

INVESTIGATION OF THE REACTION KINETICS OF CONSECUTIVE REACTIONS BY TGA

KLAUS HEIDE

Friedrich-Schiller-Universität Jena, Sektion Chemie, Otto-Schott-Institut, DDR-69 Jena (G.D.R.)

GERHARD KLUGE and VIOLA HLAWATSCH

Friedrich-Schiller-Universität Jena, Sektion Physik, DDR-69 Jena (G.D.R.)

(Received June 19th, 1979)

ABSTRACT

The dependence of the decomposition of kaolin, limestone and gypsum, on heating rate m and sphere diameter L is investigated. It is shown that the shape of the TG curve and the temperature of maximum reaction rate T_m are changed significantly as m and L vary. In this way information about the rate-controlling process is obtained. The decomposition of kaolin and limestone is determined both by a diffusion process and a chemical reaction under a wide range of conditions. The decomposition of gypsum cannot be described by such a reaction mechanism.

INTRODUCTION

Theoretical calculations of TA curves for several reaction models have shown that interpretation of the experimental results of the kinetic process is very difficult or in many cases impossible unless other information is available [1,2]. Various examples are given in the literature of homogeneous consecutive reactions and concurrent reactions [1,3,4]. Investigations about the interference phenomena of first-order chemical reaction and diffusion processes are rare [5–7]. These cases are of great importance for solid-state reaction. We have shown that a dimensional analysis provides information about the influence of experimental parameters on reaction rate.

From such an analysis a simple method was evolved for determining the experimental parameters which control the reaction rate or diffusion rate. The results depend on a few dimensionless quantities such as the reduced frequency factor of chemical reaction K

$$K = \frac{Ek_0}{Rm}$$

the reduced diffusion coefficient H

$$H = \frac{ED_0}{RmL^2}$$

and the reduced coefficient of thermal conductivity

$$\Lambda = \frac{E\lambda}{RmL^2}$$

Here E , D_0 , λ , L , R , m and k_0 denote activation energy, diffusion coefficient, coefficient of thermal conductivity, characteristic length of the sample, gas constant, heating rate and frequency factor, respectively. Variations in the sample size (L) do not change the reduced frequency factor K , but the quantities H and Λ . Therefore it is possible to decide by variation of L if a chemical reaction or a diffusion process is responsible for the slope of TA curves. In cases where the TA curve is unchanged by variation of L , the reaction rate is controlled by a chemical process. If the TA curve is unchanged by variation of L and m in such a way that mL^2 is constant, a diffusion process controls the reaction rate.

The aim of this work was to study the influence of the variation of L and m on the shape of the TG curves. We were especially interested in determining if it is possible to confirm the theoretical results by thermoanalytical methods. For this purpose the rate-controlling process was determined for some well known decomposition reaction by the method described in ref. 4.

EXPERIMENTAL

To get reproducible experimental results, the samples must fulfil the following conditions:

- (1) the reaction mechanism should be as simple as possible;
- (2) samples with differences in geometrical shape and size must have the same internal structure, e.g. the same grain size, density and porosity;
- (3) the material should be easy to form in different geometrical shapes.

After preliminary experiments we selected kaolin, limestone and gypsum for the investigations.

From the kaolin (technical product from Kemmlitz DDR), spheres and plates were shaped after wetting. The proportion of water and kaolin was kept constant. After drying in vacuum (10^{-2} torr) the thermal decomposition was started. Only in this way was it possible to obtain reproducible results. Spheres and cylinders were formed from limestone and gypsum on a turning lathe without difficulty. The limestone samples were from Solnhofen Bavaria ("Plattenkalk") and from Rügen island (chalk, "Schreibkreide"). Alabaster from Rübeland, in the Harz mountains, was used to form the gypsum samples. Reproducible results were obtained from these samples under constant analytical conditions.

The determination of reaction rate was done by thermogravimetric analysis with a thermoanalyzer TA 1 (Mettler Instr. AG). The experiments were started when the pressure fell below 10^{-2} torr. The sample was fixed on the sample holder with a thin platinum wire. In this way degassing was possible without obstruction. The quantity of sample taken was 40 mg to 1 g. The temperature-measuring Pt/PtRh thermocouple was calibrated by ICTA temperature standards. The heating rate was varied in the range 0.2 – 25 K min^{-1}

TABLE 1

Decomposition of kaolin: experimental conditions and temperature of the maximum reaction rate T_m

L (mm)	m (K min ⁻¹)	T_m (°C)
7.5	0.2	432—442
8	0.5	457
8	1	472
7.5	1.5	488
7.5	2	505
7.5	4	526
7.5	6	525

in steps of 0.5, 1, 2, 4, 6, 10 and 15 K min⁻¹. In all cases the weight loss was constant at 1000°C.

RESULTS

Kaolin

In the first series of tests the heating rate was varied at a constant sample size. The experimental conditions and results are given in Table 1. Figures 1 and 2 show that the temperature of maximum reaction rate depends loga-

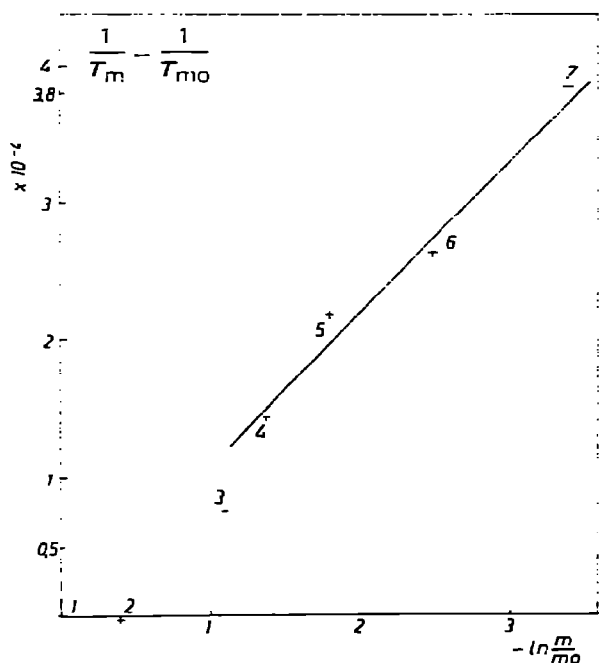


Fig. 1. Dependence of T_m on heating rate m in the decomposition of kaolin at a constant sphere diameter $L \approx 7.5$ –8 mm. Reference temperature $T_{m0} = 525^\circ\text{C}$, reference heating rate $m_0 = 6$ K min⁻¹. Heating rates are (1) 6, (2) 4, (3) 2, (4) 1.5, (5) 1, (6) 0.5, and (7) 0.2 K min⁻¹.

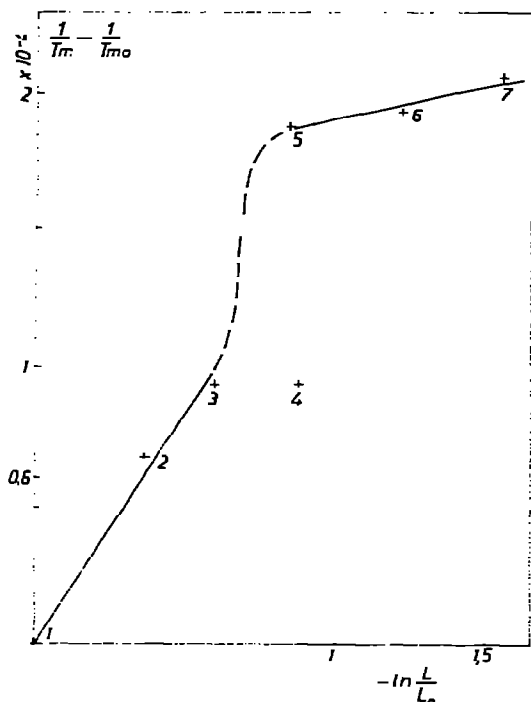


Fig. 2. Dependence of T_m on sphere diameter L in the decomposition of kaolin at a constant heating rate m of 1 K min^{-1} . Reference temperature $T_{m0} = 494^\circ\text{C}$, reference diameter $L_0 = 14.5 \text{ mm}$. Sphere diameters are (1) 14.5, (2) 10, (3) 8, (4) 6, (5) 6.2, (6) 4.3, and (7) 3 mm.

rithmically on the heating rate. This dependence is significant for spheres with a diameter of 7–8 mm, but a logarithmic dependence is expected for smaller and greater diameters also. In a second series of tests sphere diameter was varied at constant heating rate. The results are given in Table 2.

Limestone

Two natural limestones were suitable for the investigations. The following results of the first series of tests with "Plattenkalk" from Solnhofen are

TABLE 2

Decomposition of kaolin: temperature of maximum reaction rate T_m for sphere diameter L at constant heating rate m of 1 K min^{-1}

L (mm)	T_m ($^\circ\text{C}$)
3	443–452
4.3	446–457
6	468–477
6.2	452
8	472
10	478
14.5	494

TABLE 3

Decomposition of limestone ("Pattenkalk"): experimental conditions and temperature of maximum reaction rate T_m

L (mm)	m (K min ⁻¹)	T_m (°C)
11.5	1	890
8.3	1	854—870
8.0	1	843—850
7.0	0.5	842—848
6.4	1	842—849
6.0	1	838—844
4.5	1	822—832

TABLE 4

Decomposition of limestone ("Schreibkreide"): experimental conditions and temperature of maximum reaction rate T_m

L (mm)	m (K min ⁻¹)	T_m (°C)	mL^2 (mm ² K min ⁻¹)
2	25	837	100
5	4	735	100
8	0.2	580	12.8
8	10	755	640
8	25	837	1600
7	2	721	98
10	1	650—665	100
10	15	883	1500
13	10	920	1690

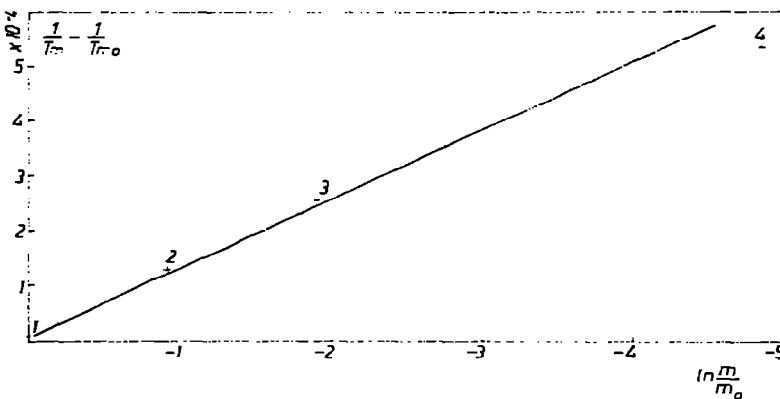


Fig. 3. Dependence of T_m on heating rate m in the decomposition of limestone ("Schreibkreide") at a constant sphere diameter $L \approx 7-8$ mm. Reference temperature $T_{m0} = 837^\circ\text{C}$, reference heating rate $m_0 = 25$ K min⁻¹. Heating rates are (1) 25, (2) 10, (3) 2, and (4) 0.2 K min⁻¹.

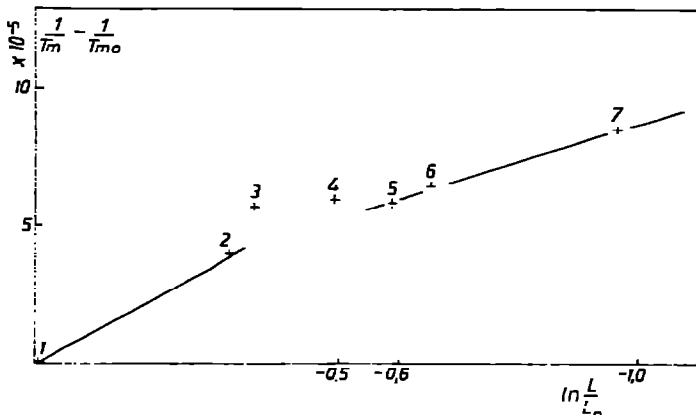


Fig. 4. Dependence of T_m on sphere diameter L in the decomposition of limestone ("Solnhofer Plattenkalk") at a constant heating rate m of 1 K min^{-1} . Reference temperature $T_{m0} = 890^\circ\text{C}$, reference diameter $L_0 = 11.5 \text{ mm}$. Sphere diameters are (1) 11.5, (2) 8.3, (3) 8, (4) 7, (5) 6.4, (6) 6, and (7) 4.5 mm.

shown in Table 3. Because of difficulties in forming spheres with different diameters, we looked for other limestones with better homogeneity and porosity. Chalk from Rügen island was found to be suitable for the experiments. The results are given in Table 4; see also Figs. 3 and 4.

Gypsum

Decomposition of gypsum, under the same experimental conditions, gives results which differ from those of kaolin and limestone. Figure 5 shows how the decomposition rate varies with increasing temperature. The theoretical models in general use cannot describe this effect. Probably phase-boundary and reverse reactions control the reaction rate in these cases. At present, theoretical considerations of this more complicated case are incomplete.

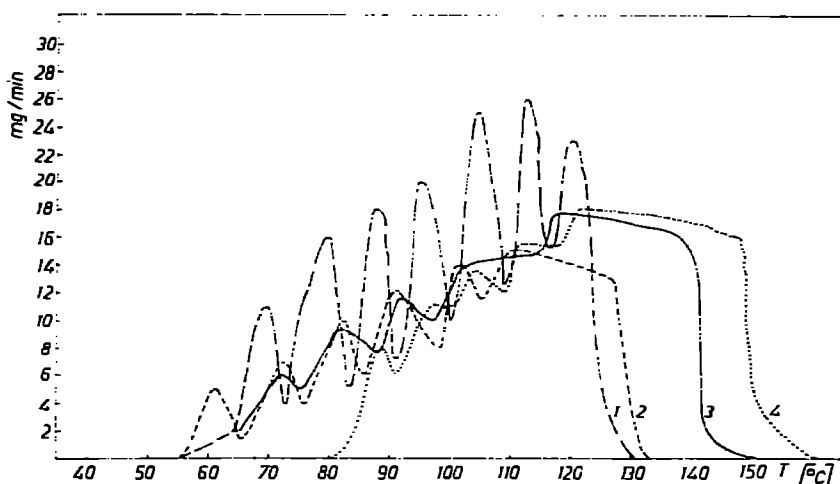


Fig. 5. Decomposition rate of gypsum at a heating rate of 1 K min^{-1} for (1) a monocrystal (46.1 mg), (2) a sphere (36.1 mg), (3) a plate (47.6 mg), and (4) a cylinder (50.5 mg).

DISCUSSION

To explain the measurements and get information about kinetic parameters from the TGA curves, a reaction mechanism is assumed which is controlled simultaneously by a first-order chemical and a diffusion process. From TGA curves it is possible to deduce the temperature of maximum reaction rate T_m and degree of decomposition in the temperature run. In this paper we shall concentrate on the behaviour of T_m under different experimental conditions.

In the case of spheres the temperature T_m can be calculated from the equation [5,8]

$$\sum_{n=1}^{\infty} \frac{(-1)^n}{n} \left\{ \int_0^{T_m} \left[\frac{E_D}{RT_m^2} + \frac{D_0}{m} \left(\frac{2^n \pi}{L} \right)^2 \frac{\partial}{\partial T_m} \left(\frac{R(T_m - T)^2}{E_D} e^{-E_D/R(T_m - T)} \right) \right] \right. \\ \left. \exp \left[-\frac{E}{RT} - \frac{k_0}{m} \frac{RT^2}{E} e^{-E/RT} - \frac{D_0}{m} \left(\frac{2^n \pi}{L} \right)^2 \frac{R(T_m - T)^2}{E_D} e^{-E_D/R(T_m - T)} \right] \right\} dT \\ - \exp \left[-\left(\frac{E}{RT_m} + \frac{k_0}{m} \frac{RT_m^2}{E} e^{-E/RT_m} \right) \right] = 0 \quad (1)$$

where L is the sphere diameter.

In this equation the approximation

$$\int_0^T e^{-E/RT'} dT' \approx \frac{RT^2}{E} e^{-E/RT} \quad (2)$$

is used already. The solution of eqn. (1) and the calculation of $T_m = T_m(m, L)$ (where m is the heating rate) is very complicated even in the case where only the first term is considered. Therefore we looked at the two borderline cases — the homogeneous first-order reaction and the diffusion-controlled reaction. The first case is given by [3]

$$\frac{m}{T_m^2} = \frac{Rk_0c_0^{n-1}}{E} e^{-E/RT_m} \quad (3)$$

or

$$\ln m - 2 \ln T_m = \ln \left(\frac{Rk_0c_0^{n-1}}{E} \right) - \frac{E}{RT_m} \quad (4)$$

where c_0 is the concentration at the start of the reaction. Within the limits of the temperature range the term $\ln T_m$ can be considered as constant. Under this assumption the expression

$$\frac{1}{T_m} = -\frac{R}{E} \ln m + C \quad (5)$$

is obtained, where the value of C depends on the reaction order n , the pre-exponential factor k_0 and the activation energy E . For discussion of the experimental results it is significant that $1/T_m$ is directly proportional to

ln m and almost independent of reaction order. For diffusion-controlled reactions, the following equation is derived

$$\sum_{n=1}^{\infty} \left\{ \left(\frac{E_D}{RT_m^2} - \frac{D_0}{m} \frac{4n^2\pi^2}{L^2} e^{-E_D/RT_m} \right) \exp \left(-\frac{D_0}{m} \frac{4n^2\pi^2}{L^2} \int_{T_0}^{T_m} e^{-E_D/RT} dT \right) \right\} = 0 \quad (6)$$

By truncation of the series and retaining only the first term in eqn. (6) for T_m

$$\frac{E_D}{RT_m^2} = \frac{D_0}{m} \frac{\pi^2}{L^2} e^{-E_D/RT_m} \quad (7)$$

or

$$\ln m + 2 \ln L - 2 \ln T_m = \ln \frac{RD_0\pi^2}{E_D} - \frac{E}{RT_m} \quad (8)$$

With the approximation $\ln T_m = \text{constant}$, it follows that

$$\frac{1}{T_m} = -\frac{R}{E_D} \ln m - \frac{2R}{E_D} \ln L + C \quad (9)$$

where C depends on the diffusion coefficient D_0 and the activation energy of diffusion E_D . It is evident that a plot of $\ln(L/L_0)$ vs. $(1/T_m)$ calculated from the experimentally obtained data is approximately linear only for diffusion-controlled reactions. From the slopes of plots of $\ln(m/m_0)$ vs. $1/T_m$ at constant L , of $\ln(L/L_0)$ vs. $1/T_m$ at constant m , the activation energy can be obtained. The slope of the plot of $\ln(m/m_0)$ vs. $1/T_m$ is the half-value of the plot of $\ln(L/L_0)$ vs. $1/T_m$ when diffusion alone controls the reaction rate. Since the rate of the first-order reaction is independent of L , in this way it can be resolved whether the chemical or diffusion process is the rate-determining step. A further possibility of distinguishing between a first-order reaction and a diffusion process is the variation of m and L . If the product mL^2 is constant, T_{\max} is constant and the diffusion process controls the reaction (eqn. 7). This result is of particular interest in practice, since it is possible to get information about the experimental conditions at which diffusion controls the reaction rate.

The experimental results are given in Figs. 1–4. The decomposition of kaolin is controlled both by a chemical reaction and a diffusion process, as shown in Figs. 1 and 2. For small diameters ($L < 6$ mm) the chemical reaction predominates, whereas for spheres larger than 8 mm diameter the diffusion process is dominant. Equation (7) is suitable for obtaining a rough value of activation energy E . When the diameter of the spheres is small ($L < 6$ mm) the activation energy is about 18 kcal mole⁻¹, and for large spheres ($L > 8$ mm) about 24 kcal mole⁻¹.

The decomposition of limestone is more complicated, as shown in Fig. 4. It is obvious that there are two stages in the diffusion-controlled reaction. When the diameter is 6–8 mm it is not possible to assign the experimental results significantly to a chemical reaction or to a diffusion process. This un-

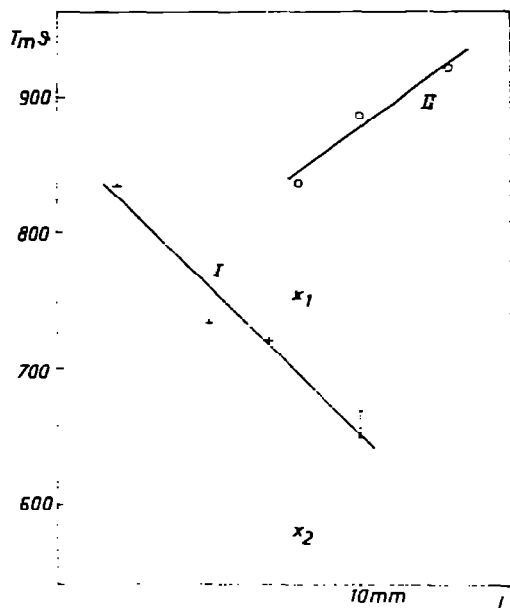


Fig. 6. Dependence of T_m on sphere diameter in the decomposition of limestone ("Schreibkreide") with $mL^2 = 100 \text{ mm}^2 \text{ K min}^{-1}$ (curve I), $mL^2 = 1600 \text{ mm}^2 \text{ K min}^{-1}$ (curve II), and $mL^2 = 640$ and $12.8 \text{ mm}^2 \text{ K min}^{-1}$, denoted by 1 and 2, respectively.

expected result can be explained as follows. For spheres with $3 \text{ mm} < L < 6 \text{ mm}$ diffusion is rate-controlling. (It was not possible to produce spheres with $L < 3 \text{ mm}$, for which the diffusion process could be neglected.) With increasing diameter the intergranular-gas partial pressure also increases and hence the internal structure is changed. Therefore a large increase of porosity is possible and the influence of diffusion decreases. Perhaps this effect is overlapped by a sintering reaction, which decreases porosity when $L > 8 \text{ mm}$. In this way the diffusion process also controls the reaction rate for large spheres. Further experiments are necessary to confirm these results.

From the slopes of plots of $\ln(L/L_0)$ vs. $1/T_m$ (Fig. 4) at constant m , the activation energy obtained from eqn. (9) as $E = 32 \text{ kcal mole}^{-1}$ for $L > 8 \text{ mm}$ and $E = 55 \text{ kcal mole}^{-1}$ for $L < 6 \text{ mm}$.

From the slopes of plots of $\ln(m/m_0)$ vs. $1/T_m$ at constant L the activation energy E is about $15 \text{ kcal mole}^{-1}$. It is probable that the value of $55 \text{ kcal mole}^{-1}$ represents the activation energy of the diffusion-controlled process. An interpretation of the other values is not possible because further processes may be involved (e.g. catalytic and sintering processes).

The plot of T_m vs. sphere diameter shows an interesting connection for curves with constant mL^2 (Fig. 6). If diffusion alone controls the reaction rate, T_m must be constant for constant mL^2 . This does not correspond to the experimental results. It is possible to estimate the experimental conditions at which a diffusion process will predominate. Figure 6 shows that T_m is independent of L if mL^2 is about $900 \text{ mm}^2 \text{ K}^{-1}$. This is the case, for example, at $L = 2, 9, 11, 20 \text{ mm}$ and $m = 200, 10, 8, 2 \text{ K min}^{-1}$, respectively. These results are a good starting point for further experiments in process control and optimization.

SUMMARY

The decomposition of kaolin and limestone is determined both by a diffusion process and a chemical reaction under a wide range of conditions. In practice, discrimination between the two processes is difficult and only possible under special conditions. Determination of the kinetic parameters in the range where both diffusion and the chemical reaction are taking place is not possible without extensive calculations.

The decomposition of gypsum cannot be described by a homogeneous chemical reaction together with a diffusion process. It is likely that phase-boundary and reverse reactions also take place. Further theoretical considerations are necessary.

Where only one process controls the reaction rate, the kinetic parameters can be calculated from eqns. (5) and (9). In this way the following activation energies are obtained: 18 kcal mole⁻¹ (chemical reaction) and 24 kcal mole⁻¹ (diffusion) for kaolin; 15 kcal mole⁻¹ (chemical reaction) and 55 kcal mole⁻¹ (diffusion) for limestone. The problem, however, is not in obtaining kinetic parameters in agreement with the literature, but the physical interpretation of these parameters. For solid-state reactions the processes are very much more complicated than the commonly used models suggest. Experimental results are therefore essential to obtain better understanding of the rate-controlling processes.

In interpreting the experimental results we have concentrated on the temperature T_m of the maximum reaction rate. This temperature can be measured with an error of ± 5 K to ± 10 K. The experimental data include much more information about the processes considered. Therefore further theoretical investigations are necessary.

Experimental limitations restrict the variation of parameters L (sphere diameter) and m (heating rate). At sphere diameters >10 mm and sample masses >1000 mg, heat conduction must be taken into consideration. Extrapolation of the results to larger technical equipment is possible only with caution. However, knowledge of general trends can be of great practical benefit.

REFERENCES

- 1 E. Koch, *Non-Isothermal Reaction Analysis*, Academic Press, London, 1977.
- 2 K. Heide, G. Kluge, W. Reiprich and H. Hobert, *Thermal Analysis*, Vol. 1, Proc. IV ICTA, Budapest, 1974, p. 123.
- 3 J. Šesták, V. Satava and W.W. Wendlandt, *Thermochim. Acta*, 7 (1973) 333.
- 4 K. Heide, *Dynamische Thermische Analysenverfahren*, VEB Dt. Verlag für Grundstoff-industrie, Leipzig, 1979.
- 5 G. Kluge and K. Heide, *Thermochim. Acta*, 21 (1977) 423.
- 6 T. Ozawa, *J. Therm. Anal.*, 5 (1973) 563.
- 7 W. Mauss, *Beiträge zur Theorie anisothermer Zersetzungsreaktionen*, Diplomarbeit FSU Jena, 1974.
- 8 V. Hlawatsch, *Experimentelle Untersuchungen zum Problem der Übertragbarkeit kinetischer Berechnungen*, Diplomarbeit FSU Jena, 1978.