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Determination of the equilibrium dissociation pressure of inorganic solids from TG: Application to the calculation of the enthalpy change of the reaction $Pb_3O_2(CO)_3 \Leftrightarrow PbO + CO_2$

J.M. Criado*, M. González

Instituto de Ciencia de Materiales de Sevilla, Centro Mixto Universidad de Sevilla – C.S.I.C., c/Américo Vespucio s/n, Isla de La Cartuja, 41092 Sevilla, Spain

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Abstract

A procedure is developed for determining the equilibrium constants of reactions of the type:

$$\mathrm{A(solid)} \Leftrightarrow \mathrm{B(solid)} + \mathrm{C(gas)}$$

from TG data. The method is based upon the overlapping of both formation and decomposition TG diagrams when an appropriate heating rate is applied. This procedure has been checked by determining the equilibrium constants at different pressures of the calcium carbonate dissociation products.

The method outlined here has been used for determining the thermodynamic parameters of the following reaction:

$$Pb_3O_2CO_3 \Leftrightarrow 3PbO + CO_2$$

The results obtained suggest that the phase diagram reported in literature for the PbO–O–CO_2 system should be reviewed.

Keywords: Lead oxicarbonate decomposition; Thermodynamic parameters; Equilibrium constant from TG

1. Introduction

Single and mixed metal carbonates have been widely employed for the synthesis of oxides used as catalysts [1,2] or in the manufacture of cathode coatings [3]. On the other hand, they have been very often used as geological thermometers [4]. Thus, the information concerning the equilibrium constant for the thermal decomposition of carbonates at different temperatures is highly valuable for the above applications. The thermal decomposition of metal carbonates is a reversible reaction of the type:

$$\mathrm{A(solid)} \Leftrightarrow \mathrm{B(solid)} + \mathrm{C(gas)} \quad (1)$$

The equilibrium constant of this kind of reaction has been frequently determined from direct measurements in which the solids, A and B, are allowed to equilibrate with the gas, C, at different temperatures.

Stern and Weiss [5] have pointed out that such direct measurements are frequently unreliable since in many cases 'pseudo-equilibria' appear, i.e. different

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*Corresponding author. Tel.: +34 95 4489547; fax: +34 95 4460665; e-mail: jmcriado@cica.es

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constant pressures are obtained depending on whether the equilibrium is approached from above or below. This behaviour can be understood by considering that when the forward and reverse reactions (1) are proceeding, a progressive decrease of their rate take place; thus equilibrium is not reached and the reaction merely becomes very slow. Moreover, Lvov [6] has shown, in a very recent paper, that the thermal decomposition of alkali-earth carbonates can be improved by water vapour. This statement is in agreement with results obtained in a previous work [7] that shows that the recarbonation of CaO under dry carbon dioxide atmosphere starts at temperatures >600°C, in spite of the fact that the calcium oxide conversion into calcium carbonate under CO_2 atmosphere is thermodynamically favoured from room temperature. However, it has been pointed out that the recarbonation temperature is dramatically decreased if humid carbon dioxide is used, which suggests [7] that, in this case, the reaction takes place through $Ca(OH)_2$ as an intermediate product that is rapidly converted into calcium carbonate.

The scope of the present paper is to develop a TG method for determining the equilibrium partial pressure of reactions such as [1] at different temperatures in such a way that 'pseudo-equilibria' would be avoided. This method would take advantage of the fact that the recarbonation of metal oxides under dry CO_2 atmosphere does not seem to take place at low temperatures.

The thermal decomposition of $CaCO_3$ has been taken as a test reaction because accurate thermodynamic data of this reaction are available [5]. On the other hand, this method will be used for the determination of the thermodynamic constants of the reaction:

$$Pb_3O_2CO_3 \Leftrightarrow 3PbO + CO_2 \tag{2}$$

To our knowledge, the thermodynamic data reported by Grisafe and White [8] are the only ones available in literature for this reaction. However, it is noteworthy that these authors have determined the equilibrium constants by following the decrease of the CO_2 pressure during the conversion of lead monoxide into oxycarbonate from a starting pressure selected to be higher than the one expected for the equilibrium. The value recorded for the CO_2 pressure when the steady state is reached was taken by Grisafe and White as the equilibrium pressure at the temperature at which the experiment was carried out. It has been previously shown that this method would lead to unreliable equilibrium pressure because 'pseudo-equilibrium' would be reached for kinetic reasons.

2. Experimental

2.1. Materials

$CaCO_3$ and $PbCO_3$ D'Hemio a.r have been used. CaO was proceeding from the thermal decomposition of the corresponding carbonate.

2.2. Apparatus

A Cahn electrobalance, model RG, was employed. The balance was connected to a conventional vacuum system and to a gas storing system. The temperature was measured with a thermocouple located inside the electrobalance very close to the sample. The system can be operated under isothermal conditions or under heating rates that can be selected in the range from 0.5 to 25 K/min. The system can be operated at pressures ranging from vacuum to 400 torr. This upper limit is chosen because the noise becomes very high at higher pressures.

3. Results and discussion

When the temperature of a sample of CaO is progressively raised under a defined pressure of CO_2, a continuous increase in the sample weight would be expected until the equilibrium for reaction [2] is reached. Above the equilibrium temperature, $CaCO_3$ will not be thermodynamically stable, and a weight loss should be recorded in the TG diagram.

Fig. 1 includes a TG diagram obtained for a sample of CaO at a heating rate of 10 K/min and a CO_2 pressure of 30 torr. As can be observed in this figure, under the experimental conditions used, the sections of the thermogravimetric curve corresponding to the thermal formation and the decomposition of $CaCO_3$ do not overlap, as might be expected if a real equilibrium situation would be reached. The sections are connected by a broad zone of 'pseudo-equilibria' temperatures from 680° to 740°C in which no detect-

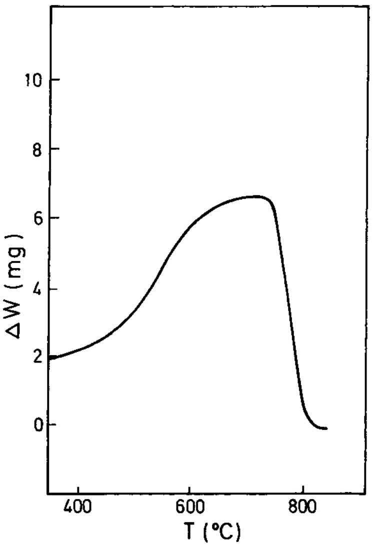

Fig. 1. TG diagram of a CaO–$CaCO_3$ sample. Heating rate=10 K/min. Pressure of CO_2=30 torr.

able change of weight has been recorded, although the oxide is not completely recarbonated.

For the determination of the equilibrium temperature of the reaction, it is therefore necessary to develop an experimental procedure which allows the overlapping of both sections.

In order to achieve this, we must recall that, when a chemical reaction is carried out under a heating programme, the plot of the reacted fraction vs. temperature shifts towards higher temperatures as the heating rate increases. In this way, the equilibrium temperature of $CaCO_3$ thermal decomposition could be determined at different pressures of CO_2 by changing the heating rate in the proper way for achieving the overlapping of the sections of the thermogravimetric curves corresponding to the reactions of formation and decomposition of the salt, respectively.

TG diagrams of CaO–$CaCO_3$ included in Fig. 2 have been recorded at different pressures of CO_2 by changing the heating rate until overlapping of both, the forward and the reverse reactions is reached. It is noteworthy that, as is well known, the temperature at which a particular value of the reacted fraction is reached increases by increasing the heating rate; in other words, the conversion of the oxide into the corresponding carbonate depends not only on the CO_2 partial pressure but also on the heating rate.

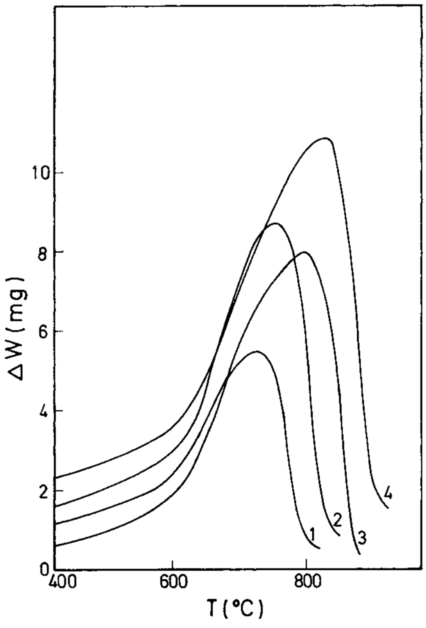

Fig. 2. TG diagrams of a CaO–$CaCO_3$ sample obtained at different CO_2 pressures. The heating rate has been changed until overlapping is reached. Pressures of CO_2: (1) 30; (2) 61; (3) 134; and (4) 184 torr.

Thus, provided that the TG curves shown in Figs. 2 and 4 have not been recorded using the same heating rate, we must not expect that the total carbonation of

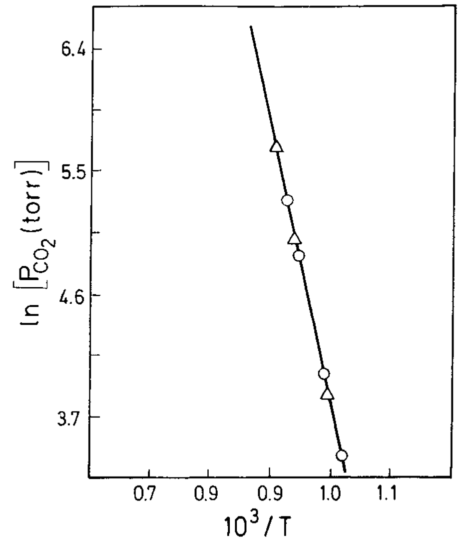

Fig. 3. Clausius–Clapeyron plot of CO_2 equilibrium pressures of $CaCO_3 \Leftrightarrow CaO+CO_2$. (○), This work; (D), Ref. [5].

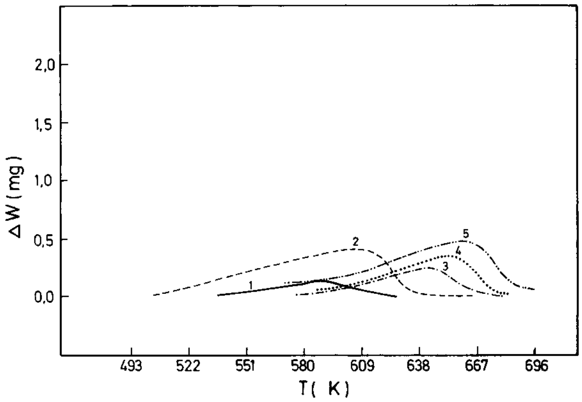

Fig. 4. TG diagrams of PbO under different CO_2 pressures. (1) 109; (2) 150; (3) 270; (4) 317; and (5) 371 torr.

the respective oxides, at the temperature at which the two section of the TG curves overlap, increases by increasing the CO_2 pressure.

From the diagrams of Fig. 2, $CaCO_3$ equilibrium dissociation temperatures have been determined at different pressures. Both parameters have been represented in Fig. 3 by means of the Clausius–Clapeyron equation. In this figure, our results for the dissociation pressures of $CaCO_3$ are compared with those tabulated by Sterm et al. [5]. The excellent agreement of both sets of data supports the validity of the method here outlined.

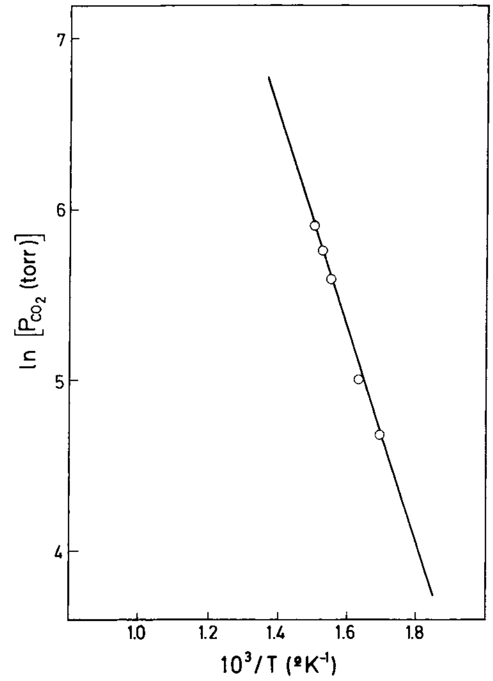

Fig. 6. Clausius–Clapeyron plot of the equilibrium pressure taken from Fig. 4 for the reaction: $Pb_3O_2CO_3 \Leftrightarrow 3PbO+CO_2$.

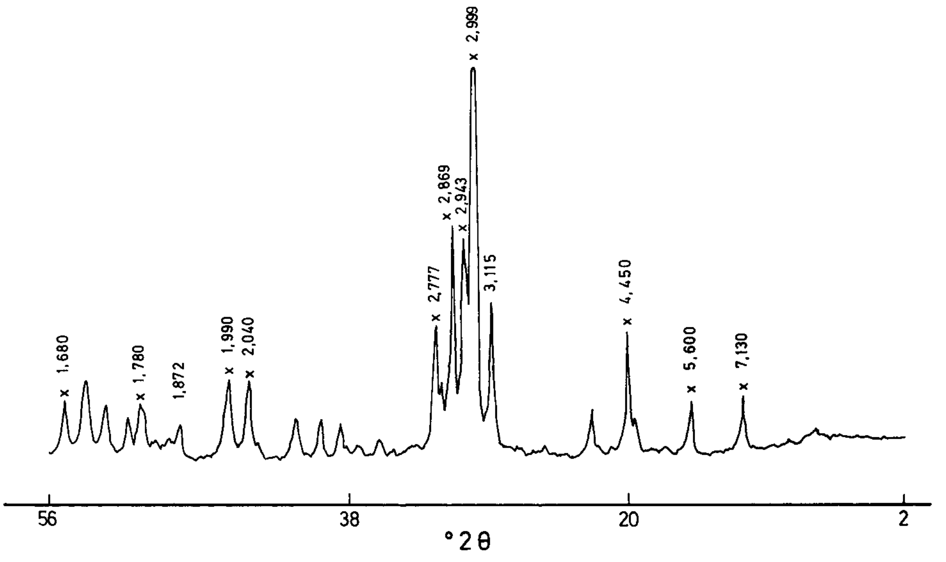

Fig. 5. XRD diagram of PbO carbonated at a CO_2 pressure of 150 torr at 320°C. (X), $Pb_3O_2CO_3$

The described procedure has been used for determining the equilibrium pressures of reaction [2]. Fig. 4 shows the TG diagrams recorded for PbO at different CO_2 pressures by changing the heating rate (in the range from 12 to 2 K/min) until overlapping of both, the forward and reverse reaction is reached. Fig. 5 shows a typical X-ray diagram recorded for the carbonated PbO sample that is constituted of a mixture of Pbo and $Pb_3O_2CO_3$. This compound has been the unique product found by heating PbO up to 700°C under CO_2 pressures <400 torr. We must bear in mind that higher pressures cannot be used in our experimental system.

The equilibrium dissociation temperatures determined from Fig. 4 have been represented in Fig. 6 according to the Clausius–Clapeyron equation. The values calculated for the changes of enthalpy and entropy of reaction [2] are ΔH_0=53.9 kJ/mol and ΔS_0=18 u.e. These values do not agree with those reported by Grisafe and White [8] (ΔH_0=99.5 kJ/mol and ΔS_0=15 u.e.). We must bear in mind that these authors have identified the equilibrium constants with the CO_2 pressure recorded when the steady state between carbon dioxide and lead monoxide is reached at a particular temperature. It has been shown in the present work that this method would lead to unreliable equilibrium pressures because 'pseudo-equilibria' would be reached as a result of kinetic reasons.

In summary, the results reported in this paper show that the phase diagram of the $PbO–O_2–CO_2$ system reported by Grisafe and White needs to be reviewed.

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