	1770
This work, Fig. 4	EGD	≈ 1120	≈ 1400	≈ 1500

Data for lower pressures are rather scarce in the literature. Wolk[1] has published a decomposition curve of a comparable triple carbonate which resembles curve c, Fig. 2, but he studied a very fast decomposition, with a rate of heating of 800 K min^{-1}. He found a peak value at about 1140 K, for 10^{-3} Torr pressure. This temperature is about 100 K above the value found in Fig. 2. The difference may perhaps be attributed to the incomparable dissociation rates. In Table 2 the dissociation temperatures reported by Judd and Pope[2-7], for 10^{-1} Torr pressure, are compared with the values deduced from Fig. 4.

TABLE 2

DISSOCIATION PEAK TEMPERATURES (K) OF ALKALINE-EARTH CARBONATES AT 10^{-1} TORR

Source	*Ca-peak*	*Sr-peak*	*Ba-peak*
Judd–Pope[2]	920	1230	1390
This work, Fig. 4	900	1060	1150

The differences seen in the two tables above are quite unexpected, after the observation that the Sr- and Ba-peaks, as given in Fig. 2, were not very much dependent on the chemical history and morphology of the carbonate, both at higher and lower pressure.

The most intriguing difference between literature values and observations made in this investigation is found in Table 1 when one compares the thermodynamic data of Stern and Weise[8] with the extrapolated data of this work. Taking into account the uncertainty around the possibility of this extrapolation, the agreement for the Ca- and Si-peaks is reasonable. However, no agreement at all is found for the Ba-peak. This fact is also disclosed in Fig. 4, where the pressure during dissociation exceeds the equilibrium pressure for $T > 1200$ K. This is of course impossible. In search for an explanation we first note that the carbonates exist in different crystal modifications in the temperature range considered. As to $BaCO_3$ this is indicated in Fig. 4. This can cause complications in the dissociation behaviour. But probably more relevant is the existence of the compound $BaO \cdot BaCO_3$, or a eutectic mixture of this composition[5]. It may be an intermediate product in the decomposition of $BaCO_3$ to BaO. In the past this compound was considered to be the cause of an often observed melting process which occurred during the processing of vacuum tube cathodes in which $BaCO_3$ was exclusively used as an electron-emissive coating. The melting has also been observed by Judd and Pope[5] in their DTA experiments. It was found in the past that the addition of $SrCO_3$ to $BaCO_3$ could prevent the melting during the processing of electron tube cathodes, whereas Judd and Pope also found that at pressures much below 10^{-1} Torr no melting could be observed. It is in the context of these known facts that the observation of the two-step decomposition of $BaCO_3$ at pressures below 10^{-3} Torr is of interest. One probably observes in this case the two-step reaction

$$2BaCO_3 \rightarrow BaO \cdot BaCO_3 + CO_2 \rightarrow 2BaO + 2CO_2$$

It is evident that a more detailed analysis of the rather complex decomposition of $BaCO_3$ is necessary, in order to clear up the uncertainty concerning the pressure above the dissociating $BaCO_3$, in certain cases probably mixed with the intermediate compound.

In such an investigation the EGD technique should preferably be combined with simultaneous X-ray analysis.

REFERENCES

1 B. Wolk, *J. Electrochem. Soc. (New York)*, 105 (1958) 89.
2 M. D. Judd and M. I. Pope, in R. F. Schwenker and P. D. Garn (Eds.), *Proc. 2nd Conf. Thermal Analysis*, Vol. 2, Academic Press, New York, 1969, p. 1423.
3 M. D. Judd and M. I. Pope, *J. Appl. Chem. (London)*, 19 (1969) 191.
4 M. D. Judd and M. I. Pope, *J. Appl. Chem. (London)*, 20 (1970) 69.
5 M. D. Judd and M. I. Pope, *J. Appl. Chem. (London)*, 20 (1970) 384.
6 M. D. Judd and M. I. Pope, *J. Appl. Chem. Biotechnol. (London)*, 21 (1971) 149.
7 M. D. Judd and M. I. Pope, *J. Appl. Chem. Biotechnol. (London)*, 21 (1971) 285.
8 K. H. Stern and E. L. Weise, *High Temperature Properties and Decompositions of Inorganic Salts*, Vol. 2, Nat. Bur. Standards, Washington D.C., NSRDS-NBS 30, 1969.
9 T. L. Webb and J. E. Krüger, in R. C. Mackenzie (Ed.), *Differential Thermal Analysis*, Vol. I, Academic Press, London, 1970, p. 303.
10 A. Bouwknegt, J. de Kok and J. A. W. de Kock, *Thermochim. Acta*, 9 (1974) 399.
11 T. L. Webb and J. E. Krüger, in R. C. Mackenzie (Ed.), *Differential Thermal Analysis*, Vol. I, Academic Press, London, 1970, p. 323.
12 C. Duval, *Inorganic Thermogravimetric Analysis*, Elsevier, Amsterdam, 2nd ed., 1963, pp. 277–279, p. 440, pp. 533–534.