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DETERMINATION OF EQUILIBRIUM CONSTANTS OF SOLID THERMAL DECOMPOSITION REACTIONS BY THERMOGRAVIMETRY

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ABSTRACT

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

A (solid) $\rightleftharpoons$ B (solid) + C (gas)

from TG data. The method is based upon the overlapping of both formation and decomposition TG diagrams when an appropiate heating rate is applied.

INTRODUCTION

The equilibrium constants of reversible thermal decomposition of solids of the type:

$$\text{A (s)} \rightleftharpoons \text{B (s)} + \text{C (g)} \qquad (1)$$

are frequently determined[1] from direct measurements in which the solids A and B are allowed to equilibrate with the gas, C, at different temperatures.

Stern and Weiss[2] have pointed out that such direct measurements are frequently unreliable since in many cases "pseudo-equilibria" appear, i.e., different 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 of reaction (1) are going on, a progressive decrease of their rates takes place; then the equilibrium has not been reached, and the reaction is merely very slow.

In order to avoid these "pseudo-equilibria", a method is developed in the present paper which allows the determination of equilibrium constants of reversible thermal decomposition of solids from TG data. The method is based on the effect of heating rate change on the TG curves.

The thermal decomposition of $CaCO_3$ has been chosen as test reaction to carry out this study:

$$CaCO_3 \rightleftarrows CaO + CO_2 \tag{2}$$

EXPERIMENTAL

Materials

$CaCO_3$ D'Hemio a.r. and CaO proceeding from its decomposition have been used.

Apparatus

A Cahn electrobalance, model RG, has been employed. The balance was connected to a conventional vacuum system and to a gas storing system. The temperature has been measured with a thermocouple located outside the electrobalance hangdown, very near to the sample. A furnace of 15 of resistance connected to a temperature programmer of an Aminco thermoanalyser makes possible to obtain lineal heating rates from 2 to 25°C min^{-1}.

The TG diagrams have been plotted with an X–Y Plotomatic 690 recorder.

Sample weights of 20–21 mg of CaO have been used in all the experiments. The large volume of the electrobalance avoids pressure changes during the experiments.

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 could 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.

Figure 1 includes the TG diagrams obtained for a sample of CaO at a heating rate of 11°C min^{-1} and a CO_2 pressure of 29 Torr. As can be observed in this Figure, under the experimental conditions used, the thermogravimetric curves corresponding to both the thermal formation and decomposition of $CaCO_3$ do not overlap, as could be expected if a real equilibrium situation would be reached. The curves are separated by a broad zone of "pseudo-equilibria" temperatures from 680 to 740°C in which no detectable change of weight has been recorded, although the oxide is not completely recarbonated.

Therefore, for the determination of the equilibrium temperature of the reaction, it is necessary to develop an experimental procedure which allows the overlapping of both curves.

In order to achieve this, we must recall[3-5] that when a chemical reaction is carried out under a heating programme, the plot of the reaction progress parameter vs. temperature shifts itself towards higher temperatures on increasing the heating rate. 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 until

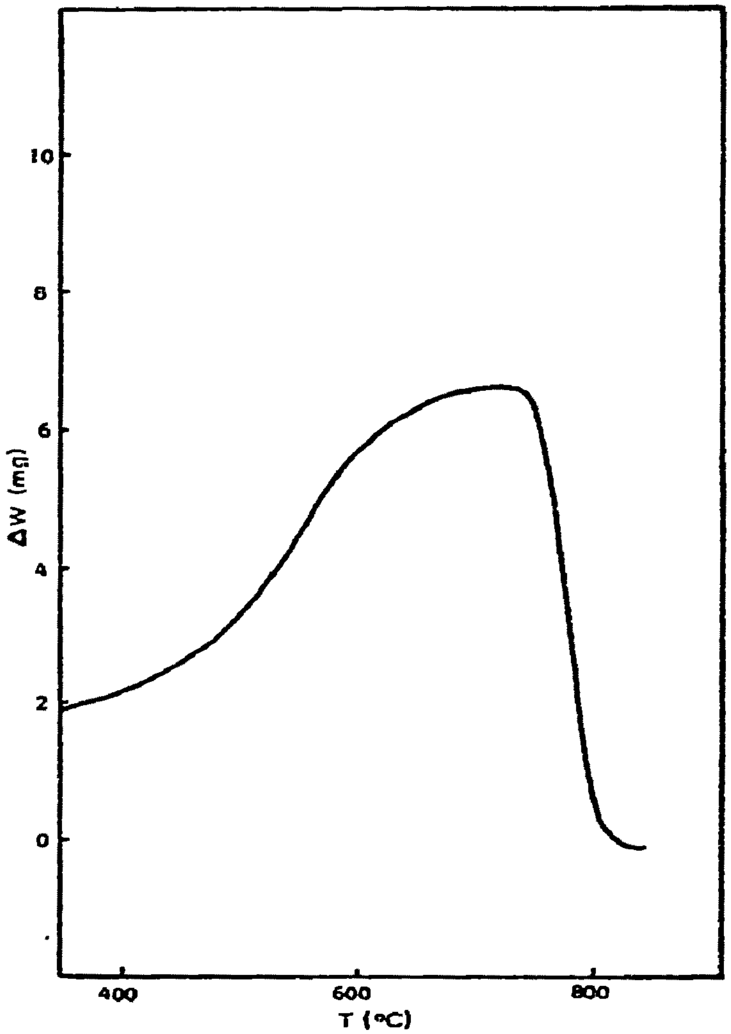

Fig. 1. TG diagram of a sample of CaO–CaCO$_3$. β = 11 °C min^{-1}, P_{CO_2} = 29 Torr.

overlapping of the thermogravimetric curves corresponding to the reactions of formation and decomposition of the salt occurs.

Therefore, 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 reverse reactions is reached. Optimum values of heating rate are always in the range 14–17 °C min^{-1}.

From the diagrams of Fig. 2, CaCO$_3$ equilibrium dissociation temperatures have been determined at different pressures. Both magnitudes have been represented in Fig. 3 by means of the Clausius-Clapeyron equation. In this Figure our results are compared with those tabulated by Stern et al.[2] for the dissociation pressures of CaCO$_3$, determined at different temperatures by classical equilibrium methods.

The small desplacement of the lines observed for the two sets of data of Fig. 3 may be accounted by considering the difference between the actual temperature of the sample and that measured by the thermocouple (~ 20 °C). Unfortunately, it has not been possible to determinate the temperature inside the sample container of the

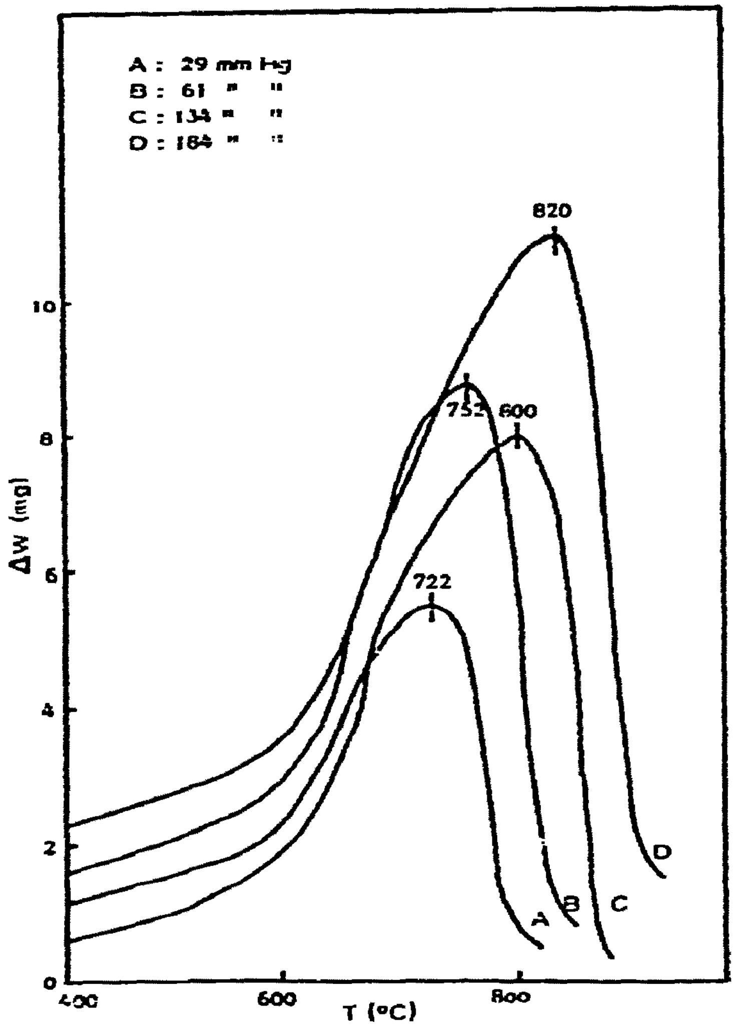

Fig. 2. TG diagrams of a CaO–$CaCO_3$ sample, obtained at different CO_2 pressures. β has been changed until the overlapping is reached.

electrobalance. However, if the experiment is performed in a DTA apparatus, using the same furnace and sample weight and a heating rate of 16°C min^{-1}, a difference of temperature between the thermocouple located inside the sample and the reference thermocouple close to 20°C is recorded.

From the slope of the plot of our data (see Fig. 3), the reaction enthalpy of $CaCO_3$ thermal decomposition has been calculated in the temperature range 990–1080 K. Then, taking into account the "free energy function" values given at different temperatures in ref. 2, a standard enthalpy of 42 kcal mol^{-1} has been obtained. The good agreement of this result with the value of 42.61 kcal mol^{-1} given in ref. 2, seems to support the validity of the method developed in the present paper for the determination of equilibrium constants.

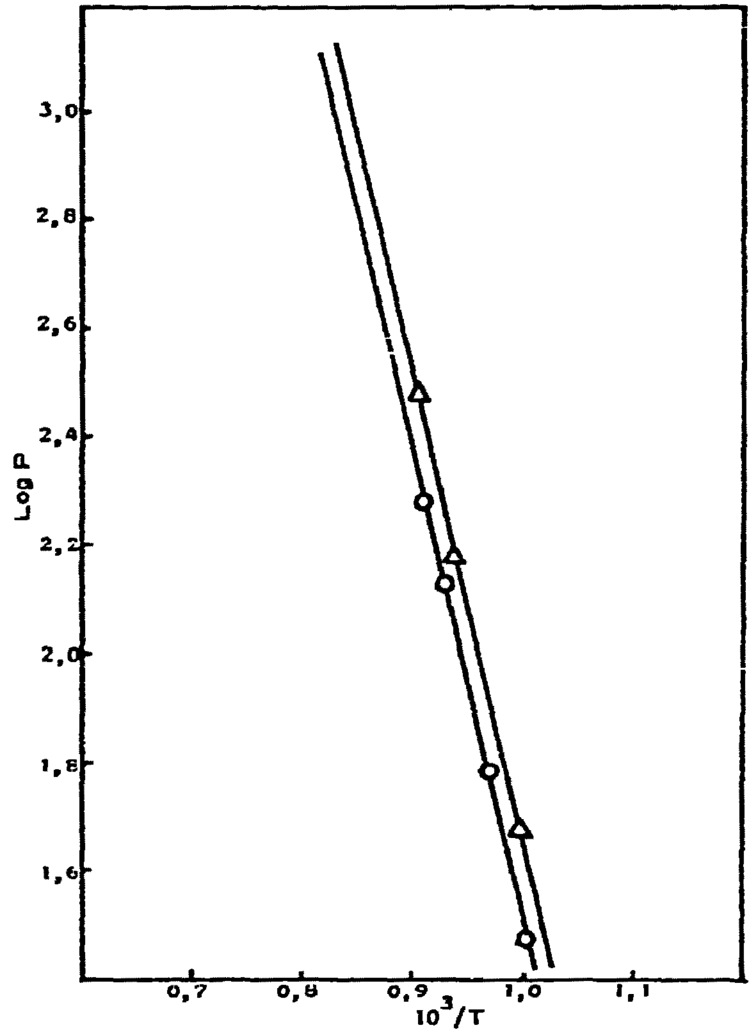

Fig. 3. Clausius-Clapeyron plot of CO_2 equilibrium pressures of $CaCO_3$ thermal decomposition reaction. ○, This work; △, ref. 2.

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