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ALUMINUM SULPHATE HYDRATES
Kinetics of the thermal decomposition of aluminum sulphate using different calculation methods

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Abstract

Three different calculation methods of deriving kinetic parameters (activation energy and preexponential factor) from dynamic TG data have been applied for the sulphate decomposition stage of the aluminum sulphate octadecahydrate. The constant rate experiments were carried out by Derivatograph and DuPont thermobalances. The three parameters estimation methods included a simple differential method, the classical Coats-Redfern and a new direct integral method. The fits of the curves obtained by these procedures were compared both graphically and numerically. It was found that the direct integral method gave the most satisfactory results. With the order type reaction models this method in each case produced the smallest residual deviation values and the best fitting curves compared to those obtained by the other two methods. The activation parameters calculated by the differential method were not acceptable at all, for the estimated curves were very far from the measured ones.

Keywords: aluminum sulphate hydrates, kinetics

Introduction

Decomposition of aluminum sulphate hydrates have been studied by thermogravimetry, simultaneous thermal analysis and differential scanning calorimetry. The structure of hydrate phases and their intermediate products have been characterized by X-ray diffraction and infrared spectroscopy. This article presents the kinetics of the thermal decomposition of aluminum sulphate.

The objective of our is to determine the kinetic parameters, activation energy and preexponential factor from dynamic TG data obtained by the derivatograph

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and DuPont system for the sulphate decomposition stage of the aluminum sulphate octadecahydrate and to compare the results of three calculation methods.

Dynamic thermogravimetry (TG) for deriving kinetic parameters of solid state decompositions has become popular because of its advantages [1],

(i) considerably fewer data are required;

(ii) the kinetics can be calculated over an entire temperature range in a continuous manner;

(iii) only a single sample is required.

We have chosen the dynamic TG data of sulphate decomposition to obtain kinetic parameters.

Kinetic parameters were calculated by three different methods and the results were compared. Calculation techniques used in this study had been worked out by Sharp and Wentworth [2], Coats and Redfern [3], and Valkó and Vajda [4]. In principle, each of the methods combines the apparent order rate equation with the Arrhenius equation.

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \tag{1}$$

$$f(\alpha) = (1-\alpha)^n \tag{2}$$

and

$$k = A \exp(-E/RT) \tag{3}$$

$$\frac{d\alpha}{dt} = A \exp(-E/RT)\ (1-\alpha)^n \tag{4}$$

where α= fraction reacted, t = time, k = rate constant, n = reaction order, A = preexponential term, E = activation energy, R = gas constant, and T = absolute temperature. The exponents n = 1/2, 2/3 and 1.0 were used in this study. In the following, a brief description of each parameter estimating method applied is presented.

Method I

The general differential technique was derived by Sharp and Wentworth [2]. In this method the data for each of the selected models are plotted, and the linearity is compared in order to find the best model. The defining equation is:

$$\lg\left(\frac{\mathrm{d}\alpha/\mathrm{d}T}{f(\alpha)}\right)=\lg\frac{A}{\beta}-\frac{E}{2.3RT}$$

where $\beta = \mathrm{d}T/\mathrm{d}t$ is the heating rate. By plotting log $[(\mathrm{d}\alpha/\mathrm{d}T)/f(\alpha)]$ *vs.* $1/T$ one can calculate the activation energy and preexponential term from the slope and intercept.

Method II

This is an integral method developed by Coats and Redfern [3]. The orders (n = 1/2, 2/3, 1.0) have been used since each of these correspond to a simple model of solid state decomposition. Using this, the Coats and Redfern equation became

$$\lg\left(\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right)=\lg\left(\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right)-\frac{E}{2.3RT}\quad \text{for } n\neq 1$$

$$\lg\left(\frac{-\ln(1-\alpha)}{T^2}\right)=\lg\left(\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right)-\frac{E}{2.3RT}\quad \text{for } n=1$$

This approach uses the fact that

$$\lg\left(\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right)$$

is nearly constant, because $\left(1-\frac{2RT}{E}\right)$ is close to one. Regressing the appropriate left side of the above equations using the least square criteria *vs.* $1/T$, the slope is $-E/2.3R$ and the intercept is equal to

$$\lg\left(\frac{AR}{\beta E}\right),$$

thus allows calculation of the activation energy E and preexponential term A.

Method III

A general numerical procedure for parameter estimation of common differential equation sets designed and implemented by Valkó *et al.* [4] was used. This so-called direct integral method is based on the iterative procedure of

Gauss-Newton-Marquard's nonlinear regression, and application of natural cubic splines to interpolate all of the functions involved in the calculation.

In our case we used the following equation set

$$d\alpha / dt = A \exp(-E/RT) f(\alpha)$$

$$dT/dt = \beta$$

where β (heating rate) was constant.

In this method, the integration of the original differential equation set is executed only after the last step, but not in each step of iterative process. The iteration was finished when the relative change of the estimated parameters became less than a certain limit.

We used a fourth order numerical integration method to get back the α-t curves. To characterize the merit of fit a residual deviation was generated from the differences between the original curve and the estimated one. In each case we calculated the s_r values as follows:

$$s_r = \sqrt{\frac{\sum [\alpha_m(t_i) - \alpha_c(t_i)]^2}{n-p}}$$

where s_r = residual deviation, α_m = measured α at t_i time, α_c = calculated α at t_i time, n = number of data points from TG curve, p = number of estimated parameters and n-p is the degree of freedom.

The value of s_r generally makes it possible to compare different types of the model or models with different exponents. From the values of s_r obtained as above, the best fitting model has the least s_r value.

These values can also be used to compare different estimation methods.

Experimental and calculations

MOTIM aluminum sulphate hydrate, $Al_2(SO_4)_3 \cdot 18H_2O$ (manufactured by Mosonmagyaróvár Alumina and Synthetic Corundum Works, Hungary) was used in this work. The dynamic TG and DTG measurements were carried out with a derivatograph and a DuPont 990 thermal analysis system. In the derivatograph powder of weight of 22.52 mg was heated with 5 deg·min^{-1}. Dry nitrogen flowing at 20 l/h was used throughout this study. This sample was decomposed by heating up to 1000°C. In the DuPont system powder of weight of 10.10 mg was decomposed in dry nitrogen by heating up to 1000°C. In both cases only the sulphate decomposition stage was examined.

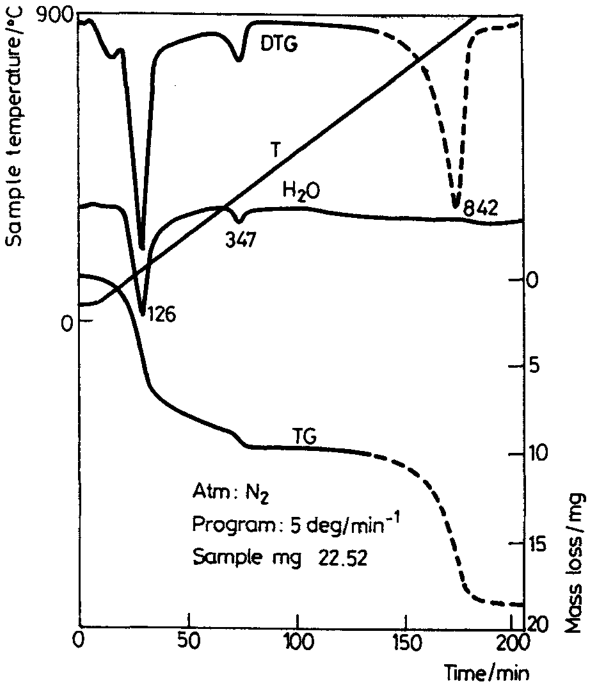

Fig. 1 Thermoanalytical curves of MOTIM aluminum sulphate sample obtained by derivatograph

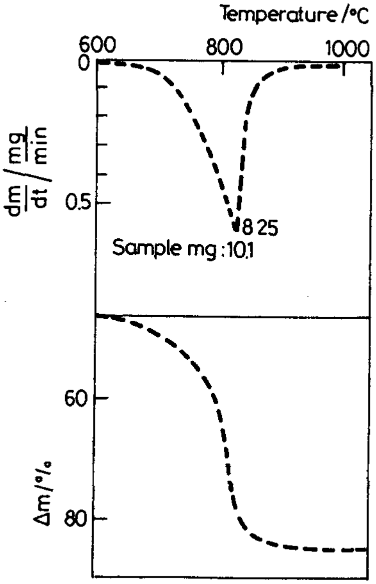

Fig. 2 A part of the thermoanalytical curves of MOTIM aluminum sulphate sample obtained by DuPont 990

Illustrative complete simultaneous thermal curves of the sample are shown in Fig. 1 by dashed line. Inspection of the TG and DTG curves show the decomposition stages of aluminum sulphate octadecahydrate. There are three dehydration stages and the fourth stage represents the sulphate decomposition. Only the sulphate decomposition stage of the DuPont measurement is given in Fig. 2.

Table 1 Kinetic parameters and residual variances from method I, II, III for the sulphate decomposition stage* of MOTIM sample using $f(\alpha) = (1 - \alpha)^n$

Method	Order n	Residual variance	E / kJ·mol^{-1}	A / sec^{-1}
I	$n = 1/2$	0.192	287	$9.3 \cdot 10^{12}$
	$n = 2/3$	0.203	327	$1.1 \cdot 10^{15}$
	$n = 1.0$	0.178	348	$1.3 \cdot 10^{16}$
II	$n = 1/2$	0.059	154	$1.0 \cdot 10^{6}$
	$n = 2/3$	0.049	167	$4.8 \cdot 10^{6}$
	$n = 1.0$	0.045	196	$1.96 \cdot 10^{8}$
III	$n = 1/2$	0.025	178	$1.75 \cdot 10^{7}$
	$n = 2/3$	0.018	211	$8.1 \cdot 10^{8}$
	$n = 1.0$	0.016	274	$1.2 \cdot 10^{12}$

* Data obtained by the derivatograph

Table 2 Kinetic parameters and residual variances from method II and III for the sulphate decomposition stage* of MOTIM sample using $f(\alpha) = (1 - \alpha)^n$

Method	Order	Residual variance	E / kJ·mol^{-1}	A / sec^{-1}
II	$n = 1/2$	0.069	148	$1.53 \cdot 10^{6}$
	$n = 2/3$	0.067	153	$3.2 \cdot 10^{6}$
	$n = 1.3$	0.069	166	$1.89 \cdot 10^{7}$
III	$n = 1/2$	0.026	215	$4.45 \cdot 10^{9}$
	$n = 2/3$	0.030	239	$7.8 \cdot 10^{10}$
	$n = 1.0$	0.036	284	$1.38 \cdot 10^{13}$

* Data obtained by the DuPont

In the dehydration stages the difficulties in base line correction and the presence of overlapping steps caused great uncertainties in the calculation of α values, that's why we deal in the present work only with the sulphate decomposition stage where α values can be determined precisely.

In the calculations, first of all, the weight data are converted into α, fraction reacted. In this study we used 16 randomly selected data points from the derivatograph and 29 equidistantly selected points from the DuPont curves covering the whole range of α from 0 to 1.

The residual deviations and plots of the estimated curves were used for the comparison among the different models and the three applied methods. The residual deviations for methods I and II were calculated after Runge-Kutta integration; for method III it was determined by the estimation procedure itself.

Results and discussion

Table 1 shows the kinetic parameters and residual deviations from methods I, II and III for the derivatograph sulphate decomposition stage of aluminum sulphate octadecahydrate. According to the TG curve of the DuPont system, Table 2 shows the parameters obtained from the two integral methodsII and III.

Method I (Differential)

Figure 3 shows the graphical plots used to get the activation energy E and preexponential factor A listed in Table 1, lines 1–3. With each exponents this method gives large residual deviation and bad fit compared to the results of the other two methods. This may be due to the inevitable uncertainties of derivation itself. These parameters are not acceptable at all.

Method II (Coats-Redfern)

Lines 4–6 of Table 1 summarize the results with apparent orders 1/2, 2/3 and 1 using the derivatograph TG data. In this case the first order model gave the smallest residual deviation. An apparent activation energy of 196 kJ/mol and preexponential factor of $1.96\cdot10^{8}$ s^{-1} were determined.

A comparison of the experimental and calculated curves of the three models used is illustrated in Fig. 4. This method gives small residual deviations but the disagreement between the calculated curves and the original one are significant, so we can not consider any of them as a perfect fit.

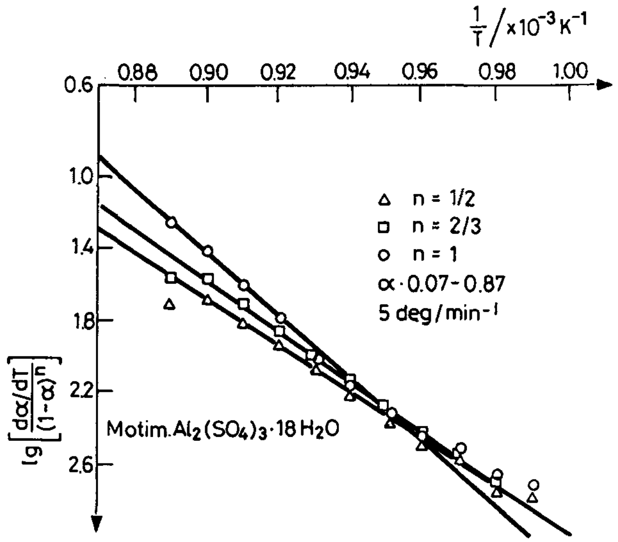

Fig. 3 Samples of data sets using various models with method I (Decomposition stage of the MOTIM sample)

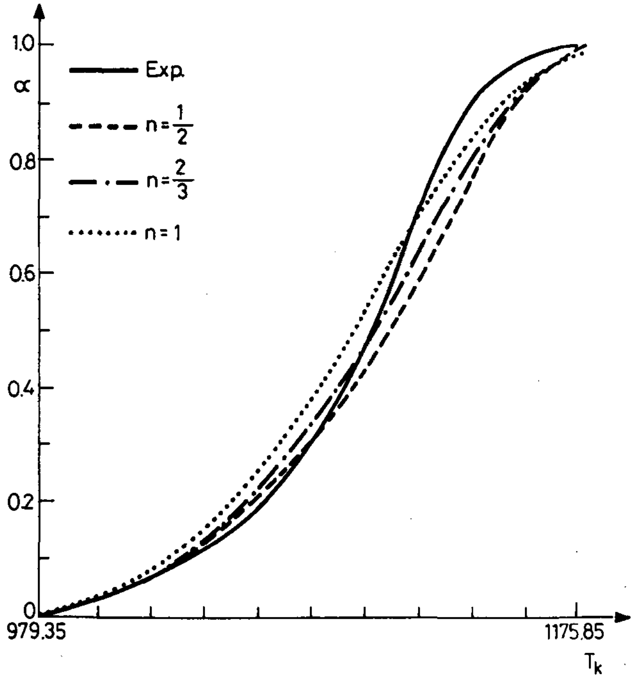

Fig. 4 Comparison of experimental and calculated α values according to Coats-Redfern method with (1–α) model (derivatograph)

Method III (New Direct Integral Method)

In this method the iteration procedure has been started with a random initial value and the optimized fitting has been reached after more than 250 steps. During these steps the square sum of the deviations decreased continuously. The iteration was finished when the relative change of the estimated parameters became less than $\varepsilon = 1.0 \cdot 10^{-7}$. Table 1, lines 7–9 show the results obtained. These final residual deviations obtained, may represent the deviation of experimental error. The iteration procedure was repeated using different initial values but better fitting could not been reached, they gave the same kinetic parameters. The exponent $n = 1.0$ yielded the best fit corresponding to a minimum residual deviation of 0.016, yielding kinetic parameters $E = 274$ kJ/mol and $A = 1.2 \cdot 10^{12}\ \mathrm{s}^{-1}$.

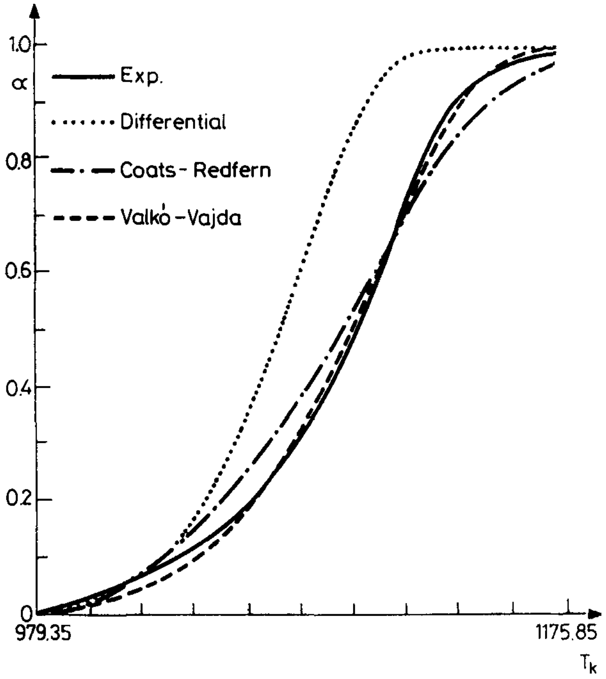

Fig. 5 Comparison of experimental and calculated α values of the three methods according to (1–α) model (derivatograph)

Comparison of the results of the three methods

Analysing the results summarized in Table 1 one can see the differences among the residual deviations calculated by a certain method using different model exponent, and also the differences among the three methods using the same models. The residual deviations range from 0.178 to 0.203 in the case of the differential method, from 0.045 to 0.059 in the case of Coats-Redfern integral method and from 0.016 to 0.025 in Valkó and Vajda integral method. The largest residual deviations were calculated by the differential type method. Derivation methods generally contain uncertainties which may be related to the calculation of differential quotients. In our case the $d\alpha/dT$ was calculated from the tangent of the TG curve manually in Method I. The residual deviations obtained by the other two integral methods are significantly smaller than that the differential method. The fits of the same model (e.g. $n = 1.0$) yielded by the three methods are demonstrated in Fig. 5. This figure contains the measured curve and the curves calculated by the three methods. The corresponding activation energies are significantly different.

Comparison of the results obtained by DuPont and derivatograph

Table 2 summarizes the results of the two integral methods (II and III) obtained with the data of DuPont apparatus.

Lines 1–3 of Table 2 show the results obtained by the Coats-Redfern method. The 2/3 order model gave the smallest residual deviation but we can say that the results practically show no significant difference concerning the residual deviation among the three orders used 1/2, 2/3 and 1. An apparent activation energy of 153 kJ/mol and preexponential factor of $3.2\cdot10^{6}$ s^{-1} were determined by 2/3 order model.

Lines 4–6 of Table 2 show the results of the Valkó-Vajda method. In this case the 1/2 order model yielded the best fit corresponding to a minimum residual deviation of 0.026, yielding kinetic parameters $E = 215$ kJ/mol and $A = 4.45\cdot10^{9}$ s^{-1}.

Comparing the results obtained by the two integral methods from the data measured on the two thermobalances we can the Coats-Redfern method gave bigger residual deviations calculated from DuPont system, bigger than those calculated from the derivatograph. The kinetic parameters are close to each other but the fit of the curves significantly different.

The Valkó-Vajda method in both cases gave the least residual deviations, but the calculated kinetic parameters of the two systems are different (Tables 1 and 2).

Comparison of the present results with the literature data

The activation energy calculated here by Method I are close to that reported by Johnson and Gallagher [5]. The activation energy obtained by the two integral methods are lower than 74 kcal/mol reported by Johnson and Gallagher or 95 kcal/mol by Papazian and coworkers [6].

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Zusammenfassung — Für den Sulfat-Zersetzungsschritt bei Aluminiumsulfat-Oktadekahydrat wurden an den DTG-Daten drei verschiedene Rechenmethoden zur Ermittelung der kinetischen Parameter (Aktivierungsenergie, präexponentieller Faktor) angewendet. Die Versuche mit konstanter Geschwindigkeit wurden mittels Derivatograf und DuPont Thermowaagen durchgeführt. Die drei Methoden zur Schätzung der Parameter waren eine einfache Differentialmethode, die klassische Coats-Redfern-Methode und eine neue direkte Integralmethode. Die Übereinstimmung der durch diese Verfahren erhaltenen Kurven wurde sowohl graphisch als auch numerisch verglichen. Man fand, daß die direkte Integralmethode die besten Resultate lieferte. Verglichen mit den beiden anderen Methoden ergab diese Methode in allen Fällen den geringsten Nullpunktsfehler und die besten Kurvenübereinstimmungen. Die mit Hilfe der Differentialmethode berechneten Aktivierungsenergien waren vollständig unakzeptabel und lagen für die geschätzten Kurven sehr weit von den gemessenen Werten entfernt.