Thermochimica Acta, 16 (1976) 339–344

THERMAL DECOMPOSITION OF ALKALINE-EARTH CARBONATE SAMPLES OF EXTREME THICKNESS

S. GÁL, Gy. POKOL AND E. PUNGOR
Institute for General and Analytical Chemistry, Technical University, Budapest (Hungary)
(Received 20 January 1976)

ABSTRACT

Forward and reverse reactions were studied of the type $MCO_3 = MO + CO_2$, $(M = Mg, Ca, Sr$ and $Ba)$. The samples were of three types: (1) thick (some mm) crystals; (2) powders; (3) thin layers (about 10 nm).

Pressure–temperature data of the reactions are reported from the point of view of reversibility and equilibrium. The effect of repeated isothermal reaction cycles resulted in decreasing conversion of CO_2 uptake.

Isothermal and non-isothermal thermal measurements were completed with studies on an electron microprobe analyzer to explain the results.

INTRODUCTION

Solid–gas reactions are one of the main subjects of thermal analysis. Alkaline-earth carbonates seemed to be a good example to study some general characteristics of this type of reaction. Besides, the investigations reported here belong to the studies on high temperature reactions, which have been one of the activities of our Institute's research for two decades.

There are a number of papers on the thermal behaviour of alkaline-earth carbonates[1–6]. Our aims were: (1) To improve the data and to study the thermodynamics of the reactions under different, controlled conditions. (2) To study microscopic mechanisms of the processes. (3) To study the kinetics and at the same time to improve the methods for kinetic evaluation.

The present report concerns points (1) and (2). Some conclusions on kinetics have been published elsewhere[7].

EXPERIMENTAL RESULTS AND DISCUSSION

Most of our data were obtained by the TG method, using a Sartorius Thermo-Gravimat in controlled and programmed atmospheres. Our samples were of different geometry: (1) Thick samples (of some mm size). They were natural carbonate crystals. (2) Powdered analytical grade materials (usually of 45 μm maximum grain size). (3) Thin samples (in the order of 10 nm, mean thickness).

These thin layers were obtained by processing an evaporated metal layer of about 60 cm^2 geometric surface in oxygen and carbon dioxide[8].

Both non-isothermal and isothermal measurements were carried out in carbon dioxide atmospheres, the former under constant pressures, the latter under gradually programmed pressures. The isothermal circumsances permit to come closer to the equilibrium if it exists at all.

From the point of view of reversibility, it is interesting to consider the pressure and temperature parameters of both the decomposition and the reverse reaction. Figure 1 shows the data for starting the strontium carbonate decomposition and the carbon dioxide uptake of the resulting oxide. The empty circles and crosses are non-isothermal (10°C min^{-1} heating rate, about 20°C min^{-1} cooling) and isothermal data of about 20 mg powdered samples. Full circles and squares apply to thin layers.

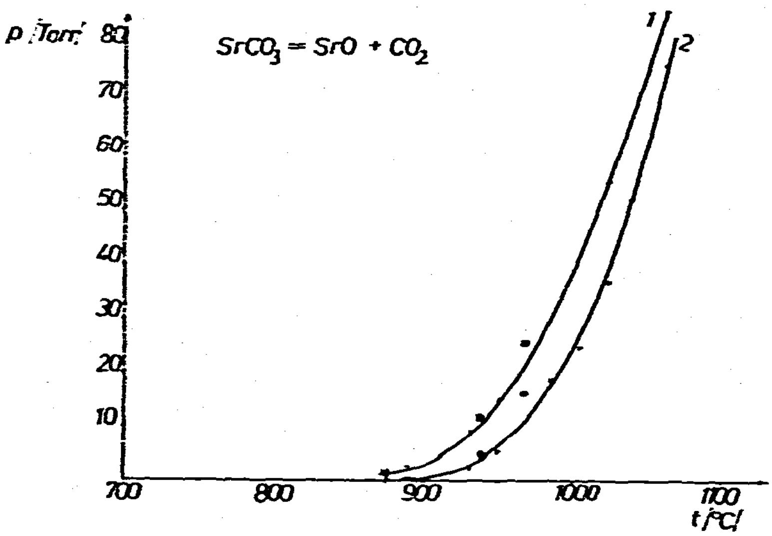


Fig. 1. Pressure and temperature of strontium carbonate decomposition (2) and recombination (1).

It can be seen that the data for powders and thin layers fit well but there is a remarkable difference between the two directions.

For barium carbonate we have similar but only a few data because of the high temperature range of the reaction. In some cases, it decomposes in two steps as reported previously by Judd and Pope[4], and De Kok et al.[5].

The effect of sample size and experimental conditions can be seen in Fig. 2 showing temperature–pressure data for the reaction $CaCO_3 = CaO + CO_2$. Powders (about 15 mg) and thin layers, the data of which are marked with full circles and squares again, were measured under isothermal conditions. The thick calcite samples (about 80 mg) were investigated non-isothermally, under the same conditions as strontium carbonate. This case is farther from the possible equilibrium as the curves also show.

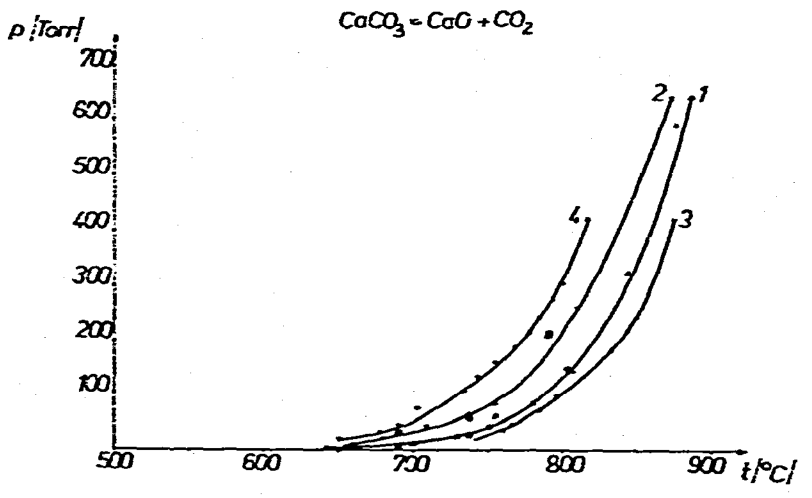


Fig. 2. Pressure and temperature of calcium carbonate decomposition and recombination. 1 = Decomposition of powder and thin layer samples; 2 = recombination of powder and thin layer samples; 3 = decomposition of calcite samples; 4 = recombination of calcite samples.

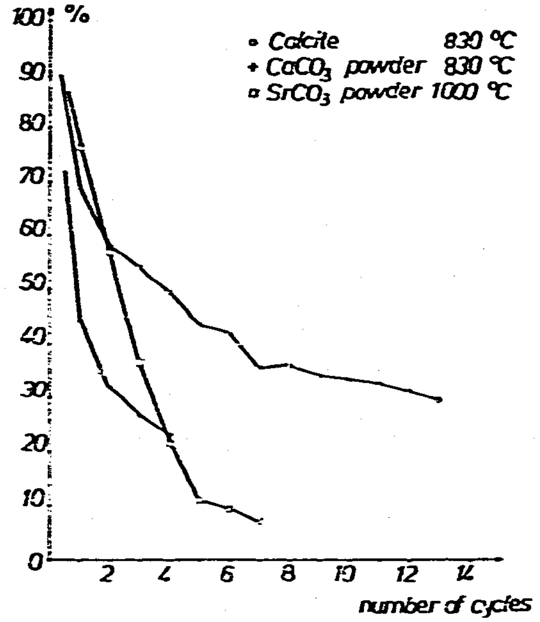
In our opinion, confirmed by curves 1 and 2, even the data of our most cautious experiments cannot be considered as equilibrium data. Points of possible equilibrium must be between curves 1 and 2.

Results found in the literature—reported as equilibrium data—are mostly between curves 1 and 3.

Enthalpy changes of the reactions are often calculated from pressure–temperature parameters, with the aid of the $\log p$–$1/T$ plots. This evaluation needs equilibrium data which of course should be the same for the decomposition and the reverse reaction. Considering this, we might determine only the range of enthalpy change. The limits of these ranges were found to be 39 and 45 kcal mol^{-1} for calcium carbonate, 55 and 60 kcal mol^{-1} for strontium carbonate, 60 and 65 kcal mol^{-1} for barium carbonate.

This method is inefficient for magnesium carbonate decomposition, since the oxide—as also reported in previous work[2]—cannot be converted into carbonate again. The enthalpy change of this decomposition was found to be 19.1 kcal mol^{-1} with the DSC method.

In order to know if reversibility was connected with changes in surface area, the surface area of some samples was determined. For this purpose gravimetric argon adsorption measurements were also carried out on the Thermo-Gravimat. It was found that the relation between the two factors was not close: specific surfaces of calcium, strontium and barium carbonates and the related oxydes were some m^2 g^{-1}—or in some cases undetectable, i.e., below 0.1 m^2 g^{-1}. Magnesium carbonate had no detectable surface, but for magnesium oxide, not reacting with carbon dioxide, at 615°C it was 130, at 480°C it was 200 m^2 g^{-1} specific surface. (It's worth mentioning that the kinetics can be much more correlated with the surface.)



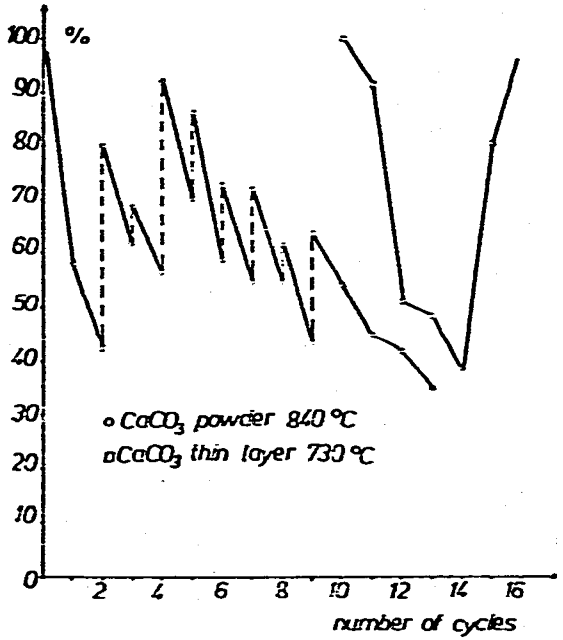


Fig. 3. Conversion of CO_2 uptake in repeated cycles I.

Fig. 4. Conversion of CO_2 uptake in repeated cycles II.

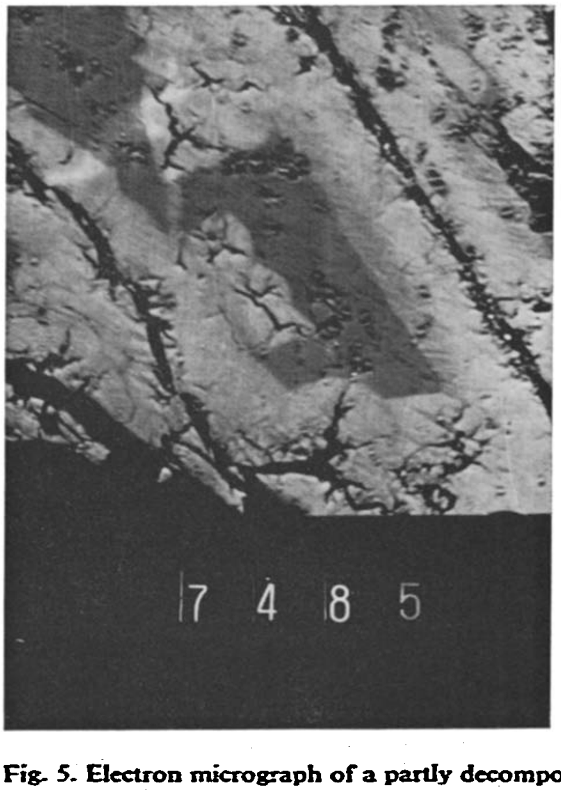
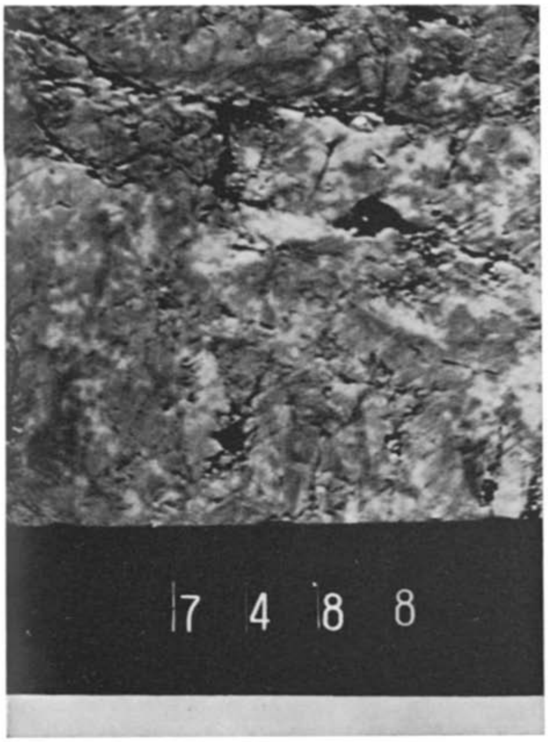


Fig. 5. Electron micrograph of a partly decomposed calcite.



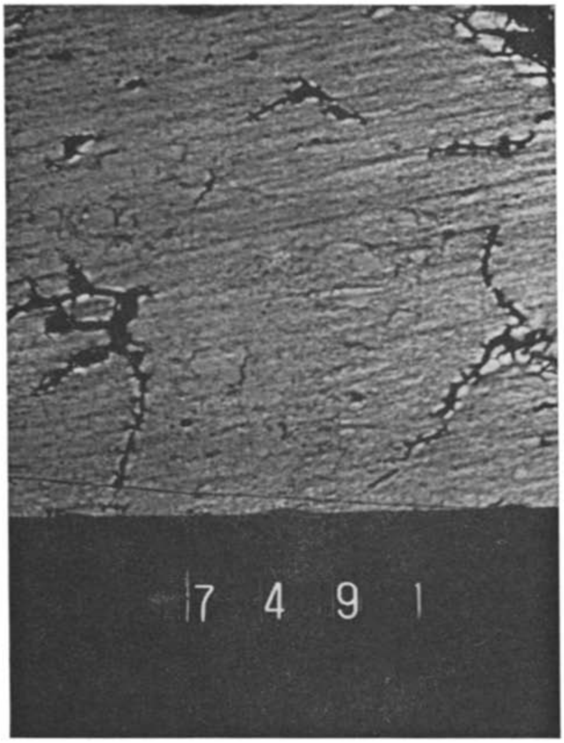


Fig. 6. Electron micrograph of a partly reformed calcite after one decomposition.

Fig. 7. Electron micrograph of a partly reformed calcite after ten decompositions.

Reversibility was also investigated from the aspect of conversion of carbon dioxide uptake. Figure 3 shows the change of the conversion in question for repeated isothermal decomposition—reformation cycles for calcite single crystal and powders.

For calcium carbonate Speros and Woodhouse[9] reported about this decrease in the conversion. In our experiences the process of the uptake can be well divided into fast and slow periods. In these measurements the carbon dioxide uptakes were performed till the end of the fast period. The first curve in Fig. 4 demonstrates another run for calcium carbonate powder. In some cycles the reaction was continued in the slow period for several hours. The conversion changes during the slow periods are marked with broken lines. (Cooling and heating again have a similar effect.) So we can expect that the conversion will complete if we continue the reaction long enough.

The other curve relates to a thin layer. Usually the uptake of thin-layer samples was complete, but when we made very fast cycles—about some minutes long—the process had two parts similar to powders or thick samples, and the conversion decreased in the cycles if we performed them till the end of the fast part. In slower reactions the full conversion could be reached easily.

To study the mechanism of the reactions and explaining the changes in the conversion of carbon dioxide uptake some samples were investigated in an electron microprobe analyzer. Figures 5–7 are electron micrographs of calcite crystals prepared in a different way. The full width of the photographs corresponds to 300 μm. The changes in the structure can be seen well. In the partly decomposed calcite (Fig. 5) the unchanged carbonate (inner, dark part) and the oxide (outer part) can be distinguished easily. Both of them form relatively large, compact phases, and there are relatively wide cracks in the crystal. An investigation of the phase boundary between the carbonate and oxide has been reported very recently by Beruto and Searcy[10]. Comparing the micrographs of partly reformed calcites in the first and the tenth cycles (Figs. 6 and 7, respectively) to that of the partly decomposed original the shrinking process can be observed. It can be seen that the channels became shorter and smaller, and the material became more compact. This may explain the decrease of the fast part of the reaction.

Our further aims are:

(1) To go on with electron microscopic and microprobe analyses, to investigate the differences between materials and reactions further.

(2) To interpret the processes in detail, including the aspects of mechanism and kinetics.

REFERENCES

1 H. Mauras, *Bull. Soc. Chim.*, (1959) 16.
2 D. A. Young, *Decomposition of Solids*, Pergamon Press, London, 1966.
3 M. D. Judd and M. I. Pope, *J. Therm. Anal.*, 4 (1972) 31.
4 M. D. Judd and M. I. Pope, *J. Appl. Chem. (London)*, 20 (1970) 384.
5 J. de Kok, J. A. W. de Kock and A. Bouwknegt, *Thermochim. Acta*, 9 (1974) 409.
6 P. K. Gallagher and D. W. Johnson, *Thermochim. Acta*, 6 (1973) 67.
7 Gy. Pokol, S. Gál, J. Sztatisz, L. Domokos and E. Pungor, in Preprints of *8th Int. Conf. on the Reactivity of Solids, Gothenborg*, 1976, p. 179.
8 Gy. Pokol, S. Gál, K. Tomor and L. Domokos, in I. Buzás (Ed.), *Proc. 4th ICTA, Budapest 1974*, Vol. I, Akadémiai Kiadó, Budapest, 1975, p. 479.
9 D. M. Speros and R. L. Woodhouse, *J. Phys. Chem.*, 72 (1968) 2846.
10 D. Beruto and A. W. Searcy, *Faraday Trans. I*, 70 (1974) 2145.