

## **THERMAL DECOMPOSITION OF A DOLOMITIC LIMESTONE WITH BRUCITE UNDER QUASI-ISOTHERMAL CONDITIONS USING A QUASI-ISOBARIC CRUCIBLE AND ASSOCIATED NON-ISOTHERMAL KINETIC PARAMETERS**

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### **ABSTRACT**

The recorded thermoanalytical curves of a natural brucite were used to distinguish the thermal decomposition steps from 20 to 1000°C. In order to identify the crystal phases of the original material as well as of the decomposition intermediates, X-ray diffraction was used. The non-isothermal kinetic parameters of the thermal decompositions of brucite and magnesium carbonate from dolomite were determined.

### **INTRODUCTION**

Much research has been devoted to the thermal behaviour of carbonatic rocks, which have various industrial uses [1–3]. In this paper the results concerning the thermal decomposition of a natural powdered dolomitic rock as well as some associated non-isothermal kinetic parameters are reported.

### **EXPERIMENTAL**

The thermoanalytical curves were recorded with a Paulik–Paulik–Erdey type derivatograph (MOM Budapest Q-1500). The X-Ray analyses were performed with a Philips PW 1140 diffractometer using Cr  $K_{\alpha}$  radiation. The mean crystallite sizes of the original powder determined with the Scherrer formula [4] were between  $9.9 \times 10^2$  and  $5.6 \times 10^2$  Å.

### **RESULTS AND DISCUSSION**

From the powder diffractograms of the original material brucite ( $\text{Mg}(\text{OH})_2$ ), dolomite ( $\text{MgCO}_3 \cdot \text{CaCO}_3$ ) and calcium carbonate (as calcite and aragonite, in traces) were identified.

On the TG curves recorded in quasi-isothermal conditions with a quasi-isobaric crucible, four decomposition steps can be distinguished (Fig. 1a). These steps occur in the following temperature intervals

(I) 427–450°C

(II) 723–765°C

(III) 915–948°C

(IV) 952–983°C

The diffractogram of a sample heated under the above conditions up to 450°C shows the diffraction lines of the magnesium oxide but not the brucite. Thus, the first step occurring in the thermal decomposition of brucite is



From diffractometric and derivatographic data it follows that

(1) step (II) corresponds to the thermal decomposition of dolomitic

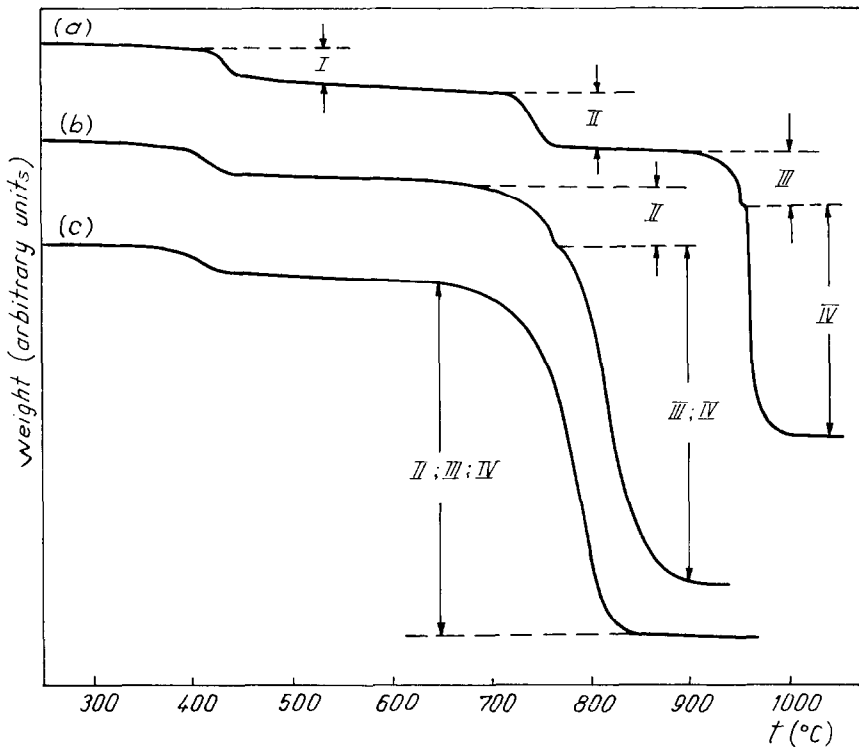
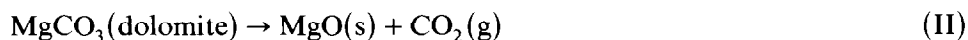
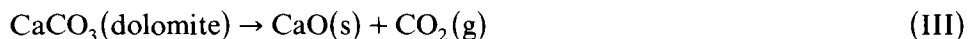


Fig. 1. The thermal decomposition curves of a dolomitic limestone with brucite powder in quasi-isothermal conditions. (a) Quasi-isobaric crucible; (b) covered crucible in the shape of a truncated cone; (c) uncovered flat crucible. Sample weight  $m = 0.1057$  g decomposition rate  $dm/dt = 0.2$  g  $\text{min}^{-1}$ .

magnesium carbonate



(2) step (III) can be assigned to the thermal decomposition of dolomitic calcium carbonate



(3) step (IV) corresponds to the decomposition of calcitic calcium carbonate



The final decomposition product consists of a mixture of CaO(s) and MgO(s).

From the weights of water and carbon dioxide evolved, the composition (in weight %) of the original material is evaluated as follows

Mg(OH) <sub>2</sub>	(brucite)	10.2%
MgCO <sub>3</sub>	(dolomite)	16.2%
CaCO <sub>3</sub>	(dolomite)	18.0%
CaCO <sub>3</sub>	(calcite)	54.2%
Impurities		1.4%

The corresponding molar ratios are Mg(OH)<sub>2</sub>(brucite) : MgCO<sub>3</sub>(dolomite) : CaCO<sub>3</sub>(dolomite) : CaCO<sub>3</sub>(calcite) = 0.91 : 0.91 : 1.00 : 3.02. The shape and position of TG quasi-isothermal-isobaric curves are very sensitive to the change of working conditions: as is evident on comparing Fig. 1b, recorded with a crucible in the shape of a truncated cone, with Fig. 1c, recorded with a flat crucible, the powder being spread in a thin layer. In quasi-isothermal conditions with a quasi-isobaric crucible all the decomposition steps are well separated; however, in non-isothermal conditions steps (I) and (II) are still separated but steps (III) and (IV) overlap (Fig. 2). Nevertheless to determine the kinetic parameters for reactions (I) and (II), non-isothermal conditions were used at a heating rate of 5 K min<sup>-1</sup>, because under such conditions a negligible contribution of the reverse reactions is expected.

The conversion function,  $f(\alpha)$ , for steps (I) and (II) was determined by the use of the pair of iso-kinetic points method, based on the equation [5]

$$\log \frac{f(\alpha)}{f(\alpha')} = \frac{E}{2.303 R} \left( \frac{1}{T} - \frac{1}{T'} \right) \quad (1)$$

where  $\alpha$ ,  $\alpha'$  and  $T$ ,  $T'$  are the conversion degrees and temperatures, respectively, corresponding to the pair of iso-kinetic points;  $E$  is the activation energy; and  $R$  is the gas constant.

Considering two different forms of the conversion function  $f_1(\alpha) = (1 - \alpha)^n$

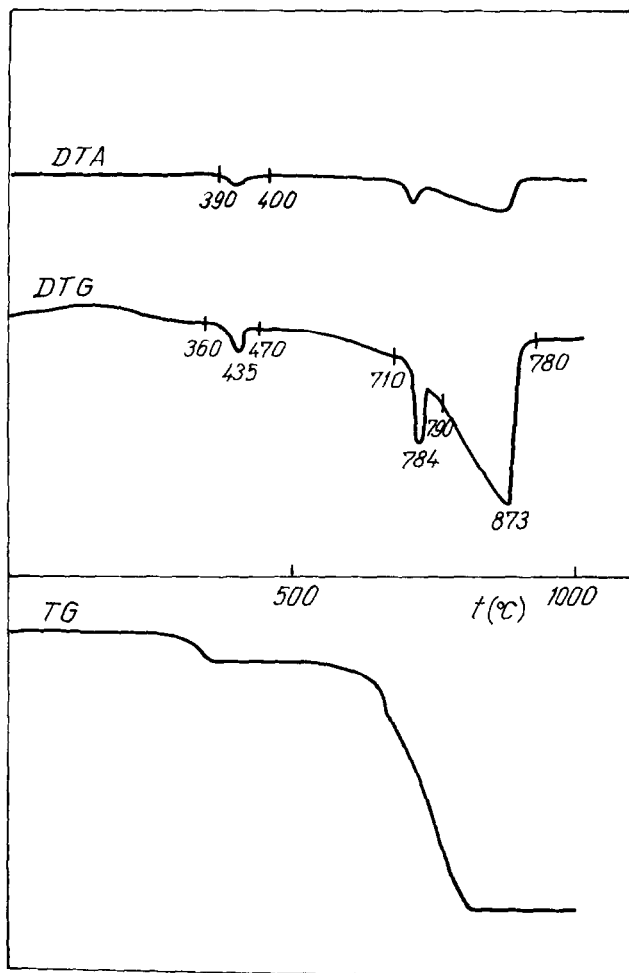


Fig. 2. Non-isothermal decomposition curves of the dolomitic limestone with brucite powder.  $m = 1.0845$  g;  $dT/dt = 5$  K  $\text{min}^{-1}$ . Uncovered crucible in the shape of a truncated cone.

and  $f_2(\alpha) = \alpha(1 - \alpha)$ , from eqn. (1)

$$\log \frac{1 - \alpha}{1 - \alpha'} = \frac{E}{2.303 Rn} \left( \frac{1}{T} - \frac{1}{T'} \right) \quad (2)$$

$$\log \frac{\alpha(1 - \alpha)}{\alpha'(1 - \alpha')} = \frac{E}{2.303 R} \left( \frac{1}{T} - \frac{1}{T'} \right) \quad (3)$$

where  $n$  is the reaction order.

The linear plots of eqns. (2) and (3) for reaction (I) are given in Fig. 3. It is evident that eqn. (2) describes more clearly the kinetics of decomposition. From the slope of the straight line the value  $45 \text{ kcal mol}^{-1}$  was obtained for

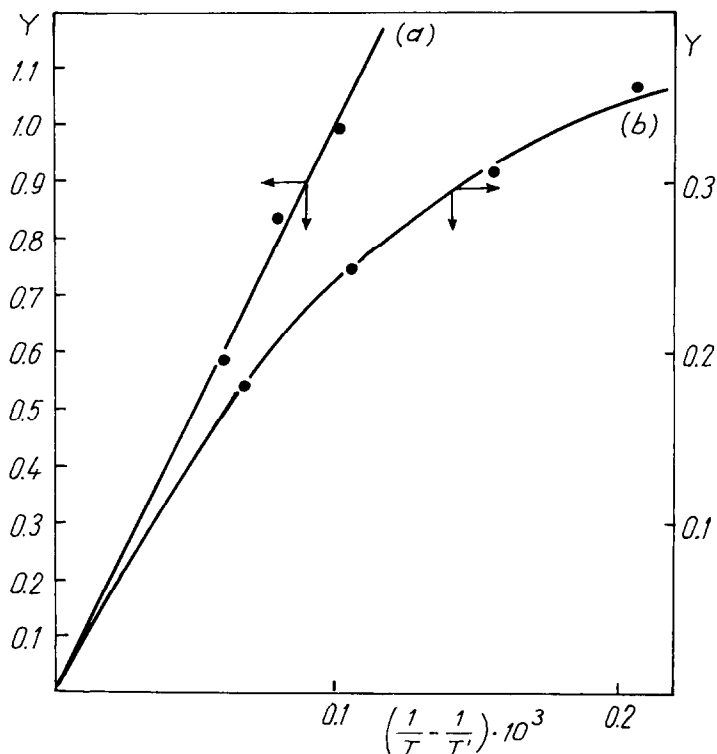


Fig. 3. (a) Plot of eqn. (2) for step (I).  $Y = \log \frac{1-\alpha}{1-\alpha'}$ . (b) Plot of eqn. (3) for step (I).  $Y = \log \frac{\alpha(1-\alpha)}{\alpha'(1-\alpha')}$ .

$E/n$ . The activation energy can be estimated from the initial portion of the TG and DTG curves. In such conditions

$$\log \frac{d\alpha}{dt} = B - \frac{E}{2.303 RT} \quad (4)$$

where  $B$  is practically constant. From the slope of the straight line ( $d\alpha/dt$ ,  $1/T$ ) the value of  $E$  is  $38 \text{ kcal mol}^{-1}$ . The value of the reaction order can be obtained as follows

$$n = \frac{E}{E/n} = \frac{38}{45} = 0.84$$

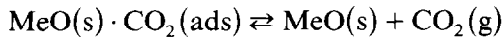
The heterogeneous decompositions which occur according to the contracting sphere model are characterized by  $n = 2/3$  while the decompositions with equal probability of each crystalline grain should give  $n = 1$  [6]. The intermediate value of the reaction order can be assigned to a combined decomposition regime with contributions due to the displacement of the interface as well as to the random nucleation in the crystalline grains.

Using the values of  $E$  and  $d\alpha/dt$  measured from the slope of the TG curve the pre-exponential factor  $A$  can be obtained from the equation

$$\log \frac{d\alpha}{dt} = \log A + \log f(\alpha) - \frac{E}{2.303 RT} \quad (5)$$

which leads to the value  $A = 5.1 \times 10^9 \text{ s}^{-1}$ . The values of the kinetic parameters were checked with the Coats–Redfern integral method [7]. The shifts of the kinetic parameter values with respect to those mentioned are  $\Delta E = 2 \text{ kcal mol}^{-1}$ ;  $\Delta n = 0.12$ ;  $\Delta A = 10 \text{ s}^{-1}$ . Quite good agreement is obtained between the kinetic parameters determined by help of the two different methods.

In the same way for step (II), which consists of the decomposition of magnesium carbonate, the following values of the kinetic parameters are obtained:  $n = 1.2$ ;  $E = 229 \text{ kcal mol}^{-1}$ ;  $A = 1.9 \times 10^{46} \text{ s}^{-1}$ . The high value of the activation energy can be attributed to the quite strong influence of the reverse reaction. The increase of the apparent activation energy with the partial pressure of carbon dioxide was reported by Zavadski and Bretsznajder for the isothermal decomposition of  $\text{CaCO}_3$  [8]. This effect can be explained by taking into account the increase of the equilibrium dissociation pressure with temperature and the desorption of carbon dioxide from the surface of the solid product according to the following sequence



Based on such a mechanism Prodan et al. [9] derived the following relationship

$$E_a = E_2 \pm \lambda + mQ \frac{P_0^m}{P_0^m - P^m} \quad (6)$$

where  $E_a$  and  $E_2$  are the apparent activation energy of the direct reaction and the true activation energy of the reverse reaction, respectively;  $\lambda$  is the heat of adsorption of  $\text{CO}_2$  onto  $\text{MeO}(\text{s})$ ;  $m$  is a constant;  $p_0$  is the equilibrium pressure of  $\text{CO}_2$ ; and  $p$  is the actual value of  $\text{CO}_2$  pressure [9]. According to eqn. (6) the change in  $p$  value between 0 and  $p_0$  corresponds to a change in  $E_a$  value between  $(E_2 \pm \lambda + mQ)$  and  $\infty$ .

The rather high value of the pre-exponential factor compensates for the high value of the activation energy.

Due to the overlap of steps (III) and (IV) the corresponding non-isothermal kinetic parameters were not determined.

The Zavadski–Bretsznajder effect was put in evidence to the decomposition of strontium carbonate in the presence of  $\text{H}_3\text{BO}_3$  [10] as well as to the decomposition of calcium oxalate [11].

## CONCLUSIONS

(1) A thermoanalytical study of the decomposition steps of a limestone with brucite was performed.

(2) For the well resolved steps of decomposition the non-isothermal kinetic parameters were determined.

(3) The high value of the activation energy for the decomposition of magnesium carbonate is an indication of the accumulation of  $\text{CO}_2$  at the reaction interface, which determines the occurrence of the reaction near equilibrium.

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