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INFLUENCE OF CO_2 PRESSURE ON THE KINETICS OF THERMAL DECOMPOSITION OF $CdCO_3$

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ABSTRACT

Kinetic analysis was performed on TG and DTG diagrams for the reaction $CdCO_3 \rightarrow CdO + CO_2$ recorded at different pressures of CO_2 up to 26.66 kPa. The results obtained show that the thermal decomposition of $CdCO_3$ follows a first order kinetic law, regardless of the CO_2 pressure used for the experiments. The activation energy was found to increase upon increasing the pressure of CO_2 until a maximum is attained at 14 kPa. At higher pressures the activation energy decreases on increasing the CO_2 pressure. These results cannot be explained by considering the influence of the reverse reaction of formation of $CdCO_3$ because, under the experimental conditions, the ratio $PCO_2/P\text{eq}$ is very close to zero. A mechanism that takes into account both the adsorption of CO_2 on the phase boundary and the influence of the heat transfer phenomena is proposed in order to interpret these results.

INTRODUCTION

A number of authors [1–5] have paid attention to the study of the thermal decomposition of carbonates having a calcite–aragonite structure because of their interest in ceramic reactions and as starting material for the preparation of oxides. There are a number of papers [6–11] on the kinetics of the decomposition of $CdCO_3$ whose results are summarised in Table 1. This table completes and updates the data reported by Brown, et al. [12].

TABLE 1

Kinetic data of the thermal decomposition of $CdCO_3$ selected from the literature

Atmosphere	Mechanism	E (kJ mol^{-1})	Ref.
Air	A_3	91	6
Air	R_3	94	7
Vacuum	–	151	8, 9
CO_2	–	163	10
CO_2	–	151–669	10
N_2	R_3	150	11

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Table 1 shows the lack of agreement among the kinetic parameters obtained by different authors. This behaviour could be explained by considering the influence of CO_2 generated during the salt decomposition that is strongly dependant on the experimental conditions [13,14].

The scope of the present paper is to study the influence of the CO_2 pressure on the thermal decomposition of $CdCO_3$ in order to achieve a better understanding of the reaction mechanism.

EXPERIMENTAL

The $CdCO_3$ used was supplied by Merck (r.a. grade). DTG curves were obtained by using a Cahn electrobalance, model RG, equipped with a derivation adapter Mark II. This system permits work both in high vacuum and under a gas atmosphere.

RESULTS AND DISCUSSION

Several isothermal thermogravimetric curves of the $CdCO_3$ recorded under a vacuum of 1.33×10^{-5} kPa at temperatures ranging from 550 to 610°C and weights of 23 mg are included in Fig. 1. The DTG curve of $CdCO_3$ obtained under a vacuum of 1.33×10^{-5} kPa at a heating rate of 6°C min^{-1} and a starting sample of about 23 mg is shown in Fig. 2 together with the DTG curves obtained at different pessures of CO_2; all the other experimental conditions being identical.

The thermogravimetric analysis of $CdCO_3$ and the X-ray diffraction analysis of the final product of its thermal decomposition show that this reaction takes place through a single step yielding CdO. It has been demonstrated in a previous work [15] that the activation energy, E, obtained from isothermal experiments is independent of the kinetic model previously assumed for performing the calculation, while the value of E determined from non-isothermal experiments is strongly dependant on the previous assumptions regarding the kinetic model. Thus, an agreement between the values of these two parameters calculated from both isothermal and non-isothermal experiments is achieved when the proper reaction kinetic model is assumed for carrying out the calculations.

The best agreement between the kinetic parameters of the thermal decomposition of $CdCO_3$ determined from both isothermal and non-isothermal measurements has been obtained by assuming that this reaction fits a first order kinetic as shown in Tables 2 and 3.

For the kinetic analysis of the DTG curves of $CdCO_3$ in Fig. 2, obtained at different CO_2 pressures, the equation of Sharp and Wentworth [16] for a first order kinetics law must be modified in order to consider the presence of

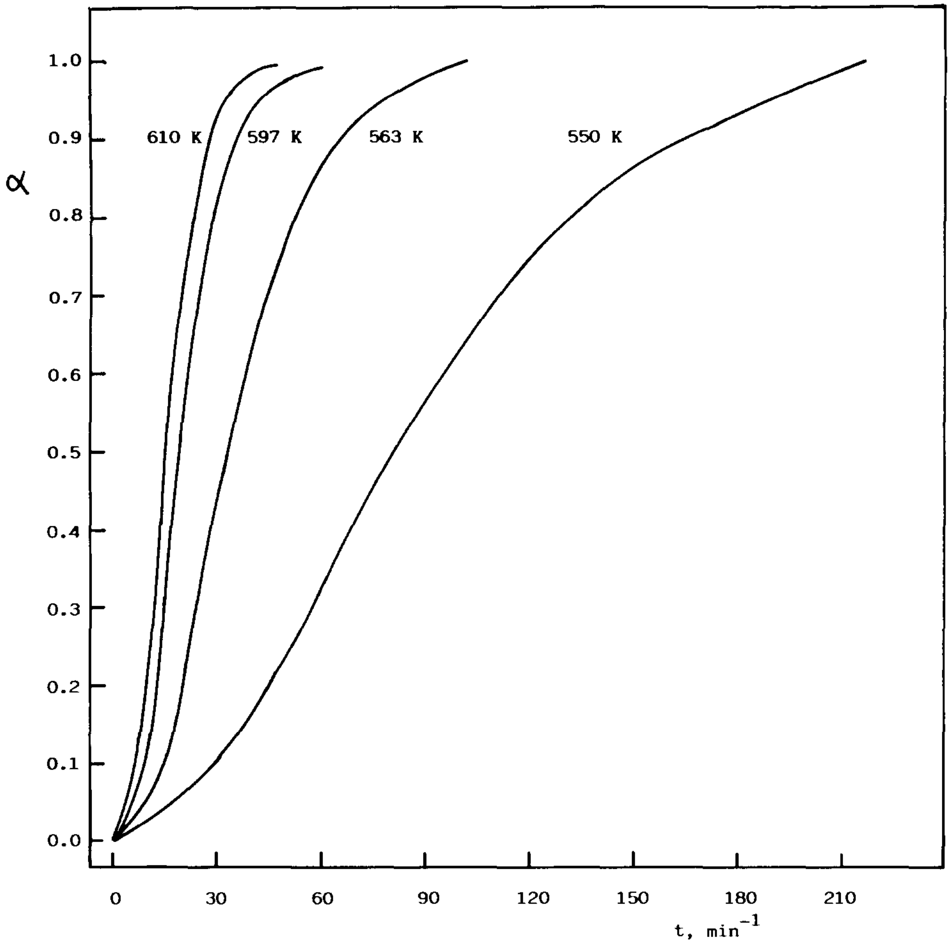

Fig. 1. Isothermal thermogravimetric curves of $CdCO_3$ under a vacuum of 1.33×10^{-5} kPa at several temperatures.

CO_2. Therefore, bearing in mind the microreversibility principle, the following equation is deduced [17]:

$$d\alpha/dt = A\ \exp(-E/RT)(1-\alpha)(1-P/P_d) \tag{3}$$

where P is the pressure of CO_2 and P_d is the dissociation pressure of $CdCO_3$. From the P_d data calculated from ref. (18) the $\ln(1-P/P_d)$–$1/T$ plots included in Fig. 3 were obtained.

These plots show that, at the CO_2 pressures and temperatures at which the DTG curves in Fig. 2 were obtained, $(1-P/P_d)=1$. Therefore, eqn. (3) becomes:

$$d\alpha/dt = A\ \exp(-E/RT)(1-\alpha) \tag{4}$$

that is the same equation used for performing the kinetic analysis of the

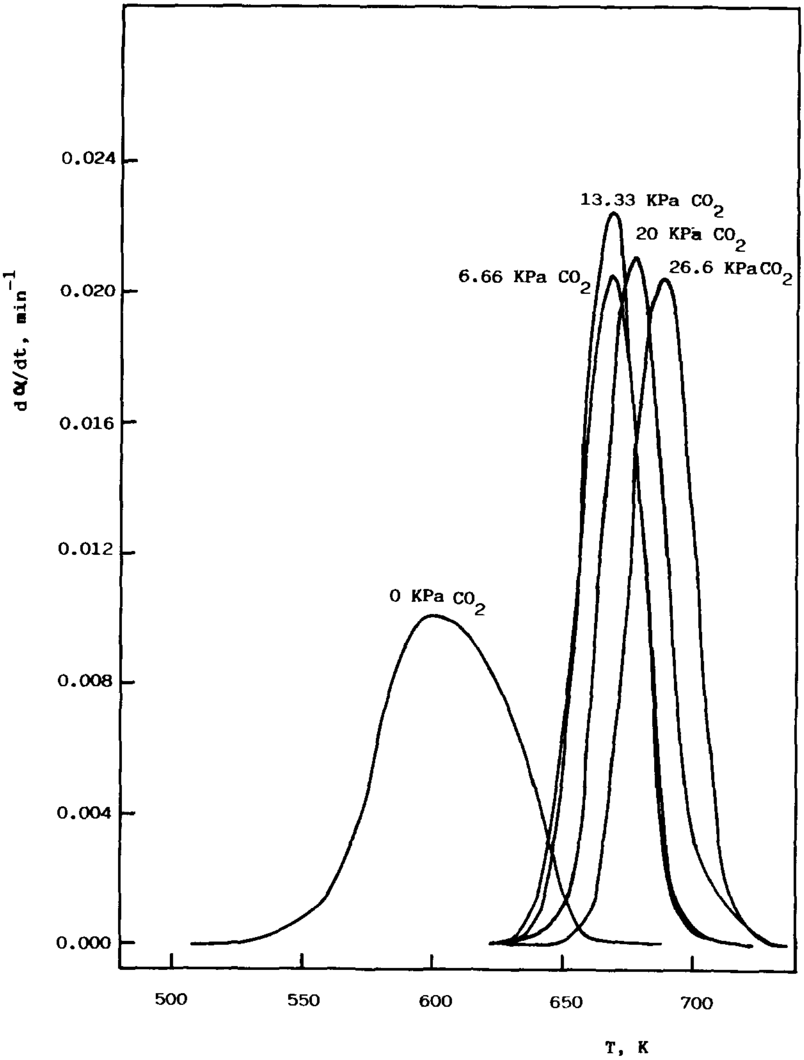

Fig. 2. DTG curves of the thermal decomposition of $CdCO_3$ under different pressures of CO_2.

data obtained under a high vacuum. The kinetic parameters calculated from the data included in Fig. 2 are shown in Table 4.

The plot of the values of the activation energy of the forward reaction of thermal decomposition of $CdCO_3$, against the pressure of CO_2, included in Fig. 4, shows that E increases upon increasing the pressure of CO_2 until an asymtotic value is attained at about 14 kPa.

It is noteworthy that these results cannot be explained by considering the influence of the reverse rection of formation of $CdCO_3$, as we have mentioned before, $P/P_d = 0$.

TABLE 2

Kinetic analysis of the thermal decomposition of the $CdCO_3$ in vacuum

Mechanism	E (kJ mol^{-1})	A (min^{-1})	Correlation coefficient
R_1	−8	2×10^{-3}	−0.39887
R_2	44	9×10^{1}	−0.98019
R_3	61	3×10^{3}	−0.99503
F_1	96	4×10^{6}	−0.99900
A_2	26	2	−0.96668
A_3	2	1×10^{-2}	−0.26120
D_1	88	3×10^{5}	−0.92921
D_2	132	2×10^{9}	−0.97784
D_3	185	2×10^{13}	−0.99491
D_4	151	2×10^{10}	−0.98666

TABLE 3

Kinetic analysis of the thermal decomposition of $CdCO_3$ from several isotherms obtained in high vacuum

Mechanism	E (kJ mol^{-1})	A (min^{-1})	Correlation coefficient
R_1	69	3×10^{4}	−0.94834
R_2	79	4×10^{5}	−0.95877
R_3	82	1×10^{6}	−0.96153
F_1	90	9×10^{6}	−0.96606
A_2	77	3×10^{5}	−0.95710
A_3	72	6×10^{4}	−0.95123
D_1	81	4×10^{5}	−0.96122
D_2	88	1×10^{6}	−0.96473
D_3	99	7×10^{6}	−0.96838
D_4	92	9×10^{5}	−0.96615

The noticeable influence of CO_2 on the thermal decomposition of $CdCO_3$ could be interpreted if we consider that CO_2 is chemisorbed on the CdO surface. Therefore, if we assume that the active phase boundary is the surface not covered by CO_2, the reaction rate would be expressed, according

TABLE 4

Kinetic parameters of the thermal decomposition of $CdCO_3$ under several pressures of CO_2

CO_2 pressure (kPa)	E (kJ mol^{-1})	A (min^{-1})	Correlation coefficient
6.66	254	2×10^{18}	−0.99634
13.33	293	2×10^{21}	−0.99777
20.00	175	5×10^{11}	−0.97430
26.66	258	6×10^{17}	−0.99408

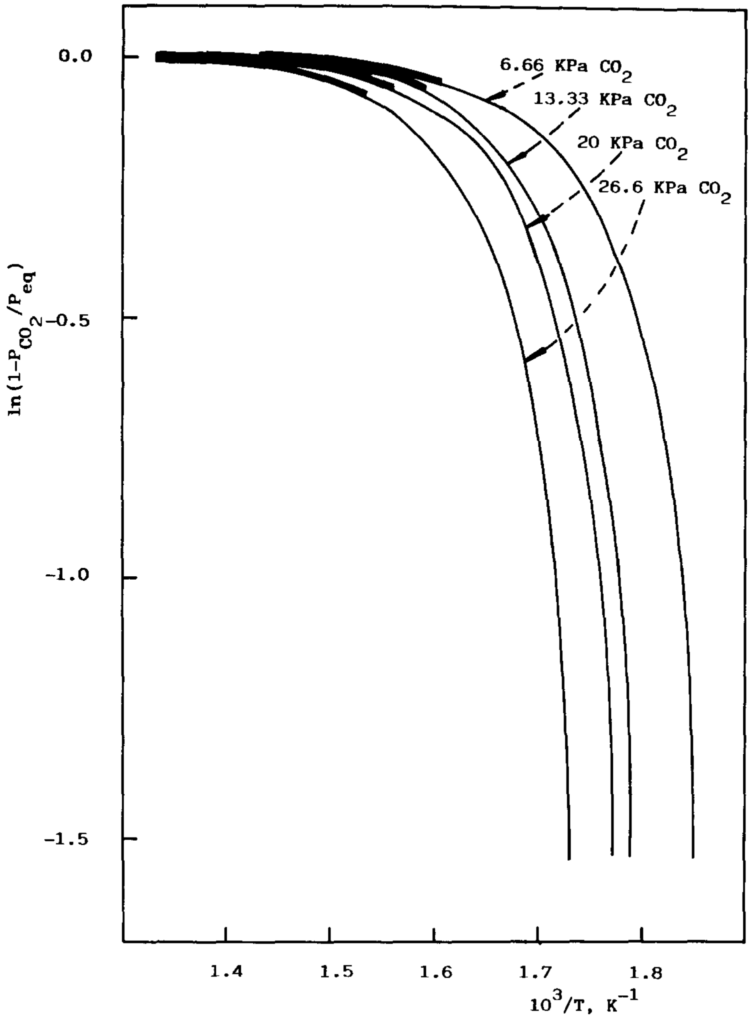

Fig. 3. Plots of the $\ln(1-PCO_2/Peq)$ values calculated for $CdCO_3$ at different pressures of CO_2 as a function of the inverse temperature.

to a previous paper [19], by means of the following equation:

$$d\alpha/dt = A\ \exp(-E/RT)(1-\alpha)[1/(1+aP)] \qquad (5)$$

where the adsorption coefficient a depends on the adsorption heat through the expression:

$$a = a_0\ \exp(\lambda/RT) \qquad (6)$$

where a_0 is constant.

As shown in ref. 19, one can deduce for eqn. (5) that the reaction decreases when CO_2 increases and, therefore, the DTG curves move to

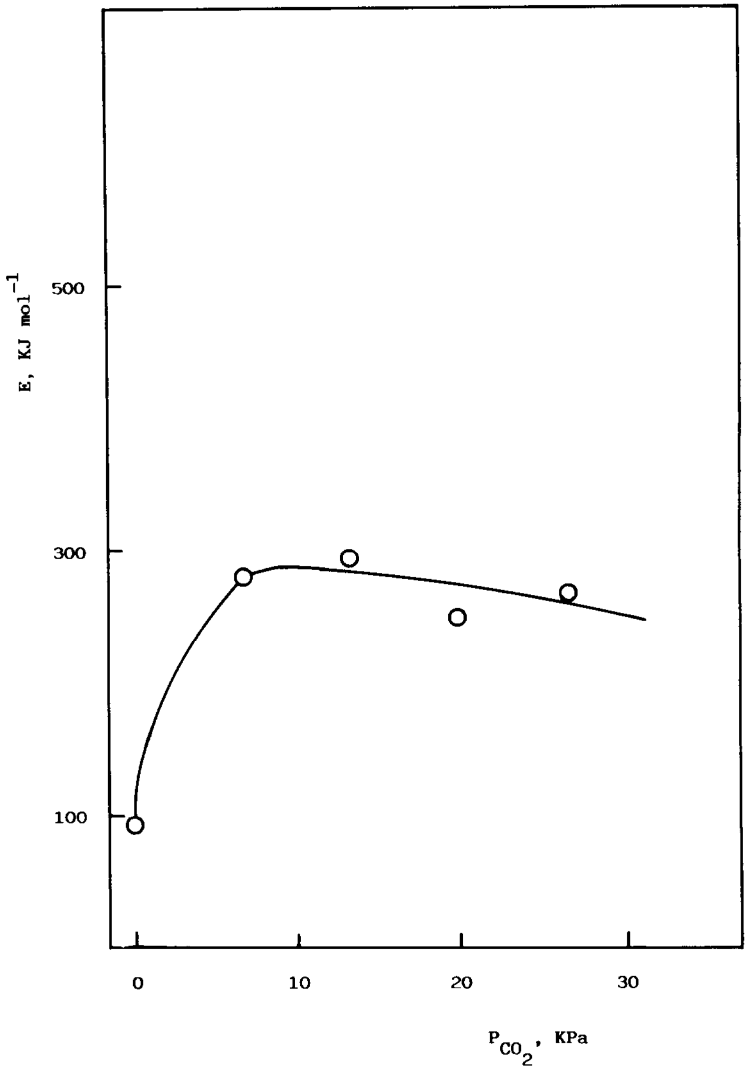

Fig. 4. Plots of the values of the activation energy of the forward reaction of thermal decomposition of $CdCO_3$ as a function of the CO_2 pressure.

higher temperatures, in agreement with our results in Fig. 2. Moreover, from eqns. 5 and 6 it would be expected that the apparent activation energy, E_a, varies from $E_a = E$ (if $aP \ll 1$) to an asymptotic value $E_a = E + \lambda$ (if $aP \gg 1$), what is in agreement with both the plot shown in Fig. 4 and previous results reported in ref. 19.

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