

THE INFLUENCE OF THE PRESSURE OF THE GASEOUS PRODUCT ON THE REVERSIBLE THERMAL DECOMPOSITION OF SOLIDS

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ABSTRACT

Results of the isothermal decomposition of  $\text{CaCO}_3$  in the temperature range 1018-1048K show greater dependence of the  $\text{CO}_2$  pressure on observed rate of reaction compared with the equations based on Langmuir or Freundlich theories of the adsorption. The mechanism of the decomposition on the basis of the Jovanovic adsorption theory has been proposed. In agreement with this mechanism the activation energy of  $\text{CaCO}_3$  decomposition is a linear function of the  $\text{CO}_2$  pressure ( $p$ ) and depends also on the ratio  $p:p_e$  ( $p_e$  - the equilibrium pressure).

INTRODUCTION

It is usually assumed that the rate of the thermal decomposition of solids can be described by the equation:

$$r = \frac{d\alpha}{dt} = k \cdot f(\alpha) \quad (1)$$

where  $k$  - rate constant dependent only on the temperature,  $f(\alpha)$  is a function of the fraction decomposed and depends on the reaction mechanism. It is worth remembering that in the reversible decomposition reaction there is one more -very important- parameter  $f(p,T)$  - function of two variables: the temperature and the pressure [1-3]. The dependence of the decomposition rate on the pressure is expressed usually by the functions based on the Freundlich or Langmuir mechanism of the adsorption [4-6]. In the literature there are a few equations describing the relation between the pressure in the system and the rate of the decomposition [7-10].

Results of our experiments show much higher influence of  $\text{CO}_2$  pressure on the decomposition rate of  $\text{CaCO}_3$  than any predicted theoretically based on the theories mentioned above.

RESULTS AND DISCUSSION

Decomposition of  $\text{CaCO}_3$  (polycrystalline calcite, Merck p.a.) has been carried out isothermally on Mettler 2000C thermoanalyser. Experiments have been made under atmosphere of pure  $\text{CO}_2$  in the pressure range 10-100 mbars at the temperatures 1018-1058K in 10K intervals. Proceedings of ICTA 85, Bratislava

tervals. When the equations based on the Langmuir theory are used the results show deviation from the expected linearity. On the fig1 there are presented our results in the coordinates according to [2] and [9] namely  $V$  vs.  $(\frac{p_e - p}{p_e})$  where:  $V$  - the reaction rate,  $p$  and  $p_e$  - pressure of  $CO_2$  in the system and equilibrium pressure respectively. In the case presented in fig.1 as a rate of the reaction the reciprocal of  $t_{0.5}$  has been taken,  $p_e$  values were calculated from the Tamaru equation [11].

Fig.1 shows that the equation proposed by Barret [2, 9] is not valid in this case. This disagreement and some remarks in the literature showing that the rate of the chemisorption differs from this predicted by a simple Langmuir mechanism induced us to consider the Jovanovic adsorption theory [12] for the thermal decomposition reactions.

Jovanovic modified the Langmuir theory taking into account the readsorption process resulting from collisions between bulk phase gas molecules and molecules desorbing from the surface. Introducing the Jovanovic's interpretations into our description of the  $CaCO_3$  decomposition we have assumed that the  $CO_2$  adsorption and readsorption processes are of the chemisorption type. The chemisorption process takes place on the initially formed  $CaO$  which has some unstable structural state between crystallographic structure of  $CaCO_3$  and the final cubic structure of  $CaO$ . This intermediate  $CaO$  is called here an active  $CaO$  and is given the designation  $CaO^+$ .

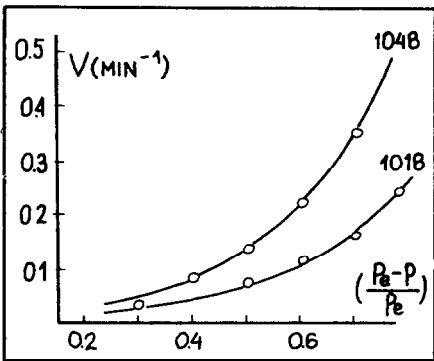


Fig.1 The rate of the decompos. of  $CaCO_3$  at 1018 and 1048K vs.  $(\frac{p_e - p}{p_e})$  where:  $p$  - pressure of  $CO_2$ ,  $p_e$  - equilibrium pressure.

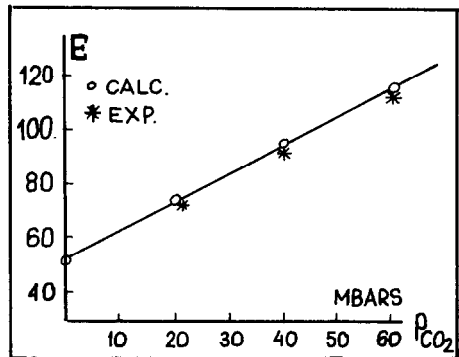


Fig.2 The activation energy  $E$  ( $kCal/mol$ ) of the decomposition of  $CaCO_3$  as a function of the  $CO_2$  pressure.

The chemisorption processes on  $\text{CaO}^+$  result in the production of  $\text{CaCO}_3$ . We have also assumed that the decomposition being the chemisorption process takes place on the  $\text{CaCO}_3$  surface not covered by  $\text{CaO}^+$ . We will show later this assumption is not important quantitatively, because the fraction of the total reaction surface occupied by  $\text{CaO}^+$  is negligible.

Our next assumption is that chemisorption processes during the decomposition are rate-controlling and the crystallisation of  $\text{CaO}$  to the stable form is fast and does not have influence on the observed rate of the decomposition (except, of course, for the initial induction period, when nucleation process is important).

Let us consider the elementary processes of the decomposition: A). In agreement with the Jovanovic ideas the rate of the chemisorption can be expressed as

$$r_{\text{DES}} = k_1(1-\Theta)e^{-bP} \quad (2)$$

with  $k_1 = k_{10} e^{\frac{-\alpha \Delta H}{RT}}$  and  $b = \frac{b_0}{\sqrt{T}} e^{\frac{\beta \Delta H}{RT}}$

where  $\alpha$  and  $\beta$  are dimensionless constants fluctuated near 1,  $\Theta$  is the fraction of the total reactive surface not covered by  $\text{CaO}^+$ ,  $\Delta H$  is the enthalpy of the decomposition of  $\text{CaCO}_3$  and  $b_0$  and  $k_{10}$  are the proportionality constants.

The assumption that  $\alpha$  and  $\beta$  values are about 1 results from the fact that the surface potential in chemisorption is generally almost equal with the heat of the reaction. Particular discussion of the eqs. (2) and (6) will be published in our next paper [13]. B). We consider the  $\text{CaO}^+$  crystallization  $\text{CaO}^+ \rightarrow \text{CaO}$  as a fast, first order process (fast in comparison with the desorption), having the rate :

$$r_c = k_c \Theta \quad \text{and } k_c \gg k_1 \quad (3)$$

Of course, also the process  $\text{CaO}_{\text{cub}} \rightarrow \text{CaO}^+$  can be considered, but in comparison with the fast decomposition process the latter seems to be not important.

C). Once again, in agreement with Jovanovic theory, we can write the equation of the adsorption rate:

$$r_{\text{ads}} = k_1 \Theta (1 - e^{-bP}) \quad (4)$$

Let us assume now that the process is fully developed (the induction period is over) and the reacting surface is in the Quasi-steady state ( the rate of the decomposition per unit area and are constant). From the equations (2), (3) and (4) we have:

$$\Theta = \frac{k_1}{k_c} \cdot e^{-bp} \quad (5)$$

$$r = k_1 \cdot e^{-bp} = k_{10} \cdot e^{-\frac{\alpha \Delta H}{RT}} \cdot e^{-\frac{b_0}{\sqrt{T}} \exp\left(\frac{\beta \Delta H}{RT}\right) \cdot p} \quad (6)$$

The equation (6) describes the influence of temperature and CO<sub>2</sub> pressure on the decomposition rate per unit area of CaCO<sub>3</sub> and the equation (5)- the influence of temperature and CO<sub>2</sub> pressure on the fraction of the reactive surface covered by CaO<sup>+</sup>.

From the eqs. 5 and (6) very interesting conclusions can be noticed:

- 1). The surface fraction is small and becomes even smaller with the increase of the CO<sub>2</sub> pressure. The result of the increase of the CO<sub>2</sub> pressure is the decrease of the number of produced CaO nuclei (see ref. 14 ).
- 2). The eq. (6) shows that in vacuum the activation energy of CaCO<sub>3</sub> decomposition is equal  $\alpha \Delta H$ , so is close to the heat of the reaction.
- 3). It can be shown that the activation energy under the constant pressure of CO<sub>2</sub> is a linear function of the pressure ( see fig.2)

$$E_p = \alpha \Delta H + b \cdot p \left( \beta \Delta H + \frac{1}{2} RT \right) \quad (7)$$

- 4). Analogically, the activation energy under constant ratio  $x = \frac{p}{p_e}$  is the linear function of x

$$E_x = \alpha \Delta H + x \cdot b \cdot p_e \cdot \left( \beta \Delta H - \Delta H + \frac{1}{2} RT \right) \quad (8)$$

All relations described above are related to the case of CaCO<sub>3</sub> decomposition under vacuum or in CO<sub>2</sub> atmosphere. However, one can expect in accordance with the influence of the collision effect on the readsorption, that the atmosphere of the inert gas can alter the decomposition rate as well as the morphology of the product.

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