

COMPREHENSIVE KINETIC STUDIES ON ISOTHERMAL AND NON-ISOTHERMAL REACTIONS OF SOME ALUMINIUM COMPOUNDS

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Residual differences after model fitting were investigated in both isothermal and non-isothermal kinetics in order to make numerical comparisons between several models and various parameter-estimating methods. Data from two independent experimental series were evaluated.

A large data set, collected earlier under isothermal conditions from decompositions and hydrothermal reactions of aluminium hydroxides and oxides, was processed first. It showed that mechanical activation of the starting gibbsite affected reactivity of samples in several subsequent reactions for all model equations tried. The relative residual deviation concept is introduced, and statistics were applied to find a model that fits a certain reaction in most of the cases.

In the second study, the sulphate decomposition step of aluminium sulphate octadecahydrate was investigated. TG curves were measured using a constant heating rate. Dynamic models were fitted by three mathematical methods, including a new general purpose one. Fitting ability of the methods with various complexity were compared on the basis of residual deviations obtained after integration of the model equations. As well as evaluating the best fit, this new parameter-estimating method provides a statistical analysis of the reliability of the whole model fitting process.

Keywords: aluminium compounds, isothermal and non-isothermal reactions, parameter-estimating methods

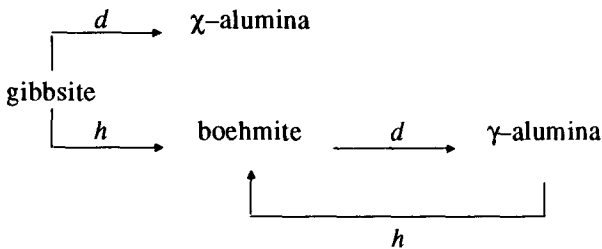
Introduction

In this paper we focus on distinguishing between various kinetic curves derived by different model equations and parameter-estimating methods. Our differentiating concept is based on the numerical fitness of the curves to the experimental curve. Choosing the most appropriate kinetic model is a common problem in solid-state chemistry, for a large number of kinetic models are known in the literature [1, 2], and also used in studies of aluminium compounds [3-5]. Here we give two examples for the application of residual deviations (definitions see below), as numerical criteria in searching for well-fitting curves.

Isotherm conversions starting from gibbsite

Thermal decompositions (*d*) and hydrothermal reactions (*h*) of aluminium hydroxides and oxides have been studied under isothermal conditions at various temperatures [6, 7]. The starting material was synthetic gibbsite pretreated by grinding in different ways ($2^3 = 8$ starting samples). Preparation details and reactions are summarized below.

Grinding mode : wet or dry
 Duration (h) : 6 or 30
 Particle size (μm) : <10 or 20–30



gibbsite	→	α-alumina	T =	250°	255°	260°C
gibbsite	→	boehmite	T =	180°	182.5°	186.5° 190°C
boehmite	→	γ-alumina	T =	490°	500°	507°C
γ-alumina	→	boehmite	T =	180°	190°	210°C

All eight samples were subjected to these isothermal treatments. Data series obtained were processed numerically in order to obtain apparent activation energies and to find model equations that fit satisfactorily the reaction in question. We fitted sixteen different kinetic models (reviewed by Pokol and Várhegyi [8], Fig. 1) to these isothermal conversion curves by linearization using the general equations below (Eqs 1 and 2). The rate constants obtained at the above temperatures served to estimate activation energies for each sample and model in each reaction.

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad \text{and} \quad \alpha(t_0) = 0 \quad (1)$$

$$g(\alpha) = \int_0^{\alpha} \frac{1}{f(\alpha)} d\alpha = k(T)(t - t_0) \quad (2)$$

Effect of long-term dry grinding

Comparison of activation energies showed that two samples which were dry ground for 30 hours had significantly lower activation energies than the other six

Abbreviation of the model	$f(\alpha)$	$g(\alpha)$
P1 power law ($m=1/2$)	α^{1-m}	$1/m \alpha^m$
E1 exponential law	α	$\ln \alpha$
B1 Prout-Tompkins	$\alpha(1-\alpha)$	$\ln(\alpha/(1-\alpha))$
F1 first order	$1-\alpha$	$-\ln(1-\alpha)$
R3 contracting volume	$(1-\alpha)^{2/3}$	$3 [1-(1-\alpha)^{1/3}]$
R2 contracting area	$(1-\alpha)^{1/2}$	$2 [1-(1-\alpha)^{1/2}]$
FIX constant rate	1	α
A033 Avrami-Erofeev ($n=1/3$)	$(1-\alpha)[- \ln(1-\alpha)]^{1/3}$	$3/2 [- \ln(1-\alpha)]^{2/3}$
A2 " ($n=1/2$)	$(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$2 [- \ln(1-\alpha)]^{1/2}$
A060 " ($n=3/5$)	$(1-\alpha)[- \ln(1-\alpha)]^{3/5}$	$5/2 [- \ln(1-\alpha)]^{2/5}$
A3 " ($n=2/3$)	$(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$3 [- \ln(1-\alpha)]^{1/3}$
A4 " ($n=3/4$)	$(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$4 [- \ln(1-\alpha)]^{1/4}$
D1 one-dimensional diff.	$1/\alpha$	$1/2 \alpha^2$
D2 two-dimensional diff.	$[- \ln(1-\alpha)]^{-1}$	$(1-\alpha) \ln(1-\alpha) + \alpha$
D3 three-dimensional diff	$(1-\alpha)^{2/3} [1-(1-\alpha)^{1/3}]^{-1}$	$3/2 [1-(1-\alpha)^{1/3}]^2$
D4 Ginstling-Brounshtein	$[(1-\alpha)^{-1/3} - 1]^{-1}$	$3/2 [1-2\alpha/3 - (1-\alpha)^{2/3}]$

Fig. 1 List of models [8] evaluated in the isothermal kinetics of aluminium hydroxides and oxides

samples (Table 1). This was observed not only in the hydrothermal decomposition of gibbsite, but also in the subsequent boehmite \rightarrow γ -alumina conversion. We can conclude that mechanical activation of the original gibbsite affected the reactivity of the samples in subsequent reactions. Activation energies calculated for the zero-order model are presented in Table 1; the other fifteen models all showed the same phenomenon, confirming the activation effect.

Table 1 Means and range of activation energies calculated for different reactions using the zero-order model

Gibbsite \rightarrow Boehmite			
Number of samples	Mean kJ·mol ⁻¹	Lowest kJ·mol ⁻¹	Highest kJ·mol ⁻¹
2 (dry 30 h grinding)	98.7	97.5	99.9
6 (Remainder)	311.5	191.6	382.0
Boehmite \rightarrow γ -Al ₂ O ₃			
Number of samples	Mean kJ·mol ⁻¹	Lowest kJ·mol ⁻¹	Highest kJ·mol ⁻¹
2 (dry 30 h grinding)	197.6	196.2	199.0
6 (Remainder)	389.0	328.8	477.1
γ -Al ₂ O ₃ \rightarrow Boehmite			
Number of samples	Mean kJ·mol ⁻¹	Lowest kJ·mol ⁻¹	Highest kJ·mol ⁻¹
8 (All)	62.3	44.0	99.8
Gibbsite \rightarrow χ -Al ₂ O ₃			
Number of samples	Mean kJ·mol ⁻¹	Lowest kJ·mol ⁻¹	Highest kJ·mol ⁻¹
8 (All)	433.9	417.4	457.8

Relative residual deviation

Comparison of our models can be made either at the stage of linearization Eq. (2) or after integration of the original differential equation Eq. (1). In the former case, the correlation coefficients are not suitable for distinguishing models, because they are always close to 1 for few numbers of data. Instead, for the various $g(\alpha) = k(T)(t-t_0)$ expressions we defined the relative residual deviation s_{rr} in the following way:

$$s_{rr} = \frac{s_{r,g(\alpha)}}{\max [g(\alpha)] - \min [g(\alpha)]} \quad (3)$$

where $s_{r,g(\alpha)}$ is the residual deviation of the linearization, calculated from the deviations of the measured and the estimated $g(\alpha)$ values:

$$s_{r,g(\alpha)} = \left[\frac{\sum_{i=1}^{nm} [g(\alpha_i) - k(T)(t_i - t_0)]^2}{nm - 2} \right]^{1/2}$$

where nm is the number of measured points.

This s_{rr} quantity shows the relative deviations about a straight line after regression, and it is a good measure of the fit of a model function. Normalization of the residual deviation $s_{r,g(\alpha)}$ is essential, because the absolute values of $g(\alpha_i)$, and consequently of $s_{r,g(\alpha)}$, are different for different models. Whilst after integration, we can make a direct comparison between experimental and calculated conversion curves. In the latter case s_r , using the residual deviation of α itself, also provides a measure of fit:

$$s_r = \left[\frac{\sum_{i=1}^{nm} [\alpha_{\text{exp},i} - \alpha_{\text{calc},i}]^2}{nm - 2} \right]^{1/2} \quad (4)$$

Choosing two levels (5% and 10%) of either of these deviations represented by Eq. (3) and Eq. (4), we treated each model and reaction statistically, counting those experiments when either s_{rr} Eq. (3) or s_r Eq. (4) were below the chosen level. The statistics obtained for two reactions are presented in Figs 2 and 3, applying the relative residual deviation Eq. (3). Generally, we obtained mainly model families providing a good fit, and the statistics did not show the same distribution using the other Eq. (4) criterion on the same level. We also present diagrams that give some indication of the curve-fitting process (Fig. 4; solid lines are experimental curves, while dashed lines are fitted ones).

Dynamic decomposition of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$

The thermal decomposition of aluminium sulphate octadecahydrate has been investigated by several authors [5, 9, 10]. Data evaluated in the present study were recorded by a Derivatograph C apparatus with a constant heating rate (Fig. 5).

Different dynamic models were fitted to the last step of the TG curve, i.e. to the sulphate decomposition process. (The dehydration steps were not dealt with,

because of uncertainties in baseline determinations and the resolution of overlapping reactions.)

Gibbsite \rightarrow boehmite

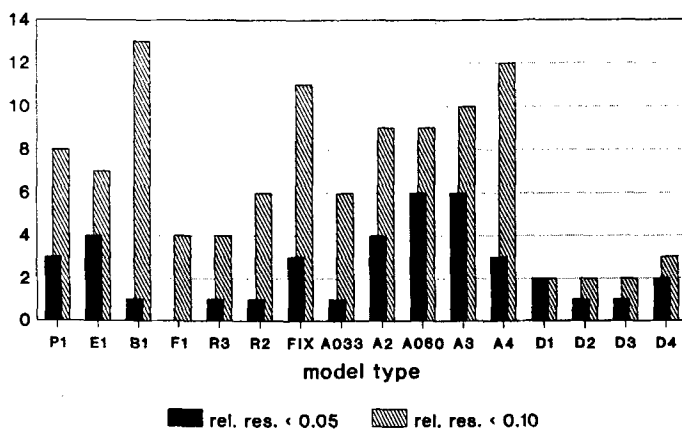


Fig. 2 Number of experiments where a model curve fits the experimental curve within 5% (solid filled column) or 10% (backslash filled column) relative residual deviation Eq. (3) in the gibbsite \rightarrow boehmite hydrothermal conversion. (Abbreviation for models are given in Fig. 1)

Boehmite \rightarrow gamma alumina

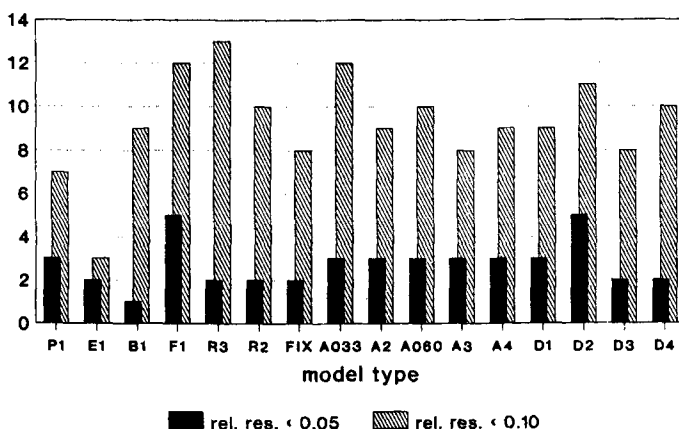


Fig. 3 Number of experiments where a model curve fits the experimental curve within 5% (solid filled column) or 10% (backslash filled column) relative residual deviation Eq. (3) in the boehmite \rightarrow γ -alumina thermal decomposition. (Abbreviation for models are given in Fig. 1)

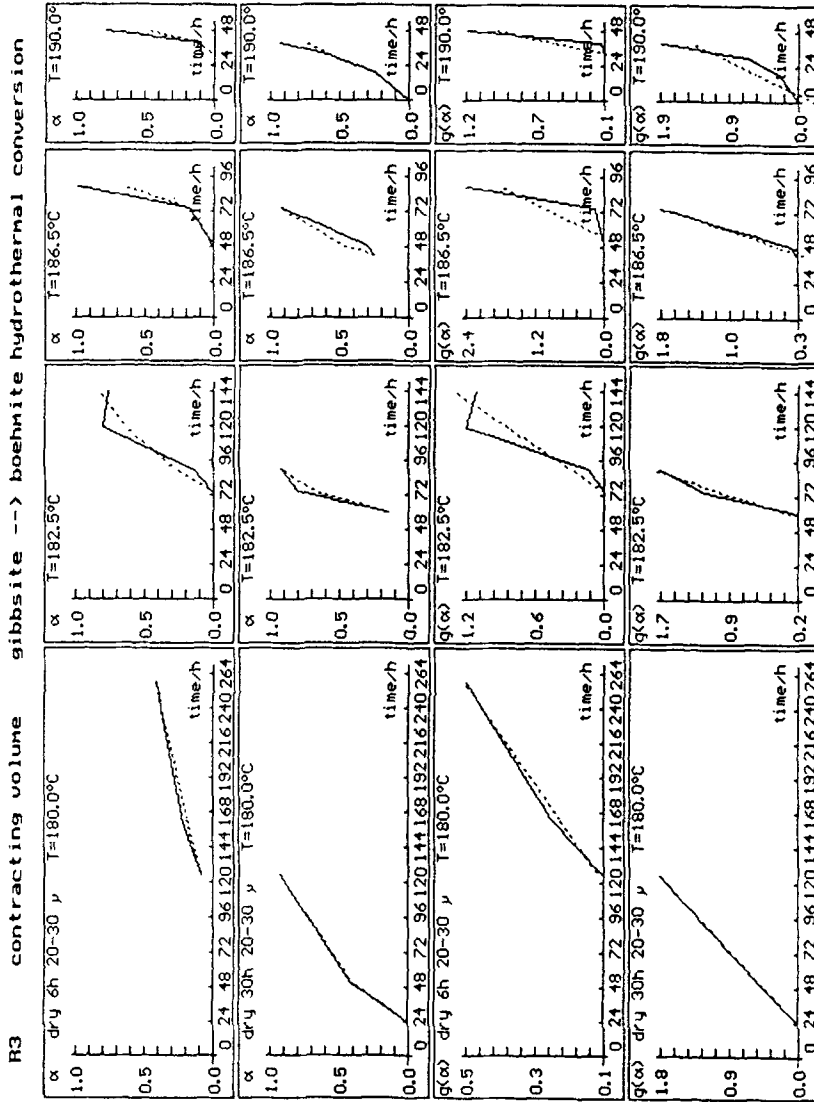


Fig. 4 Details of isothermal curve-fitting using Eqs (1) and (2). Explanations: Measured conversion points in the first row, solid lines. Transformed data points in the third row, solid lines. Fitted straight lines in the third row, dashed lines. Integrated conversion points in the first row, dashed lines. In the second and fourth row the appropriate curves of a sample subjected to long-term dry grinding can be found

The parameters of model equations were estimated by three mathematical methods:

- i) a simple differential method (Sharp & Wentworth [11]) using graphical derivation of the TG curve,
- ii) the classical integral method of Coats & Redfern [12] using numerical linear regression,
- iii) a general purpose differential equation set identifier method implemented by Valkó and Vajda [13].

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad \text{and} \quad \alpha(t_0) = \alpha_0,$$

$$\frac{dT}{dt} = \beta \quad \text{and} \quad T(t_0) = T_0,$$

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad \text{and} \quad f(\alpha) = (1-\alpha)^n$$

Each method was tested with the above equation set for three ($n = 1/2, 2/3$ and 1) exponents. Using the obtained parameters (A and E), the equation set was integrated numerically and differences between measured and fitted curves were used for calculation of the residual deviation Eq. (4), for the dynamic case. This s_r quantity served as a basis for comparison between the methods.

Residual deviation as an extent of fit

The estimated formal kinetic parameters and calculated residual deviations of the fitted curves are summarized in Table 2. The fitted curves were also compared with the experimental curve graphically. The original curve is prompted as dashed line on the left hand sides of Figs 6, 7 and 8, for the sake of comparison.

Figure 6 shows that the Coats and Redfern approximation provides curves that in our case systematically cross the experimental one, whatever exponent was chosen. The model type itself may also be questioned.

The best fit was achieved using the iterative non-linear regression method of Valkó and Vajda [13]. This is demonstrated in Fig. 7 and resulted in the lowest residual deviation values (Table 2).

Among the methods, the differential one resulted in the worst fitting curve (the most unsatisfactory curve on Fig. 8). This was confirmed by the extremely high residual deviation.

Similar qualitative observations could be made by investigation of parallel curves measured on the same or different instruments, or by changing the heating rate.

In addition to providing the best fit, Valkó and Vajda's general purpose parameter-estimating method provides a statistical analysis (including

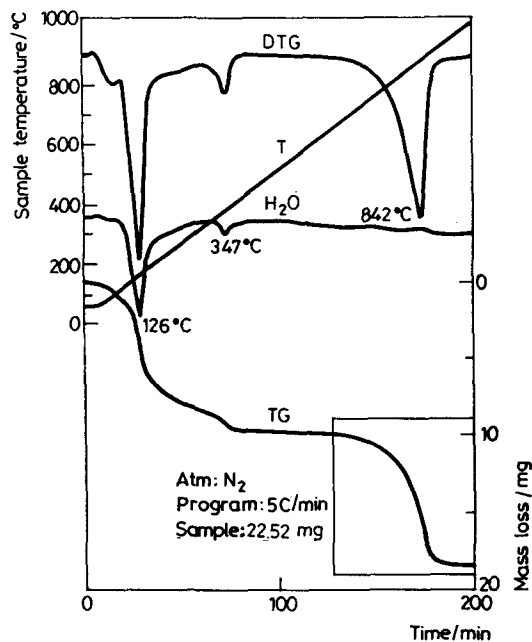


Fig. 5 Thermal curves of aluminium sulphate octadecahydrate in N_2 atmosphere, at a heating rate $5 \text{ deg}\cdot\text{min}^{-1}$, sample mass of 22.52 mg, instrument Derivatograph C. The TG step within the frame was chosen for kinetic evaluation

Table 2 Residual deviations and formal kinetic parameters obtained with three different estimating methods for three usual exponents of order model family

Method	Order n	Residual deviation	$E/$ $\text{kJ}\cdot\text{mol}^{-1}$	$A/$ sec^{-1}
Sharp & Wentworth (diff.)	1/2	0.192	287	$9.30\cdot 10^{12}$
	2/3	0.203	327	$1.10\cdot 10^{15}$
	1.0	0.178	348	$1.30\cdot 10^{16}$
Coats & Redfern (integ.)	1/2	0.059	154	$1.00\cdot 10^6$
	2/3	0.049	167	$4.80\cdot 10^6$
	1.0	0.045	196	$1.96\cdot 10^8$
Valkó & Vajda (direct integr.)	1/2	0.025	178	$1.75\cdot 10^7$
	2/3	0.018	211	$8.10\cdot 10^8$
	1.0	0.016	274	$1.20\cdot 10^{12}$

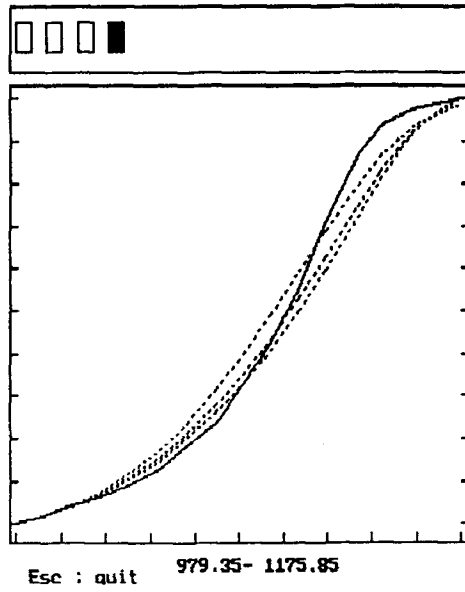


Fig. 6 Curves fitted by the Coats and Redfern method (dashed lines) together with the experimental conversion curve (solid line)

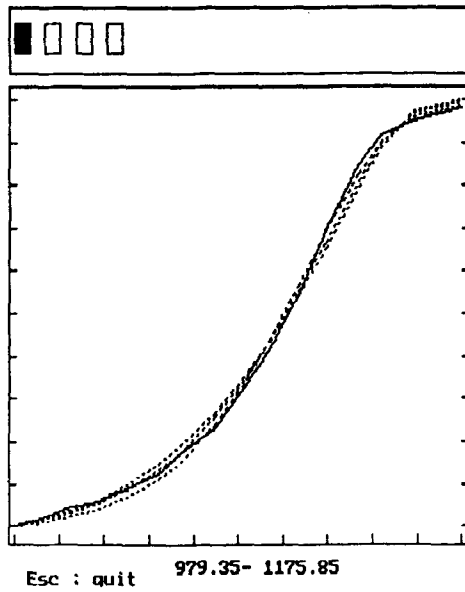


Fig. 7 Curves fitted by the Valkó and Vajda method (dashed lines) together with the experimental conversion curve (solid line)

covariance, correlation, confidence interval etc.) for characterizing the reliability of the model fitting process.

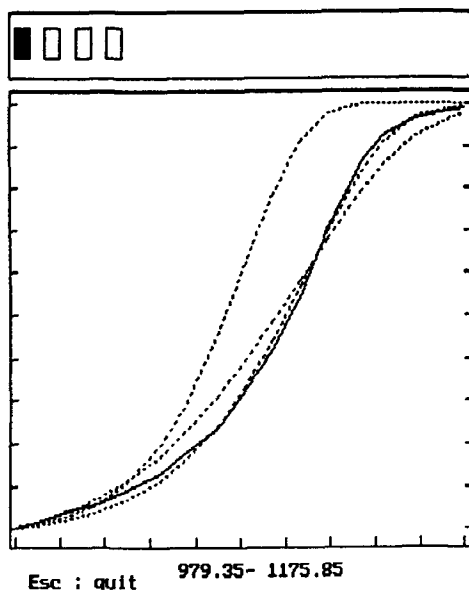


Fig. 8 Curve fitted by the three methods in the case of $n = 1$ compared to the experimental curve (solid line). The isolated curve was obtained by the Sharp and Wentworth method (differential method), the crossing one by the Coats and Redfern method, and the most satisfactory curve by the Valkó and Vajda method

Conclusion

Various kinetic models and parameter-estimating methods were compared on the basis of their fitting ability expressed numerically in isothermal and non-isothermal studies.

In the isothermal study we could confirm quantitatively a mechanical activation effect with simple tools (linear regression), and proposed two criteria to distinguish kinetic models at two different stages of calculation. Both of these are based on calculation of residual deviations.

Residual deviation also proved suitable in comparisons of fit of three parameter-estimating methods of varying complexity. In this non-isothermal study a general differential equation set identifier method provided the smallest residuals, and in addition gave a statistical analysis.

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Zusammenfassung — Für einen numerischen Vergleich einiger Modelle und verschiedener Methoden zur Parameterschätzung wurden Restdifferenzen nach dem Modellfitting sowohl bei isothermer als auch nichtisothermer Kinetik untersucht. Daten aus zwei unabhängigen Versuchsreihen wurden ausgewertet.

Zuerst wurde ein große Reihe von bereits früher, unter isothermen Bedingungen erfaßten Daten von Zersetzungs- und hydrothermischen Reaktionen von Aluminiumhydroxiden und -oxiden bearbeitet. Es zeigte sich, daß eine mechanische Aktivierung des Ausgangsmateriales Gibbsit für alle angewendeten Modellgleichungen die Aktivität der Probe in einigen Nachfolgereaktionen beeinflusste. Es wurden das Prinzip des relativen Restfehlers eingeführt und statistische Methoden eingesetzt, um ein Modell zu finden, welches im Falle einer bestimmten Reaktion für die meisten Fälle ein angemessenes Fitting bietet.

In der zweiten Studie wird der Sulfatzersetzungsschritt von Aluminiumsulfat-Oktadekahydrat untersucht. Die TG-Kurven wurden bei konstanter Aufheizgeschwindigkeit erstellt. Das Fitting dynamischer Modelle erfolgte mittels dreier mathematischer Methoden. Die Fitting-Fähigkeit von Methoden verschiedener Komplexität wurde auf der Grundlage von Restfehlern verglichen, welche man nach Integration der Modellgleichungen erhielt. Außer dem erhaltenen besten Fitting bringt diese neue Parameterschätzungsmethode eine statistische Analyse der Zuverlässigkeit des gesamten Modellfitting-Prozesses mit sich.