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KINETICS AND MECHANISM OF THERMAL DECOMPOSITION OF LEAD CARBONATE

Ž. D. ŽIVKOVIĆ

Faculty of Mining and Metallurgy in Bor, University of Beograd, 19210 Bor, Yugoslavia

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Results are given on the kinetics and mechanism of the processes in the thermal decomposition of lead carbonate with the application of TG and DTA experimental investigation methods.

The following mechanism was established:

$$3\ PbCO_3 = 2\ PbO.PbCO_3 + 2\ CO_2 \tag{1}$$

$$2\ PbO.PbCO_3 = 3\ PbO + CO_2 \tag{2}$$

$$PbO - \text{melting} \tag{3}$$

The following activation energy values were determined with TG methods for processes (1) and (2): 118.2 and 235.2 kJ/mole, respectively; and with DTA methods for processes (1), (2) and (3): 113.9, 246.6 and 294.9 kJ/mole, respectively.

Earlier investigations of the lead carbonate thermal decomposition process were mainly related to the definition of the temperature transformation and the determination of the ages which occur [1–4].

The kinetics and mechanism of the processes in the thermal treatment of lead carbonate were studied by thermogravimetry (TG) and differential thermal analysis (DTA).

The common equation for the thermal decomposition of lead carbonate can be shown in the following manner:

$$A_{(\text{solid})} = B_{(\text{solid})} + C_{(\text{gas})}$$

in which B forms at high-energy sites in the lattice of A.

Of the great number of methods existing today for the processing of thermogravimetric results with the aim of determining the kinetic parameters of the investigated processes, the author of this paper uses Chatterjee's method [5, 6], which is particularly favorable in the case when the parallel development of two or more processes is possible [7].

Borchardt and Daniels's method [8] was used for the evaluation of the DTA results obtained by continuous heating at 10°/min, which permits the investigation of the process from its beginning to its end.

Experimental

$PbCO_3$, Merck reagent grade, was used as the sample for the investigations. Thermogravimetric investigations were performed on a Netzsch thermal balance, Model 409, with the holder and a crucible for samples made from calcined alumina. The thermocouple for measuring the temperature of the furnace was of Pt – Pt/Rh, and its tip was positioned at the same level as the surface of the sample being investigated.

A Netzsch differential thermoanalyzer, Model 409, was used for the DTA measurements, with thermocouples of Pt – Pt/Rh, and the crucibles for the samples were of calcined alumina. α-Al_2O_3 was applied as reference sample. All investigations were carried out in air atmosphere.

Results and discussion

Figure 1 shows the TG and DTA curves for the tested sample of lead carbonate, obtained at a heating rate of 10°/min in air atmosphere.

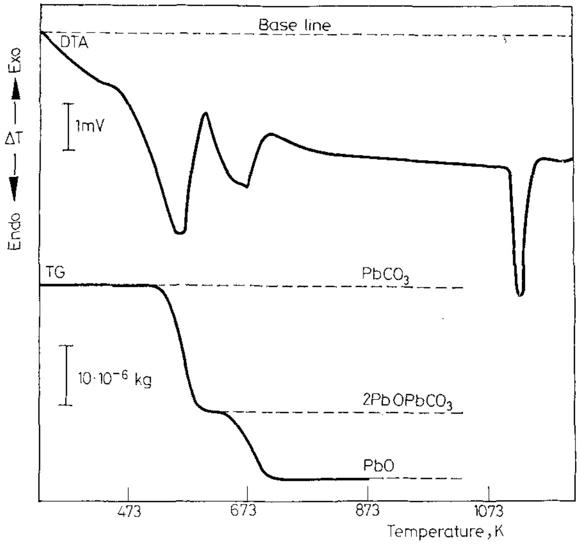

Fig. 1. DTA and TG curves of lead carbonate in air

On the basis of the curves it could be concluded that two processes occur during $PbCO_3$ decomposition and the PbO final product is obtained through the intermediate 2 PbO.$PbCO_3$. The PbO obtained melted at about 1183 K; this is presented in the DTA curve by the clearly endothermic peak. Therefore, the thermal decomposition of lead carbonate proceeds in accordance with the following mechanism:

$$3\,PbCO_3 = 2\,PbO.PbCO_3 + 2\,CO_2 \tag{1}$$

$$2\,PbO.PbCO_3 = 3\,PbO + CO_2 \tag{2}$$

$$PbO - \text{melting} \tag{3}$$

The first two transformations could be studied by using the TG and DTA results, and the third one by using only DTA results, in accordance with the fact that the first two transformations are accompanied by changes of mass and all three by measurable heat effects.

Analysis of thermogravimetric data

In our study, Chatterjee [5] simple and versatile method was employed. Chatterjee has applied his method successfully to the thermal decomposition kinetic of calcium oxalate monohydrate ($CaC_2O_4.H_2O$). The results compare favorably with the data reported in the literature.

This method is based on the general equation for the rate of a heterogeneous kinetics reaction, v:

$$v = -\frac{dm}{dt} = k \cdot m^n \tag{4}$$

where k, m, t and n are respectively the rate constant of the reaction, the active weight of the reacting material, the time elapsed from the start of the experiment and the pseudo-order of the reaction.

Substituting k from the Arrhenius equation into Eq. (4) gives:

$$v = A \cdot m^n \cdot e^{-\Delta E^\ddagger/RT}$$

or

$$n \log m - \log v = \frac{\Delta E^\ddagger}{2.303\,RT} - C \tag{5}$$

where A, $\Delta E^\ddagger$, T and R are respectively the frequency factor, the activation energy, the absolute temperature and the universal gas constant. Equation (5) gives the relationship of the reaction rate with the temperature; the activation energy ($\Delta E^\ddagger$) may be determined from the slope of the straight line ($n \log m - \log v$) versus $1/T$.

A sample mass loss of $88 \cdot 10^{-6}$ kg in the first transformation and of $44 \cdot 10^{-6}$ kg in the second transformation is accompanied by the formation of $713.63 \cdot 10^{-6}$

kg solid product in the first and $669.63 \cdot 10^{-6}$ kg in the second reaction; this remains with the unreacted starting component. On this basis the change in the active sample mass, m, was estimated as a function of time and the results obtained are shown in Fig. 2.

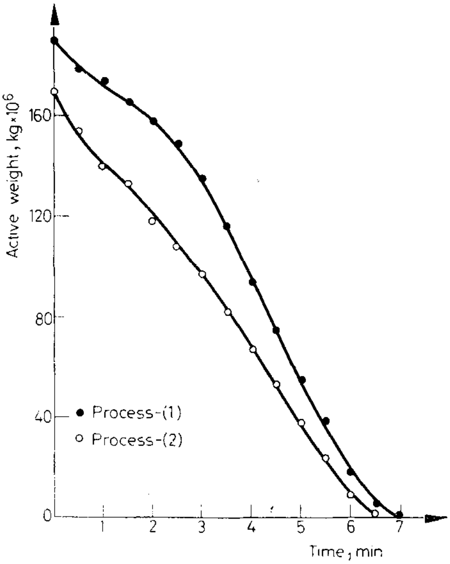

Fig. 2. Variation of active weight of sample with time for processes (1) and (2) in air

The instantaneous decomposition rate, v, for the processes (1) and (2), as defined by Eq. (4), was determined by graphical differentiation of the TG curves in Fig. 2.

Based on the thermogravimetric data required for calculation of the kinetic parameters of these processes, Fig. 3 gives ($n \log m - \log v$) as a function of the reciprocal of the reaction temperature, for both processes.

The slopes of the most probable lines were determined with the least squares statistical method and in this way the activation energies for processes (1) and (2) were estimated: 118.2 and 235.2 kJ/mole, respectively.

The temperature-dependence of the rates of processes (1) and (2) in air atmosphere at a constant heating rate of 10°/min could be represented in the following way:

for process (1):

$$n \log m - \log v = \frac{6.176}{T} - 10.435 \tag{6}$$

for process (2):

$$n \log m - \log v = \frac{12.238}{T} - 18.238 \tag{7}$$

where $n = 1$.

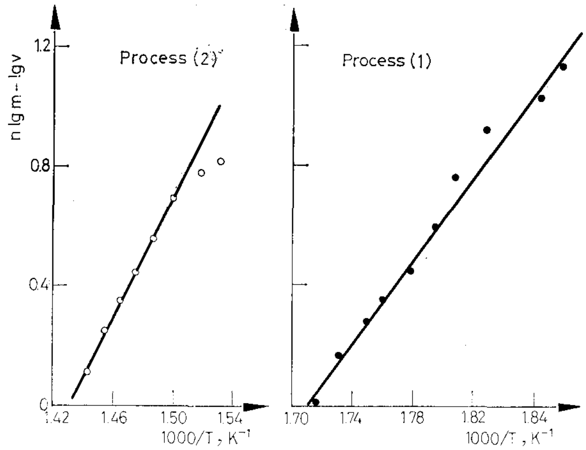

Fig. 3. Dependence of $(n \log m - \log v) = f(1/T)$ for processes (1) and (2) in air

The analysis of differential thermal data

There are many methods for the evaluation of DTA data with the aim of the determination of the reaction kinetics in the thermal decomposition of solid components. For the processes considered in the thermal treatment of $PbCO_3$ the author uses Borchardt and Daniels's method [8].

This method was originally derived for the study of homogeneous kinetics but, as will be shown later, can be applied to heterogeneous kinetics as well. This method is based upon the equation derived for a first-order reaction:

$$k = \frac{C_p(\mathrm{d}\,\Delta T/\mathrm{d}t) + K\,\Delta T}{K(A - a) + C_p\,\Delta T} \tag{8}$$

where k, K, A, C_p, ΔT, t and a are respectively the reaction rate constant, the constant characteristic of the experimental apparatus, the total curve area, the total heat capacity of the reactant or reference material, the differential temperature, time and the area under the curve up to time t.

Another approximation of the Borchardt and Daniels equation has be derived [9–12]. Since C_p is normally quite small, the equation simplifies to:

$$k = \frac{\Delta T}{A - a} \tag{9}$$

where the terms have the same notations as before. The approximation in Eq. (9) yields good results, as confirmed by the thermal decomposition of metal oxalates. An excellent correlation was found between the DTA and TG reaction kinetics data [9, 10, 13]. Also, since this approximation method is simple to use, it is the basis for the determination of the reaction kinetics described in this experiment.

The DTA results obtained with the heating rate of 10°/min in air atmosphere were used for the estimation of the reaction kinetics in processes (1), (2) and (3) occurring during the thermal decomposition of $PbCO_3$. The analyzed DTA peaks were divided into equal time intervals and the rate constants were estimated on the basis of Eq. (9). The activation energy values were determined on the basis of the Arrhenius equation from the line slopes in Figs 4, 5 and 6.

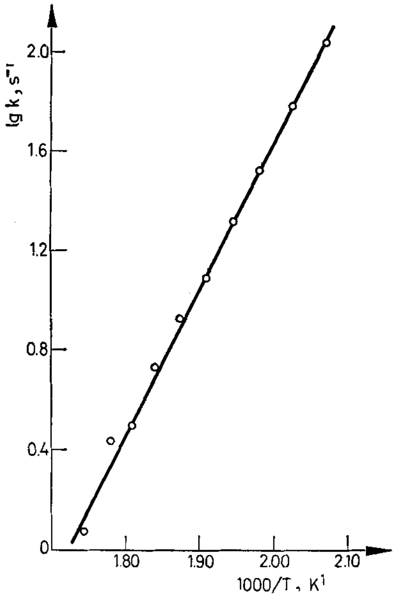

Fig. 4. Arrhenius diagram for process (1)

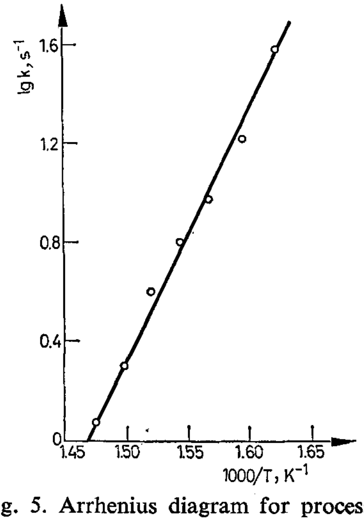

Fig. 5. Arrhenius diagram for process (2)

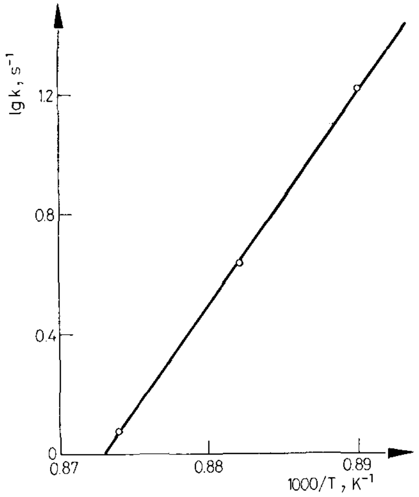

Fig. 6. Arrhenius diagram for process (3)

The following activation energy values were estimated for processes (1), (2) and (3): 113.9, 245.6 and 294.9 kJ/mole, respectively.

By the determination of the pre-exponential factor values in the Arrhenius equation it was possible to define the temperature-dependence of the rate constant for the analyzed processes in the following way:

for process (1):

$$k = 1.807 \cdot 10^{10} \cdot e^{-\frac{13704}{T}} \tag{10}$$

for process (2):

$$k = 1.016 \cdot 10^{19} \cdot e^{-\frac{29529}{T}} \tag{11}$$

for process (3):

$$k = 1.318 \cdot 10^{13} \cdot e^{-\frac{35458}{T}} \tag{12}$$

Conclusion

The results of the kinetic investigations and the mechanism of the processes during lead carbonate thermal decomposition are given in Table 1.

Table 1

Transformation	Decomposition temperature, K		Activation energy, kJ/mole	
	TG	DTA	TG	DTA
$3\,PbCO_3 = 2\,PbO \cdot PbCO_3 + 2CO_2$	528	463	118.2	113.9
$2\,PbO \cdot PbCO_3 = 3\,PbO + CO_2$	643	603	235.2	245.6
PbO — melting	—	1113	—	294.9

From the results given in Table 1 it can be seen that the beginnings of processes (1) and (2) are recorded at lower temperatures by the DTA method in relation to the results obtained by the TG method. This phenomenon is representative of many unexplained questions in the use of the DTA method for experimental investigations and the undefined beginning of the DTA peak [14].

The values obtained for the activation energy in the two ways for processes (1) and (2) present satisfactory agreement and the deviations are within the limits of experimental error. These facts show the reliability of the methods applied to process the experimental results.

For all three processes occurring during lead carbonate thermal decomposition very high activation energy values were obtained; these values show that the processes are kinetically-controlled, i.e. that their rates are limited by resistances to the chemical reaction.

References

1. F. L. Cuthbert and R. A. Rowland, Am. Mineralogist, 32 (1947) 111.
2. R. M. Gruver, J. Am. Ceram. Soc., 33 (1950) 96.
3. G. A. Collins and A. G. Swan, Bull. Canad. Inst. Min., 56 (1954) 533.
4. G. Liptay, Atlas of Thermoanalytical Curves, Akadémiai Kiadó, Budapest (1975) 255.
5. P. K. Chatterjee, J. Polymer Sci., A, 3 (1965) 4253.
6. Ž. D. Živković, D. F. Bogosavljević and V. D. Zlatković, Thermochim. Acta, 18 (1977) 235.
7. I. D. Shah and S. E. Khalafalla, Bureau of Mines, RI-7638, 1972.
8. H. J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79 (1957) 41.
9. H. J. Borchardt, J. Inorg. Nucl. Chem., 12 (1960) 252.
10. V. M. Padmanabah, S. C. Saraiya and A. K. Sundaram, J. Inorg. Nucl. Chem., 12 (1960) 356.
11. R. P. Agarwala and M. C. Naik, Anal. Chim. Acta, 24 (1960) 128.
12. W. W. Wendlant, J. Chem. Educ., 38 (1961) 571.
13. Ž. D. Živković and B. Dobovišek, Yugoslav Symposium of Metallurgy Beograd, 16—18 January 1978. M-1 p. 231.
14. B. Dobovišek, Private Communication, 1977.

RÉSUMÉ — La cinétique et le mécanisme des réactions qui se déroulent lors de la décomposition thermique du carbonate de plomb ont été étudiés par TG et ATD. Les mécanismes suivants ont été établis:

$$3\,PbCO_3 = 2\,PbO.PbCO_3 + 2\,CO_2 \quad (1)$$

$$2\,PbO.PbCO_3 = 3\,PbO + CO_2 \quad (2)$$

$$PbO - \text{fusion} \quad (3)$$

Pour les réactions (1) et (2), les valeurs de 118.2 et 235.2 kJ · mol^{-1} ont été trouvées à partir des résultats TG et pour les réactions (1), (2) et (3) l'ATD a fourni respectivement 113.9, 246.6 et 294.9 kJ · mol^{-1}.

ZUSAMMENFASSUNG — Die an Hand der TG- und DTA-Untersuchungen erhaltenen Ergebnisse über Kinetik und Mechanismus der bei der thermischen Zersetzung von Bleicarbonat auftretenden Vorgänge werden beschrieben.

Die folgenden Mechanismen des Vorganges wurden festgestellt:

$$3\,PbCO_3 = 2\,PbO.PbCO_3 + 2\,CO_2 \quad (1)$$

$$2\,PbO.PbCO_3 = 3\,PbO + CO_2 \quad (2)$$

$$PbO - \text{Schmelzen} \quad (3)$$

Die folgenden Werte der Aktivierungsenergie wurden durch TG-Versuche für die Vorgänge (1) und (2) bestimmt: 118.2, bzw. 235.2 kJ/Mol, und durch DTA-Messungen für die Vorgänge (1), (2) und (3): 113.9, 246.6, bzw. 294.9 kJ/Mol.

Резюме — Представлены результаты исследования кинетики и механизма процессов, происходящих при термическом разложении карбоната свинца с использованием ТГ и ДТА. Установлен следующий механизм этого процесса:

$$3\,PbCO_3 = 2\,PbO.PbCO_3 + 2\,CO_2 \quad (1)$$

$$2\,PbO.PbCO_3 = 3\,PbO + CO_2 \quad (2)$$

$$PbO - \text{плавление} \quad (3)$$

С помощью ТГ методов были определены значения энергии активации для процессов (1) и (2), которые соответственно были равны 118.2 и 235.2 кдж/моль. Для процессов (1), (2) и (3) методами ДТА были определены следующие значения энергии активации: 113.9; 246.6 и 294.9 кдж/моль.