

STUDIES ON THE KINETICS OF THE GIBBSITE → χ -ALUMINA REACTION

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ABSTRACT

Constant heating rate and isothermal thermogravimetric measurements, carried out in flowing air and in water vapour atmospheres, were applied in the investigations on the decomposition of mineral gibbsite. Kinetic parameters were estimated from the TG curves. The common rate equations

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \text{ and } k = Ae^{-E/RT}$$

were found to fit the dehydration to χ -alumina quite well. The apparent order of reaction showed differences depending on the experimental conditions, and the pre-exponential factor was found to be dependent on water vapour pressure. The dependence on water vapour pressure could be taken into account by including a driving force factor in the rate equation.

INTRODUCTION

It is well-known that the thermal decomposition of gibbsite (α -Al(OH)₃, also called hydrargillite), under ordinary pressures, yields two primary products, boehmite (α -AlO(OH)) and χ -Al₂O₃. In addition, thermal decomposition in vacuum leads to Al₂O₃, being almost amorphous [1].

The proportion of the amounts transformed to boehmite and χ -alumina has long been a topic of investigation. The differences in particle size and surface area and the synthetic or mineral origin of gibbsites were found to be the main reasons for the differences in this proportion [2,3]. For the two directions of transformation, a detailed model of reaction mechanism was given by Rouquerol et al. [4,5] based on the suggestion of de Boer et al. [6]: boehmite is formed in the interior of particles where hydrothermal conditions may exist even in the case of a dry atmosphere, while χ -oxide is obtained in a surface decomposition.

Recently, Sato et al. [7] reported the differences between the decomposi-

tion paths of gibbsite sub-modifications; Paulik et al. [8] and Naumann et al. [9] distinguished a reversible and an irreversible part of the gibbsite \rightarrow χ -alumina reaction by the quasi isothermal technique. In contrast to Lodding's conclusions [3] they found that an increasing concentration of lattice defects resulted in a decrease in the amount of boehmite formed, and this amount appeared independent of the amount of alkali ions in the gibbsite within a certain concentration range.

For the estimation of the activation energy of the gibbsite \rightarrow χ -alumina reaction, J. and F. Rouquerol applied both isothermal measurements and their constant decomposition rate cyclic method in the 10^{-3} – 10^{-5} Torr pressure range [10].

The isothermal measurements yielded inadequate values for the activation energy, E : 85–250 kJ mol⁻¹ depending on the temperature and pressure, the constant decomposition rate cyclic method gave a value of 85 kJ mol⁻¹. Dave and Masood [11] estimated 158 and 130 kJ mol⁻¹ for E , on the basis of non-isothermal DTG and DTA curves, respectively.

In the present work we attempted to describe the kinetics of the gibbsite \rightarrow χ -alumina reaction on the basis of different TG measurements. One of the goals was to include the pressure explicitly in the rate equation.

A gibbsite of mineral origin was chosen for the studies as its transformation to boehmite was negligible under the experimental conditions used.

EXPERIMENTAL

Mineral gibbsite from Minas Gerais, Brazil was studied. The particle size of the material after grinding was below 100 μ m. The gibbsite structure was confirmed by X-ray diffractometry. Emission spectrography showed 0.7% Fe, 0.02% Mg, 0.02% Cu, 2.5% Si, 0.1% Ca, 0.2% Mn, 1.6% Ba and 0.001% Na (related to the amount of Al).

Thermogravimetric investigations included both constant heating rate and isothermal experiments. These were partly carried out on the thermobalance (951 TGA) of the DuPont 990 thermal analysis system. Here, the mass of samples was about 12 mg, and an air flow of 10 l h⁻¹ purged the sample space.

A Sartorius Thermo-Gravimat thermobalance was used in the rest of the TG investigations. This apparatus offers a possibility to control the pressure in the sample chamber; this was applied for experiments in water vapour of different pressures. The aluminium sample holder, containing about 10 mg gibbsite powder, was hermetically sealed, then punched at the top. A small steel ball placed on the opening prevented diffusion between the inner space and the surroundings, but permitted an outflow of the evolved vapour above a very small pressure difference. This pressure difference could be neglected in the pressure range of the present work (10^4 – 10^5 Pa). Thus, during

dehydration of the gibbsite, the solid sample was surrounded by nearly pure water vapour (self-generated atmosphere), whose pressure was equal to that of the gas filling the thermobalance vessel.

Kinetic calculations were carried out on an IBM 3303 computer, with FORTRAN programs. Input data (of about 30 points of each TG run) were taken from the curves recorded by the instruments.

RESULTS OF NON-ISOTHERMAL EXPERIMENTS

Constant heating rate TG runs were evaluated with a previously published calculation method [12], which is based on the principle of least squares. Starting from the assumption that

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (1)$$

and

$$k = Ae^{-E/RT} \quad (2)$$

where α is the reacted fraction; t is the time; T is the temperature; A is the pre-exponential factor; E is the activation energy; R is the gas constant; and n is the apparent order of reaction. The difference between the solution of eqn. (1) and the measured data is minimized by the method of least squares

$$\Sigma[\alpha_i(t)_{\text{meas.}} - \alpha_i(t)_{\text{calc.}}]^2 = \text{min.} \quad (3)$$

Using a proper transformation of parameters, A , E and n values belonging to the minimum are determined. Since the dehydration of χ -alumina overlaps the effect of the gibbsite \rightarrow χ -alumina reaction (see Fig. 1), the baseline of the TG curves could not be assigned uniquely. Three possible baselines (\overline{CB} , \overline{DB} and \overline{EB}) are shown in Fig. 2. In all the three cases, the transformation of interest was assumed to take place between points A and B, as the slope of the TG curve appeared constant outside this interval. The slope of baseline \overline{CB} is equal to the slope of the TG curve before the studied section. Baseline \overline{DB} is extrapolated from the TG curve after the reaction. The real situation may be somewhere between these two extrema, thus, baseline \overline{EB} (bisecting the angle DBC) seems more realistic.

Kinetic parameters calculated from a TG measurement in flowing air are given in Table 1. Visibly, different baselines caused minor changes in the E and n values. The activation energies and pre-exponential factors change in the same direction. (Of course, this "compensation effect" has no physical meaning in this case.) In the further calculations baselines of type \overline{EB} only were used. To illustrate the overall reproducibility of the measurements and the calculations, Table 2 shows kinetic parameters calculated from three parallel measurements. Parameters calculated from measurements in self-

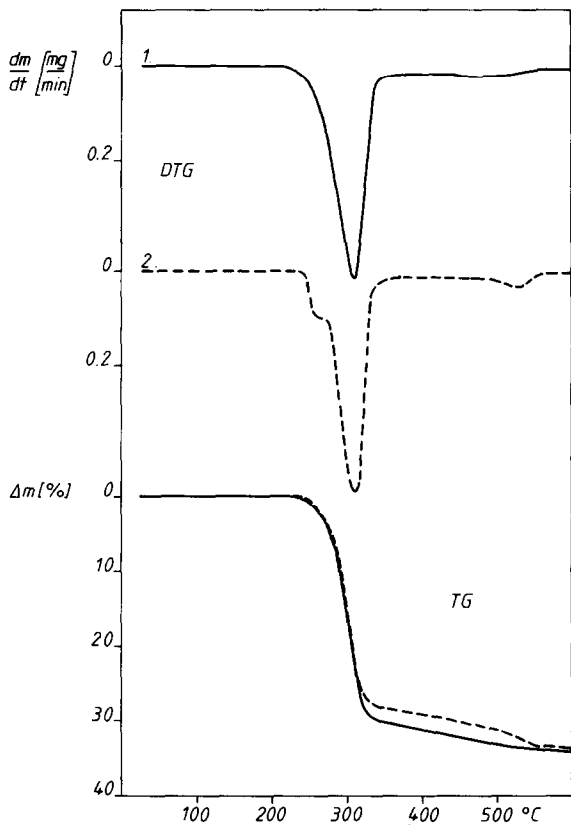


Fig. 1. Thermal decomposition of mineral (1) and synthetic (2) gibbsites in flowing air. Mass of sample = 12 mg; heating rate = $10^{\circ}\text{C min}^{-1}$.

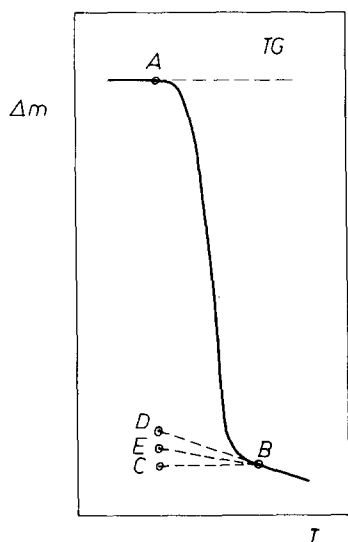


Fig. 2. The scheme of possible baselines for the evaluation of the TG curves.

generated water vapour are given in Table 3. The difference of the formal reaction orders under the two experimental conditions is the greatest. In addition, activation energies (being somewhat lower than those in Table 2) cover a significantly narrower interval than those obtained from measurements in air flow.

These observations indicate that the conditions of chemical and transport processes (including the geometry of the reacting interface) were different in the two cases, and they were far better defined when water vapour atmosphere was maintained in the sample holder.

In addition, rate constants in Table 3 (calculated from the activation energies and pre-exponential factors) clearly show that the rate constant defined by eqn. (1) is also a function of the water vapour pressure.

TABLE 1

Kinetic parameters obtained from the same TG curve with different baselines

Type of baseline (see Fig. 2)	A (s^{-1})	E ($kJ\ mol^{-1}$)	n
\overline{CB}	7.76×10^{10}	145	1.105
\overline{DB}	2.80×10^{11}	151	0.995
\overline{EB}	1.58×10^{11}	148	1.055

TABLE 2

Kinetic parameters from parallel TG runs, carried out in flowing air with $5\ K\ min^{-1}$ heating rate

No. of run	A (s^{-1})	E ($kJ\ mol^{-1}$)	n	$k(573\ K)$ (s^{-1})
1	3.29×10^{12}	161	1.005	9.78×10^{-3}
2	1.05×10^{12}	157	1.001	7.16×10^{-3}
3	5.20×10^{13}	174	1.168	1.04×10^{-2}

TABLE 3

Kinetic parameters of gibbsite dehydration in a water vapour atmosphere of different pressure at a heating rate of $5\ K\ min^{-1}$

p (kPa)	A (s^{-1})	E ($kJ\ mol^{-1}$)	n	$k(573\ K)$ (s^{-1})
11.3	1.76×10^{11}	148	0.629	7.79×10^{-3}
49.3	8.15×10^{10}	145	0.606	6.69×10^{-3}
73.7	1.16×10^{11}	148	0.593	5.13×10^{-3}

TABLE 4

Kinetic parameters calculated from isothermal runs carried out in flowing air

T (K)	k (s^{-1})	n	dev.
510	6.58×10^{-5}	0.295	0.0086
533	2.98×10^{-4}	0.370	0.0068
560	1.35×10^{-3}	0.410	0.0309

RESULTS OF ISOTHERMAL EXPERIMENTS

The isothermal measurements were evaluated by eqn. (1) as well as by a more general kinetic description. For the evaluation by eqn. (1) a simple approximation of the method of least squares was used [13,14].

By a computer program, the value of n was increased in steps of 0.005 from 0 to 2. The optimum values of n and k were obtained by the minimization of a simple expression quadratic for k . At the minimum, the deviation was calculated as follows

$$\text{dev} = \sqrt{\frac{\sum_{i=1}^M (\delta\alpha_i)^2}{M-1}}$$

where $\delta\alpha_i$ is the difference between the observed and calculated values of α_i ; i runs from 1 to M (the number of recorded points).

The parameters obtained from the measurements in flowing air are presented in Table 4. Small deviations show that eqn. (1) fits the isothermal dehydration data acceptably well. The Arrhenius plot of the calculated rate constants (Fig. 3) also confirms the applicability of eqn. (2). The slope of the plot yielded an E value of 148 kJ mole⁻¹. However, the data in Table 4 reveal a marked dependence of the apparent reaction order on temperature. To check the significance of this dependence, the calculation was repeated also assuming a constant reaction order. In this case, E was calculated from the following simple expression [15]

$$E = \frac{R \ln \frac{\Delta t_1}{\Delta t_2}}{\frac{1}{T_1} - \frac{1}{T_2}} \quad (4)$$

where Δt_1 denotes the time elapsed from an α_I to an α_{II} conversion at temperature T_1 ; Δt_2 belongs to the same $\alpha_I - \alpha_{II}$ interval at T_2 . Results obtained with eqn. (4) on $\alpha_I - \alpha_{II}$ intervals of identical and different length are presented in Tables 5 and 6. The interval covered by calculated activa-

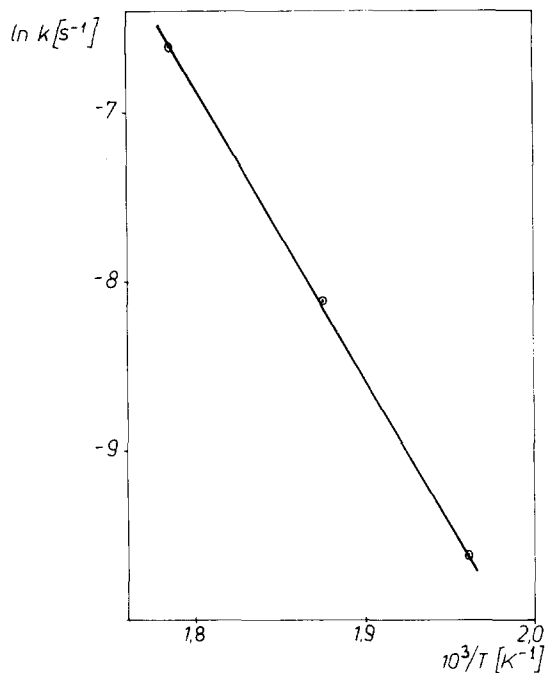


Fig. 3. Arrhenius plot of the rate constants calculated from isothermal runs in flowing air.

tion energies may be acceptable for the description of the reaction rate. However, the values of E seem to show a slight dependence on the temperature interval of the calculation. The reason for this may be the neglected dependence of the apparent order n on temperature. Nevertheless, E values of Tables 5 and 6 are close to that calculated from the rate constants of Table 4 (148 kJ mol^{-1}).

As has been mentioned already, the isothermal measurements were partly carried out in water vapour atmosphere. The kinetic evaluation of these data was first accomplished by the approximate least squares method [13]. The

TABLE 5

Activation energies calculated from isothermal runs, assuming a constant apparent order (a)

α_1	α_{11}	$E(\text{kJ mol}^{-1})$		
		$T_1(\text{K}) = 560$	560	533
		$T_2(\text{K}) = 533$	510	510
0.7	0.5	143	138	132
0.5	0.3	153	146	139
0.3	0.1	150	144	137

TABLE 6

Activation energies calculated from isothermal runs, assuming a constant apparent order (*b*)

α_I	α_{II}	E (kJ mol ⁻¹)		
		T_1 (K) = 560	560	533
		T_2 (K) = 533	510	510
0.7	0.3	148	142	136
0.7	0.1	150	143	137
0.5	0.1	151	145	138

results are shown in Table 7. Note that the rate constants and the reaction orders have proved dependent to the temperature and the pressure. The effect of the temperature on the rate constants was evaluated by $\ln k$ vs. $1/T$ diagrams of the data corresponding to the same vapour pressure. In this way, a formal activation energy of 106 kJ mol⁻¹ and a formal pre-exponential factor of 1.11×10^7 s⁻¹ were obtained at 11.3 kPa. At 49.2 kPa these values were 103 kJ mol⁻¹ and 3.36×10^6 s⁻¹, respectively. These values are significantly different from the results of the measurements in flowing air.

Since the rate constant is a decreasing function of the pressure of the water vapour, it seems reasonable to introduce a driving force factor F into the rate equation. An adequate general expression [16,17] is:

$$w = kFQ \quad (5)$$

Here w denotes the rate of reaction, and Q is the reaction cross-section, a measure of the sites geometrically suitable to react (in this case, the reacting surface of gibbsite).

For a reversible type of solid-gas reaction Bradley [18] used the $(1 - \Delta G/RT)$ driving force factor, ΔG being the Gibbs free energy difference of

TABLE 7

Kinetic parameters calculated from isothermal runs in water vapour atmosphere

p (kPa)	T (K)	k (s ⁻¹)	n	dev.
11.3	498	8.74×10^{-5}	0.250	0.011
11.3	523	2.69×10^{-4}	0.330	0.034
11.3	538	5.96×10^{-4}	0.480	0.057
49.2	498	4.30×10^{-5}	0.245	0.011
49.2	519	1.73×10^{-4}	0.360	0.024
49.2	550	4.72×10^{-4}	0.200	0.031
73.7	519	1.43×10^{-4}	0.270	0.016

the process. This factor, which was proposed by Šesták [19], and Šatava [20] to be included in the description of thermoanalytical curves, is shown to correspond to the well-known rate law of homogeneous reactions as well [17].

In the case of a $\text{solid}_I \rightarrow \text{solid}_{II} + \text{gas}$ reaction with pure phases, this driving force factor equals $(1 - p/p_e)$ (where p and p_e are the actual and equilibrium pressure of the product, respectively) as used by Jüntgen and van Heek [21] in the description of the $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ process.

The behaviour of the first part of the gibbsite $\rightarrow \chi$ -alumina transformation was like that of reversible reactions [8,9]. On the other hand, re-formation of gibbsite from χ -oxide and water has never been reported, so the process may not be reversible. Consequently, the existence of p_e (a thermodynamic equilibrium value) is questionable. So, p_e should be formally substituted by p^* , an empirical parameter dependent only on the temperature.

To decide whether the rate equation

$$w = k \left(1 - \frac{p}{p^*} \right) Q \quad (6)$$

can describe the process, data from isothermal measurements carried out with the same amount of sample at the same temperature but under two different vapour pressures may be suitable. If reaction rates belonging to an identical, arbitrarily chosen α_1 are compared, the reaction cross-section should be identical as well, and we can write

$$\frac{\left(\frac{d\alpha}{dt} \right)_{1,\alpha_1}}{\left(\frac{d\alpha}{dt} \right)_{2,\alpha_1}} = \frac{1 - \frac{p_1}{p^*}}{1 - \frac{p_2}{p^*}}, \quad (7)$$

TABLE 8

Pressure constants of the driving force factor $(1 - p/p^*)$ calculated from isothermal runs carried out in water vapour atmosphere

α	$p^*(\text{kPa})$	
	$T(\text{K}) = 498$	
	$p_1(\text{kPa}) = 11.3$	49.2
	$p_2(\text{kPa}) = 49.2$	73.7
0.3	87.4	—
0.4	84.8	—
0.5	83.9	198
0.6	87.4	186
0.7	86.5	183
0.8	86.2	209

where subscripts 1 and 2 refer to the measurements under the first and second vapour pressure. Now the question is if p^* is independent of the choice of α_1 . Conversion rates calculated from the TG curves with the methods of Savitzky and Golay [22], and Steiner et al. [23] led to the values shown in Table 8. The agreement of p^* values belonging to the same temperature seems acceptable. Consequently, the factor $(1 - p/p^*)$ may be suitable for expressing the dependency of the reaction rate on the water vapour pressure. However, these $p^* - T$ pairs could be related neither to the onset of the dehydration in non-isothermal TG runs, nor to the extrapolated onset of the DTG curves (similar to the one used in DTA).

A calculation based on average p^* values gave 90 kJ mol^{-1} for the activation energy.

CONCLUSIONS

(1) The rate equations most commonly used in thermal analysis (eqns. 1 and 2) were found to fit the dehydration of gibbsite to χ -alumina quite well. However, the apparent order of reaction showed differences depending on the experimental conditions, and the pre-exponential factor depended on the water vapour pressure.

(2) The dependence on water vapour pressure could be explicitly taken into account using a rate equation containing the $(1 - p/p^*)$ driving force factor. Since the thermodynamic reversibility of the reaction is questionable, p^* in this instance is just a temperature dependent empirical parameter.

(3) Although kinetic constants estimated from different experiments on the basis of eqns. (1) and (2) can describe the progress of the reaction under the given conditions, they are more or less formal parameters (except the apparent order n representing the geometry of the reacting surface).

In our opinion, the E value calculated with the assumption of a driving force factor, 90 kJ mol^{-1} , seems to be a better approximation of the true activation energy. However, further investigations are needed in this field.

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