

STUDIES ON ISOTHERMAL KINETICS OF SOME REACTIONS OF ALUMINUM OXIDES AND HYDROXIDES

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Thermal decomposition and hydrothermal reactions of aluminum oxides and hydroxides were studied. The starting material was gibbsite pretreated by grinding in different ways. Sixteen kinetic models were fitted and the rate constants were estimated at different temperatures. Mechanical activation of the starting gibbsite had an effect on the reactivity of samples in several subsequent reactions.

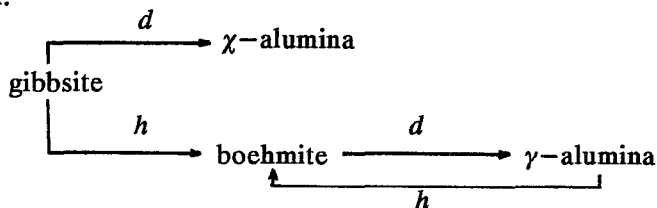
A new quantity, the relative residual variance is defined for comparison of different linearized models, and it is proposed as a criterion of fit. This was applied in making statistics in order to find the well-fitting models.

Keywords: aluminum oxides, hydroxides, hydrothermal reactions, isothermal kinetics

Introduction

Thermal reactions of aluminum hydroxides and oxides under different conditions are important objects of frequent and intensive studies [1-4]. Kinetic calculations on these reactions carried out in various ways are also available [5, 6].

Recently, some of these substances and reactions were investigated by Novák *et al.* under isothermal circumstances [3, 4]. In this paper a numerical evaluation of the isothermal conversion data measured by them, is presented.



Synthetic gibbsite was ground under dry or wet circumstances for different durations and different grain size fractions were collected. Eight fractions were compared in the experiments: 6 or 30 hours of dry or wet grinding with particle size of 20–30 μm or <10 μm [3, 4]. These fractions were the starting materials for the series of reactions, the effect of grinding and grain size of the starting gibbsite was followed in the subsequent reactions.

The reactions were carried out in air (*d*) or under hydrothermal conditions (*h*), respectively, at the following temperatures:

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

Samples were collected after different time intervals and the composition of these samples was determined by constant heating rate TG curves [3, 4]. Thus each isothermal curve consists of less than ten points.

Here we would like to describe quantitatively the decomposition (*d*) and hydrothermal (*h*) reactions, which had been qualitatively characterized earlier [3, 4]. Another goal of our investigation was to find the well-fitting kinetic models to these reactions.

Evaluation with the zero order model

Most of the isothermal reacted fraction vs. time curves ($\alpha(t)$) had a sigmoid shape that could be approximated by three linear stages. So the experimental data were divided into three sections: $\alpha < 0.05$, $0.05 \leq \alpha \leq 0.95$ and $\alpha > 0.95$. Horizontal lines $\alpha = 0$ and $\alpha = 1$ were substituted for the first and last sections, while in the second stage a constant rate of the reactions was assumed. In this way we neglected the conversion values less than 5 percent and greater than 95 percent. The remaining data were used for line fitting with linear regression according to following expression:

$$\alpha(t) - \alpha(t_0) = k(T) (t - t_0), \quad \text{and } \alpha(t_0) = 0$$

where $\alpha(t)$ is the degree of conversion at time t ,
 $k(T)$ is the constant rate at temperature T ,
 t_0 is the intersection of the straight line with the abscissa.

Table 1 Activation energies for gibbsite \rightarrow boehmite conversion depending on the grinding conditions and particle size calculated on linearized form of the Arrhenius law with linear regression

Sample features	Act. energy/ kJ mol^{-1}	Preexp. factor/ h^{-1}	Correlation factor
Dry 6h 20–30	382.0	$5.3\text{E}+41$	0.930
Dry 30h 20–30	97.5	$2.6\text{E}+09$	0.537
Dry 6h <10	191.6	$1.5\text{E}+20$	0.692
Dry 30h <10	99.9	$5.3\text{E}+09$	0.471
Wet 6h 20–30	354.4	$4.7\text{E}+38$	0.939
Wet 30h 20–30	377.5	$2.0\text{E}+41$	0.973
Wet 6h <10	286.0	$7.4\text{E}+30$	0.912
Wet 30h <10	277.4	$7.4\text{E}+29$	0.911

Mean for 'Dry 30h' samples: 98.7 kJ/mol

Mean for the other 6 samples: 311.5 kJ/mol

Table 2 Means and range of activation energies calculated for different reactions using constant rate model

Gibbsite \rightarrow boehmite			
Number of samples	Mean/ kJ mol^{-1}	Lowest/ kJ mol^{-1}	Highest/ kJ mol^{-1}
2 (Dry 30h)	98.7	97.5	99.9
6 (The rest)	311.5	191.6	382.0
Boehmite \rightarrow γ - Al_2O_3			
Number of samples	Mean/ kJ mol^{-1}	Lowest/ kJ mol^{-1}	Highest/ kJ mol^{-1}
2 (Dry 30h)	197.6	196.2	199.0
6 (The rest)	389.0	328.8	477.1
γ - Al_2O_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_2O_3			
Number of samples	Mean/ kJ mol^{-1}	Lowest/ kJ mol^{-1}	Highest/ kJ mol^{-1}
8 (All)	433.9	417.4	457.8

The rate constants obtained at different temperatures were used to calculate activation energy and preexponential factor from the linearized form of the Arrhenius law.

The Arrhenius parameters of the gibbsite \rightarrow boehmite hydrothermal conversion for each samples are presented in Table 1. In this reaction and in the subsequent boehmite \rightarrow γ -alumina decomposition too, those samples which has been ground for 30 h in dry circumstances showed much lower activation energies than the other ones. The means and the range of the activation energies obtained for each reaction are summarized in Table 2. We assume, that the lower energy values are due to the effect of mechanical activation, i.e. as a consequence of 30 hour dry grinding.

In the other two reactions similar phenomenon could not be observed, all the obtained kinetic parameters lie in one interval.

Kinetic calculations with different models

After the zero order model 15 other kinetic equations were tried to fit the experimental data in the $0.05 \leq \alpha \leq 0.95$ range. Their general differential and integral forms are the following

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

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

(the concrete forms can be found in Table 3 [7, 8]).

Using the ordinary or weighted least squares criterion the parameters ($k(T)$ and t_0) of this latter linear expression can be estimated on the basis of the measured $\alpha-t$ pairs. In the case of weighting it can be proved that the weight w_i must be square of $f(\alpha_i)$:

$$w_i = f^2(\alpha_i)$$

The linear regression between $g(\alpha)-t$ was carried out for each model type, each reaction, each sample and each temperature to obtain the $k(T)$ rate constants and the apparent activation energy. The results obtained are summarized in Table 4. All models showed again significantly lower activation values in the gibbsite \rightarrow boehmite and boehmite \rightarrow γ -alumina reactions

Table 3 List of model used

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 Avrami-Erofeev ($n = 1/2$)	$(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$2[- \ln(1-\alpha)]^{1/2}$
A060 Avrami-Erofeev ($n = 3/5$)	$(1-\alpha)[- \ln(1-\alpha)]^{3/5}$	$5/2[- \ln(1-\alpha)]^{2/5}$
A3 Avrami-Erofeev ($n = 2/3$)	$(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$3[- \ln(1-\alpha)]^{1/3}$
A4 Avrami-Erofeev ($n = 3/4$)	$(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$4[- \ln(1-\alpha)]^{1/4}$
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 Ginstiling-Brounshtein	$[(1-\alpha)^{-1/3} - 1]^{-1}$	$3/2[1-2\alpha/3-(1-\alpha)^{2/3}]$

Table 4 Means and standard deviations of activation energies for different models in the gibbsite \rightarrow boehmite hydrothermal conversion

Model	30 h dry grinding		6 other samples	
	mean/ kJ mol^{-1}	st. dev./ kJ mol^{-1}	mean/ kJ mol^{-1}	st. dev./ kJ mol^{-1}
P1	119.1	2.3	305.6	76.8
E1	183.3	2.4	299.0	98.8
B1	113.4	27.9	296.8	109.1
F1	61.1	26.4	321.8	116.9
R3	80.4	5.7	316.0	96.5
R2	86.2	1.5	313.9	88.8
FIX	98.7	1.7	311.5	73.9
A033	74.7	17.7	313.2	103.6
A2	84.6	15.1	308.9	98.3
A060	92.6	14.1	306.4	96.0
A3	99.1	13.4	304.8	94.9
A4	108.9	12.8	302.9	94.2
D1	91.5	0.8	322.3	87.1
D2	85.0	5.3	325.1	101.0
D3	89.1	0.4	349.5	126.7
D4	93.6	7.9	338.4	108.7

when the initial gibbsite sample had been ground for 30 hours in dry conditions. And similarly no such effect was observed in other cases.

Characterization of the fit

In order to select among different models we characterized the numerical fit to the $g(\alpha) = k(T)(t - t_0)$ linear equation with a new indicator called relative residual variance. It is derived from the known residual variance, s_r . In our case the residual variance can be expressed as:

$$S_r = \left[\frac{\sum_{i=1}^{nm} [g(\alpha) - k(T)(t - t_0)]^2}{nm - 2} \right]^{1/2}$$

for the ordinary least squares regression, and

$$S_r = \left[\frac{\sum_{i=1}^{nm} w_i [g(\alpha) - k(T)(t - t_0)]^2}{nm - 2} \right]^{1/2} ; w_i = f^2(\alpha_i)$$

for weighted least squares regression. In these expressions $g(\alpha)$ is calculated from the experimental data, $k(T)$ and t_0 are the regressed parameters, and nm is the number of measured points.

The $g(\alpha)$ values and the width of the interval containing them depend on the model type, that is why we normalized the s_r values with regard to the range of actual $g(\alpha)$ values. So we defined the relative residual variance in the following way:

$$s_{rr} = \frac{s_r}{\max[g(\alpha)] - \min[g(\alpha)]}$$

that is s_{rr} shows the ratio of the mean deviation and the range of $g(\alpha)$.

Drawing a limit for s_{rr} , a model can be considered as a well-fitting one, if the calculated s_{rr} is less than this limit. After evaluating all of the linearized equations, the number of cases can be counted when a model is 'well-fitting', i.e. when the relative residual variance is below the chosen limit.

Actually, we have chosen two limits, a strict one $s_{rr} = 0.05$ and a soft one $s_{rr} = 0.10$. Using both of them we got statistics showing the numbers (frequencies) of well-fitting models. The statistics obtained for each reaction are in Figs 1-4.

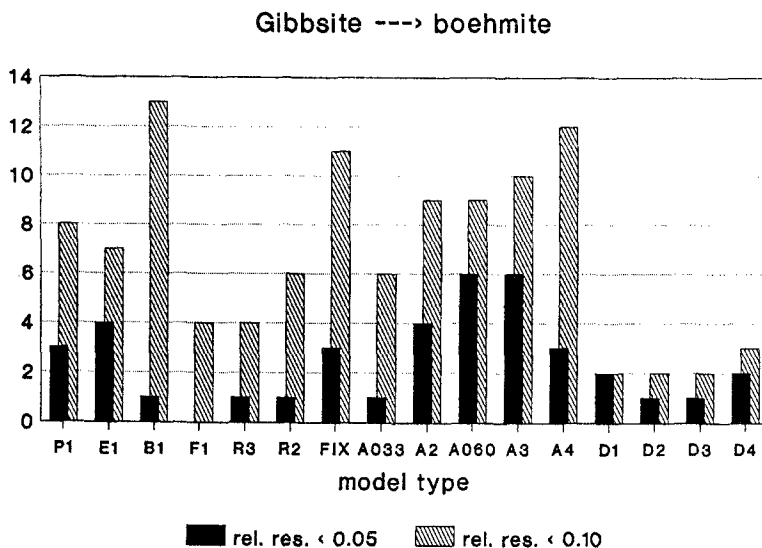


Fig. 1 Number of well-fitting lines using two different limits as criteria for the relative residual variance

In the gibbsite \rightarrow boehmite hydrothermal conversion the A3 ($n=2/3$) and A060 ($n=3/5$) models seemed to be the best ones (Fig. 1). In the boehmite \rightarrow γ -alumina decomposition we found the F1 (first order) and the D2 (two

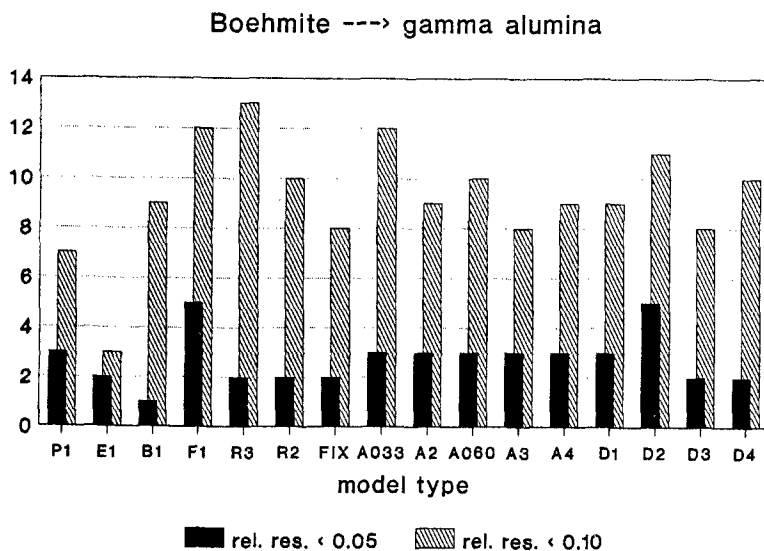


Fig. 2 Number of well-fitting lines using two different limits as criteria for the relative residual variance

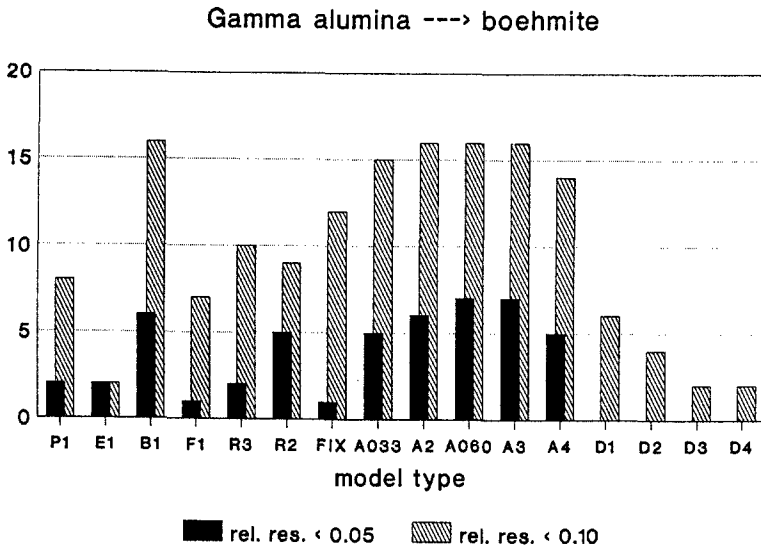


Fig. 3 Number of well-fitting lines using two different limits as criteria for the relative residual variance

dimensional diffusion) to be the best ones (Fig. 2). But it is difficult to distinguish between the various models in this case. In the reverse γ -alumina \rightarrow boehmite hydrothermal conversion the whole Avrami-Erofe'ev model family

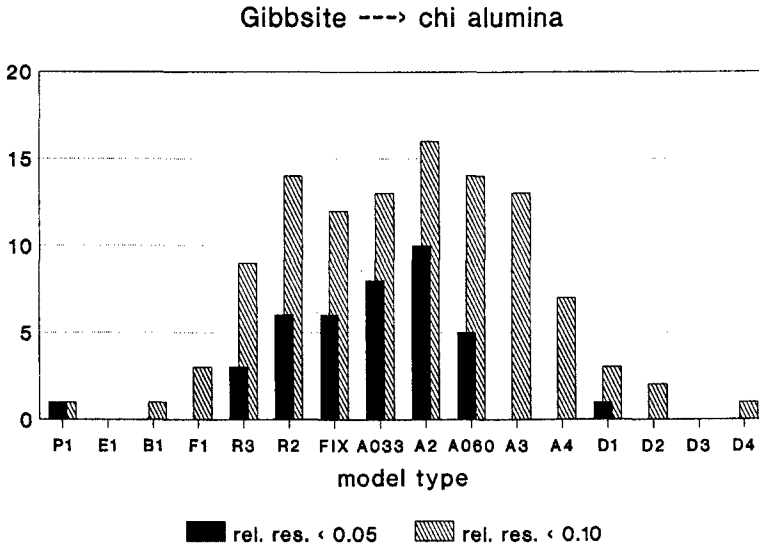


Fig. 4 Number of well-fitting lines using two different limits as criteria for the relative residual variance

gave good results (Fig. 3). In the gibbsite \rightarrow χ -alumina conversion the A2 ($n = 2/3$) can be considered the best model (Fig. 4).

The beginning and the final part of the curves which were neglected till now also have effect for the linear regression. Fortunately, it can be a distinguishing effect too, as observed in the boehmite \rightarrow γ -alumina reaction using the whole data set. Based on the newly obtained statistics (Fig. 5) we can consider the A033 ($n = 1/3$) model as a dominant one.

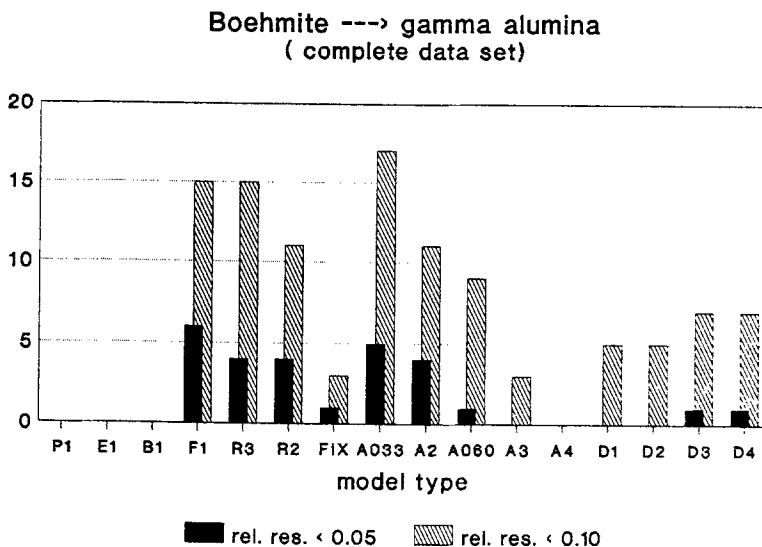


Fig. 5 Number of well-fitting lines using two different limits as criteria for the relative residual variance

The investigations extended to weighted least squares regression showed that the weighting had different effects on the various models. For example in the case of D-model family, it resulted in extra large weights, and very different rate constants. In the case of the B1 model it gave better fitting features. Generally the effect depended on the model-type.

In the following paper the results obtained using the residual variance after integration, will be presented.

Conclusions

Applying simple numeric methods we could point out an activation effect of 30-hour dry grinding of the starting gibbsite samples, in the gibbsite \rightarrow

boehmite and boehmite \rightarrow γ -alumina reactions. On the other side we defined the relative residual variance of curve fitting, which is capable to compare different isothermal models after linearization. Using certain limits for this quantity we made statistics to find dominant models for the reactions examined.

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Zusammenfassung — Es wurden die thermische Zersetzung und hydrothermische Reaktionen von Aluminiumoxiden und -hydroxiden untersucht. Das Ausgangsmaterial war Gibbsite, welches durch Zerkleinern auf verschiedene Weise vorbereitet wurde. Es wurden sechzehn kinetische Modelle angewendet und bei verschiedenen Temperaturen die Geschwindigkeitskonstanten geschätzt. Die mechanische Aktivierung des Ausgangsmaterials Gibbsite beeinflusst die Reaktivität der Proben in einigen Folgereaktionen. Für den Vergleich verschiedener Linearisationsmodelle wurde eine neue Größe, die relative Restvarianz definiert, die als Kriterium für die Anpassungsgüte vorgeschlagen wird. Dies wurde bei statistischen Untersuchungen angewendet, um die bestangepaßten Modelle zu finden.