

A NEW METHOD FOR THE DETERMINATION OF REACTION KINETICS FROM DTA AND TG CURVES. PART II. APPLICATION OF THE METHOD TO THE THERMAL DECOMPOSITION OF CARBONATES

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ABSTRACT

The method proposed in Part I [1] for the determination of the reaction kinetics was tested for the decomposition reactions of calcite and magnesite. It was shown that the mechanism of magnesite and calcite decomposition corresponds completely to reactions the total rate of which is limited by the decomposition at boundary of the phases, i.e. for which the condition $f(\alpha) = (1 - \alpha)^n$ is valid. With change of heating rate, there is also a change in the kinetic law that describes the rate of decomposition of calcite and magnesite.

INTRODUCTION

For the investigation of the kinetics of endothermic reactions, i.e. for testing the method presented in Part I [1], natural calcite and magnesite were used, bearing in mind that their decomposition reactions had been investigated by several authors and that different values of the kinetic parameters has usually been obtained. For that reason, the objective was to compare the results obtained with the existing values and to draw the appropriate conclusions.

EXPERIMENTAL

Based upon the investigations carried out and the working model proposed, we have chosen those solutions, as far as the apparatus was con-

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cerned, which give simultaneous curves of the majority of methods of thermal analysis (DTA, DTG, TG) so that all curves are obtained under the same conditions and it is possible to compare results obtained by particular methods. For this reason, for non-isothermal investigations, the Derivatograph 1500 (MOM, Budapest, Hungary) was used. For experimental investigations under isothermal conditions, the Netzch Model 409 thermobalance was used. All investigations were carried out on the same initial sample mass with the particle size $-125 + 100 \mu\text{m}$ at different heating rates in an atmosphere of air.

Investigation of the kinetics of the thermal decomposition of calcite and magnesite was carried out in two phases: (a) identification of the reaction mechanism using results obtained under non-isothermal conditions, and (b) determination of the kinetic parameters with the working model [1].

RESULTS AND DISCUSSION

Determination of reaction mechanism

In the working model [1], it was suggested that the interpretation of non-isothermal data be based upon results of isothermal investigations from the point of view of the determination of the function $f(\alpha)$ and its general form, which appears in the working equation of the model in integrated form $F(\alpha)$. According to the assumptions of the model [1], the isothermal decomposition of magnesite and calcite was first carried out at several different temperatures.

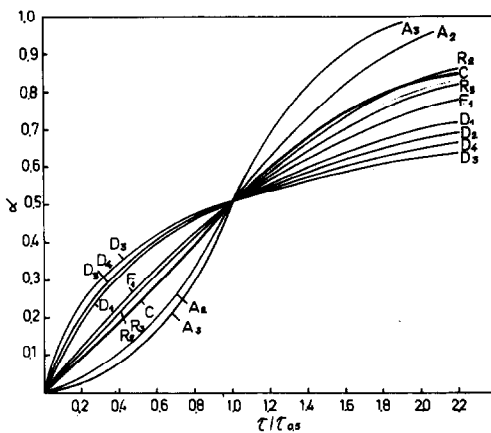


Fig. 1. The relationship between the degree of transformation and the reduced time ($\tau/\tau_{0.5}$) for the decomposition process. C, experimental curve for magnesite and calcite.

Results show that the temperature has a more pronounced influence upon the progress of the decomposition than does its duration, which is characteristic of reactions that proceed in kinetic regions. The results obtained under isothermal conditions are shown in the coordinate system $\alpha = f(\tau/\tau_{0.5})$ in Fig. 1 where they are superimposed in one curve, C, in the case of magnesite and calcite. Comparing the experimental curves with the theoretical curves, Fig. 1, it may be seen that the thermal decomposition processes of magnesite and calcite correspond to reactions, the total rate of which is limited by the decomposition process at the boundary of the phases, i.e. the mechanism of which may be best represented by a function of the general form $f(\alpha) = (1 - \alpha)^n$.

Determination of kinetic parameters

The previously identified kinetic function $f(\alpha)$, which best describes the process of decomposition of carbonates, was used in the working model equation [1] in its integrated form. Other data in the equation of the working model were obtained from experimental measurements under non-isothermal conditions for the case when the temperature was a linear function of time. Investigations were carried out at heating rates of 2.5, 5.0, 10.0 and 18.0 °C min⁻¹.

For data processing, the DTA and TG curves were used. The transformation degree was calculated using the equations given in Part I [1]. By comparing the change of the transformation degree as a function of time (Fig. 2 and 3) from data obtained from the DTA and TG curves under non-isothermal conditions at different heating rates, it may be seen that the

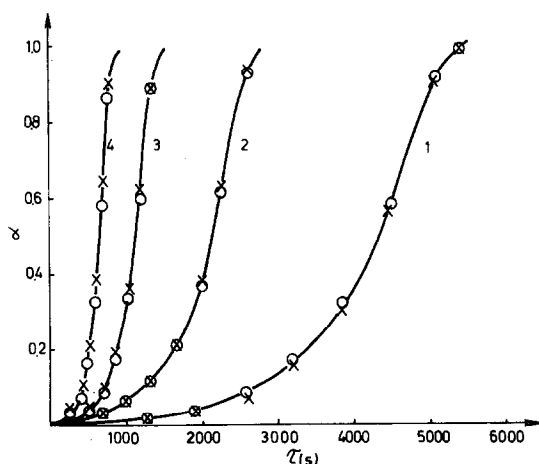


Fig. 2. Kinetic curves $\alpha = f(\tau)$ for the decomposition of magnesite under non-isothermal conditions. 1, $\Phi = 2.5$ deg min⁻¹; 2, $\Phi = 5.0$ deg min⁻¹; 3, $\Phi = 10.0$ deg min⁻¹; 4, $\Phi = 18.0$ deg min⁻¹. O, DTA; X, TG.

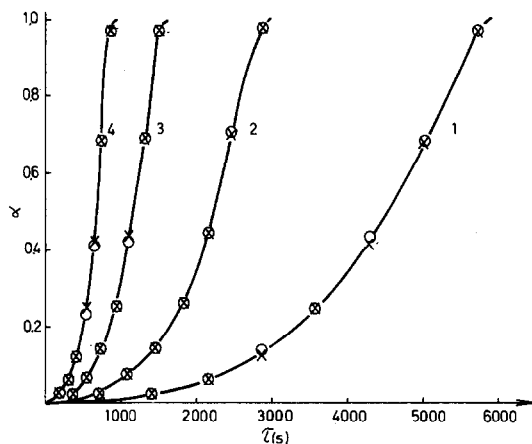


Fig. 3. Kinetic curves $\alpha=f(\tau)$ for the decomposition of calcite under non-isothermal conditions. 1, $\Phi=2.5 \text{ deg min}^{-1}$; 2, $\Phi=5.0 \text{ deg min}^{-1}$; 3, $\Phi=10.0 \text{ deg min}^{-1}$; 4, $\Phi=18.0 \text{ deg min}^{-1}$. 0, DTA; \times , TG.

values of the transformation degree are almost the same, i.e. they do not show large differences, bearing in mind the limitations which are used in their calculation from the data available from DTA.

Using the results of previous investigations for each experiment, i.e. for each heating rate using the equations of the working model, the values of the kinetic parameters, activation energy, pre-exponential factor and reaction order, were obtained for both decomposition reactions. Tables 1 and 2 show the comparative values of kinetic parameters obtained from the DTA and TG curves. The results are closely similar for both methods of analysis and there are no large deviations which would call for special comment.

Analysing the values of the kinetic parameters obtained for different heating rates, it can be seen that, in both decomposition reactions, the activation energy gradually increases with increase of the heating rate.

TABLE 1

Values of the kinetic parameters for the decomposition of magnesite at different heating rates

Φ ($^{\circ}\text{C min}^{-1}$)	$E(\text{kJ mole}^{-1})$		n		$A \times 10^4$	
	DTA	TG	DTA	TG	DTA	TG
2.5	131.0	133.0	0.510	0.560	10.921	17.855
5.0	132.0	134.0	0.570	0.650	14.976	21.194
10.0	136.0	138.0	0.510	0.650	24.749	37.720
18.0	139.5	140.0	0.590	0.730	42.206	55.716

TABLE 2

Values of the kinetic parameters for the decomposition of calcite at different heating rates

Φ ($^{\circ}\text{C min}^{-1}$)	$E(\text{kJ mole}^{-1})$		n		$A \times 10^4$	
	DTA	TG	DTA	TG	DTA	TG
2.5	155.0	157.0	0.295	0.295	1.439	1.792
5.0	157.0	158.5	0.305	0.310	2.670	3.214
10.0	163.5	164.0	0.275	0.285	6.765	7.322
18.0	176.0	175.0	0.290	0.305	30.382	28.761

According to the literature data, the heating rate may largely influence the structure of the reactants and with the higher heating rate there may appear the change of the failure density which causes the change of the activation energy at the place of failure.

If the reaction represents a surface process of distribution of reaction centres along the angles of the edges and the sample plane, the activation energy may change with the change of the heating rate. Since, for both reactions studied, the total process rate is limited by the process of decomposition at the phase boundary, according to the previous assumption, the activation energy changes with change of heating rate.

The change of activation energy with change of heating rate does not mean that the Arrhenius expression is not valid, because the activation energy in homogeneous reactions has its definite physical meaning, while in heterogeneous reactions, such as those studied, this degree of uniqueness does not hold and it is usually called "the apparent activation energy", which is different from the actual activation energy for homogenous reactions.

Decomposition reactions of solid components are also characterised by the so-called "apparent reaction order", which is included in the equation of the reaction mechanism and which is different from the reaction order for homogenous reactions. It is known from the literature that the apparent reaction order does not have to be an integer but may also be a decimal number. It is only determined by complete agreement of the experimental data with the equation for the reaction rate. Apart from this, it is important to know that there does not have to be a definite relationship between the form of stoichiometric equation for heterogeneous reactions and the reaction order. This is not the case for homogenous reactions. Investigations carried out so far on the decomposition reactions of solid components have shown that characteristic values of n are 0, 1, 1/2 and 2/3. However, Norris et al. [2] have shown that the most frequent values for the apparent reaction order for these reactions range from 0.2 to 0.6. They attribute this to asymmetry of the reaction surface.

Our investigations have shown that in the decomposition reaction of magnesite; the apparent reaction order changes over limited intervals, while in the decomposition reaction of calcite, it is almost constant for DTA as well as for TG results (Table 2). Values for the apparent reaction order for both reactions show that the mechanism of their decomposition does not correspond to any of the kinetic functions that are used in the literature. This shows that all the methods which use assumptions for the reaction order do not have enough arguments.

Deviations mentioned in the apparent reaction order from values that are considered in the model R_2 and R_3 are probably the result of the fact that the reaction phase boundary, which limits the total process rate does not proceed at the same rate along all crystal planes compared with models that consider functions R_2 and R_3 .

For comparison with the results obtained, Tables 3 and 4 give the values of the kinetic parameters for the decomposition reactions of calcite and magnesite. The results were mainly obtained under isothermal conditions. Our results are particularly close to those of Britton et al. [3].

Based upon the previous discussion, it may be concluded that for each heating rate there is a corresponding specific equation for the rate of decomposition, i.e. the reaction rate. Thus, for example, the kinetic laws for the reaction rate of the decomposition of calcite and magnesite at a heating rate of $5.0^\circ\text{C min}^{-1}$ in an atmosphere of air at linear temperature increase may be expressed as

$$\frac{d\alpha}{d\tau} = 16.47 \times 10^4 \exp\left[-\frac{15876.8}{672 + (5.0/60)\tau}\right] (1 - \alpha)^{0.57} \quad (1)$$

for magnesite and

$$\frac{d\alpha}{d\tau} = 2.98 \times 10^4 \exp\left[-\frac{18833.8}{903 + (5.0/60)\tau}\right] (1 - \alpha)^{0.30} \quad (2)$$

for calcite. In the same way, equations for other heating rates may be

TABLE 3

Summary of the literature values of the kinetic parameters of the decomposition of magnesite

Author	Method	E (kJ mole ⁻¹)	n	$\ln A$
Kissinger [4]	DTA	135.5	0.56	12.58
	isotherm	136.0	0.55	12.63
Britton et al. [3]		149.0	0.58	12.44
Piloyan and Norikova [6]		134		
Živković and Dobovišek [7]	DTA (part of curve)	106.0	1	
	TG (part of curve)	127.0	1	

TABLE 4

Summary of literature values of kinetic parameters of the process of decomposition of calcite

Author	Method	E (kJ mole ⁻¹)	n	$\ln A$
Kissinger [4]	DTA	183.0	0.32	12.31
	isotherm	179.5	0.22	12.06
Živković and Dobovišek [7]	DTA (part of curve)	126.0	1	
	TG (part of curve)	114.0	1	
Britton et al. [3]		174.0	0.3	10.61
Freeman and Carroll [8]		163.0	0.4	
Huttig and Kappal [9]		205.0	0-1	
Škavara and Šatava [10]		171.5		
Tarner [5]		146.5		

formed. Differences in eqns. (1) and (2) are the result of differences in the values of the kinetic parameters for the decomposition of calcite and magnesite.

Most frequently, in decomposition of solid components, which is probably the case in the decomposition of calcite and magnesite, the total rate is limited by the process of decomposition at phase boundaries, i.e. by resistances to chemical reaction which are the result of a decrease of reaction distributive surface. In practice, the movement of reaction distributive surface is not uniform and depends upon the strain in the crystal structure, i.e. the presence of errors-failures in the crystal grid.

However, differences in the values of the kinetic parameters are probably the result of heat transfer in the system. The decomposition reaction of calcite proceeds at higher temperatures than that of magnesite. In the decomposition of calcite, the values of the kinetic parameters are a function of heat transfer through the layer of dispersed material, since the calcite, during the process, decreases its particle size and liberates a new surface for forming the centre of the new phase. In the decomposition of magnesite, the previous relationship also includes the change of reaction surface. The lower value of the activation energy in the decomposition of magnesite may be the result of the presence of diffusion resistances and their influence upon the rate of the reaction flow, because it decomposes at a lower temperature than calcite.

Based upon the discussion presented, it may be concluded that the proposed method gives satisfactory results for the determination of the kinetic parameters of heterogenous thermal decomposition reactions of solid components based upon the results of one DTA or TG curve. The advantage of this method, compared with previously established methods, is the fact

that one does not assume the mechanism and the order of reaction but all kinetic parameters are determined from experimental results.

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