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KINETIC STUDY OF THE THERMAL DEHYDRATION OF SYNGENITE $K_2Ca(SO_4)_2 \cdot H_2O$ UNDER NON-ISOTHERMAL CONDITIONS

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Different calculation methods applied to TG, DTG and DTA curves obtained with a Mettler Thermoanalyzer at one or several heating rates have been tested. It has been shown that the dehydration of syngenite can best be described by the Avrami equation I

$$[-\ln(1-\alpha)]^{1/2} = 3.46 \cdot 10^{21} \exp\left(-\frac{2.73 \cdot 10^4}{T}\right) \cdot t$$

where α is the degree of decomposition, T the absolute temperature, and t the time.

The mean value of the activation energy is 54 kcal · mole^{-1}. This is in good agreement with the results obtained under isothermal conditions. The method of Šatava and Škvára, supplemented by the numerical tables of Zsakó, is most useful in obtaining the kinetic equations describing the thermal decomposition of solids.

In an earlier publication [1] we presented our results on the kinetics of thermal dehydration of syngenite under isothermal conditions. Analysis of the experimental data, using three different graphical methods, indicated that the process can be best described by the Avrami equation I, chosen from among nine kinetic equations taken from the literature [2–6]. In the present paper we describe the results of experiments carried out under non-isothermal (dynamic) conditions [7]. Work under dynamic conditions has now become popular for a number of reasons: the measurements can be made quickly, over a large range of temperatures, and no exploratory experiments are required (these are often necessary with isothermal techniques). Also, with the help of a single curve, several stages of the reaction can be followed.

We now present results of our investigations of the kinetics of thermal dehydration of synthetic syngenite, based on TG, DTG and DTA curves obtained at one or several heating rates. On the basis of the available literature, an attempt was made to select the most suitable method of obtaining kinetic information. Five kinetic equations were considered. They were designated by Sharp et al. [5] F_1, A_2, A_3, R_2 and R_3, and correspond to different mechanisms of nucleation and of reaction at the interphase boundary.

Experimental

Equipment and methods of measurement

Thermal analysis of syngenite $K_2Ca(SO_4)_2 \cdot H_2O$ (synthetized as described earlier [1]) under non-isothermal conditions was carried out in static air using a Mettler Thermoanalyzer. The reference substance for DTA was $\alpha-Al_2O_3$. The following heating rates were employed: 10, 6, 4 and 2° per minute. Samples of around 70 mg were used, placed in a 2 cm^3 crucible (PtRh 10%). Simultaneous TG – DTG – DTA curves shown in Fig. 1, obtained at a heating rate of $10° \cdot min^{-1}$ are typical and cover the entire process of dehydration of syngenite. The area under the DTA curve was measured using a planimeter (PZO-Warsaw).

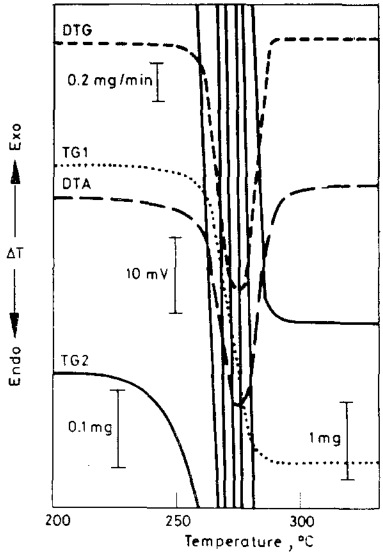

Fig. 1. Simultaneous TG DTG DTA curves for the dehydration of syngenite. Heating rate: 10°/min

Results and discussion

The evaluation of thermogravimetric data obtained under non-isothermal conditions has been discussed in a number of reviews [8 – 11]. Experimental data from TG, DTG and DTA curves were used to deduce the apparent kinetic parameters on the basis of two basic types of equations:

$$\frac{d\alpha}{dT} = \frac{Z}{q} \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{1}$$

and

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = \int_{T_0}^{T_\alpha} \frac{Z}{q} \exp\left(-\frac{E}{RT}\right) dT \tag{2}$$

where heating rate $q = \mathrm{d}T/\mathrm{d}t$. In both equations all the symbols have their usual meanings.

The kinetics of dehydration of syngenite were investigated using a number of particular equations and these are briefly considered below.

1. The final equation deduced by Coats and Redfern [12–13] has the form

$$\log \frac{g(\alpha)}{T^2} = -\frac{E}{2.303\,R} \cdot \frac{1}{T} + \log \frac{ZR}{qE}\left(1 - \frac{2RT}{E}\right) \qquad (3)$$

Figure 2 shows the dependence of $\log g(\alpha)/T^2$ on $1/T$ for functions $g(\alpha)$ – F_1, A_2, A_3, R_2 and R_3. None of the plots is a straight line.

2. Horowitz and Metzger [14] used the relationship

$$\log g(\alpha) = \frac{E}{2.303\,RT_{\mathrm{m}}^2} \cdot \Theta \qquad (4)$$

where T_{m} is the temperature corresponding to the point of inflection of the DTG curve and $\Theta = T - T_{\mathrm{m}}$. A plot of $\log g(\alpha)$ versus Θ is shown in Fig. 3. The position of the point of inflection on the TG curve could be taken to indicate that the reaction was of the first order. Because of this, the curve corresponding to the function F_1 showed the best linearity. The energy of activation deduced from this plot was

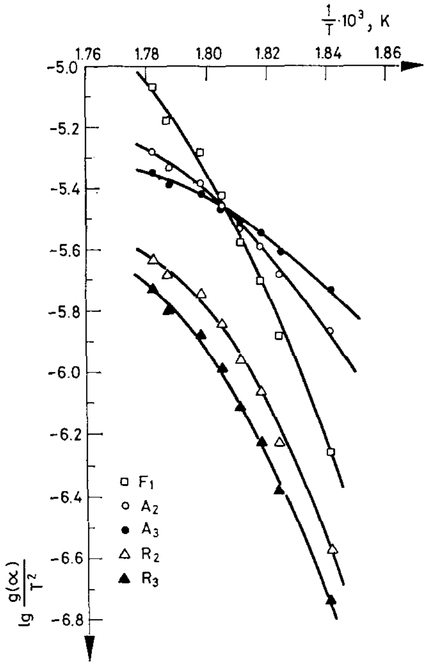

Fig. 2. Dependence of $\log \left(\frac{g(\alpha)}{T^2}\right)$ on $1/T$ according to Eq. (3) for five functions $g(\alpha)$.

93.8±4.6 kcal · mole^{-1}, and the average value of the logarithm of the pre-exponential factor was 37.09.

3. Using Eq. (2), Zsakó [15] deduced the following relationship

$$\log \frac{ZE}{qR} = \log g(\alpha) - \log p(x) = B \qquad (5)$$

For five functions $g(\alpha)$ and activation energies in the range 46–66 kcal · mole^{-1}, we calculated the standard deviations of B_i from the arithmetical mean $\bar{B}$, using the formula

$$s = \left[\frac{\sum(B_i - \bar{B})}{N}\right]^{1/2} \qquad (6)$$

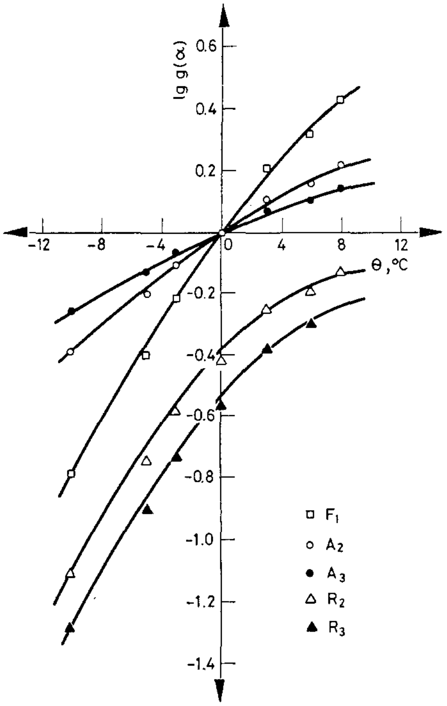

Fig. 3. Dependence of log g (α) on Θ according to Eq. (4) for five functions $g(\alpha)$. T_m = 553 K.

where N is the number of experimental data used to obtain $\bar{B}$. Tabulated values of log $g(\alpha)$ as a function of α [16] and $-\log p(x)$ of E were used [15]. The smallest standard deviation was obtained for the function A_2 with E = 57.0 kcal · mole^{-1}. The logarithm of the associated pre-exponential factor, log Z, was 22.52.

4. The method of Šatava and Škvára [16], which is based on Eq. (5), is illustrated in Fig. 4. The best correspondence between log $g(\alpha)$ and $-\log p(x)$ over the great-

est range of values of α was obtained for plots derived from the function A_2 with $E = 54 \pm 1$ kcal · mole^{-1}. The logarithm of the pre-exponential factor was then equal to 21.61 ± 0.10. The treatment of results can be made considerably easier when the tabulated values of $-\log p(x)$ given by Zsakó [15] are utilized.

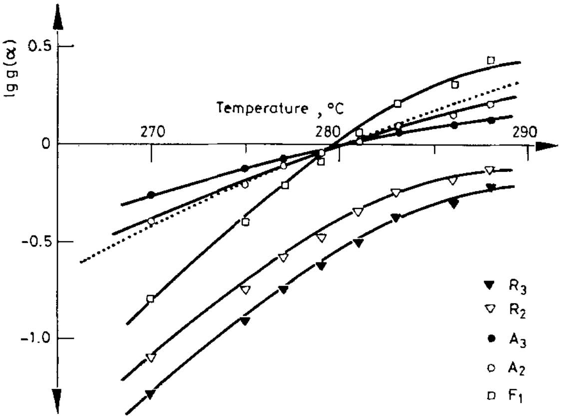

Fig. 4. Dependence of log $g(\alpha)$ on T for five functions $g(\alpha)$. Points correspond to the plot of $-\log p(x)$ versus T for $E = 54$ kcal · mole^{-1}

5. In order to evaluate the activation energy from TG curves obtained with two different heating rates, Gyulai and Greenhow [17] proposed the relationship

$$\log\left(\frac{q_1}{q_2}\right) = \log\left(\frac{i_1}{i_2}\right) \tag{7}$$

where $i = \int\limits_{T_0}^{T_\alpha} \exp\left(-\frac{E}{RT}\right) \mathrm{d}T$

Data required to obtain plots of $\log(i_1/i_2)$ as a function of E are given in Table 1 for several pairs of q values, together with the corresponding values of the activation energies. The plots are shown in Fig. 5.

6. The final equation derived by Achar et al. [18] has the form

$$\log\left(\frac{\mathrm{d}\alpha/\mathrm{d}t}{f(\alpha)}\right) = -\frac{E}{2.303\,R} \cdot \frac{1}{T} + \log Z \tag{8}$$

Plots of log $\mathrm{d}\alpha/\mathrm{d}t$. $1/f(\alpha)$ against $1/T$ are shown in Fig. 6 for five functions $f(\alpha)$. None of the plots is linear. The method is thus not suitable in our case.

7. Freeman and Carroll [19] used the equation

$$\frac{\Delta \log(\mathrm{d}\alpha/\mathrm{d}t)}{\Delta \log(1-\alpha)} = -\frac{E}{2.303\,R} \cdot \frac{\Delta 1/T}{\Delta \log(1-\alpha)} + n \tag{9}$$

Table 1

Numerical data used in plotting Fig. 5 and values of E derivated following Guylai and Greenhow [17] for $\alpha = 0.63$

q_1/q_2	$\log(q_1/q_2)$		E, kcal·mole^{-1}
	E, kcal·mole^{-1}		
	30	50	
10 : 6	0.116	0.188	58.25
10 : 4	0.255	0.414	47.75
10 : 2	0.500	0.814	42.75
6 : 4	0.139	0.226	38.50
6 : 3	0.373	0.626	38.10
4 : 2	0.246	0.396	37.25

Figure 7 shows the dependence of $\dfrac{\Delta \log(\mathrm{d}\alpha/\mathrm{d}t)}{\Delta \log(1-\alpha)}$ on $\dfrac{\Delta\, 1/T}{\Delta \log(1-\alpha)}$. The order of reaction is $n = 1.05 \pm 0.07$ and the slope of this plot gives $E = 112.0 \pm 3.2$ kcal · ·mole^{-1}.

8. On the basis of DTG curves obtained at different heating rates, Friedman [20] and Anderson [21] derived the equation

$$\log\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = -\frac{E}{2.303\,R}\cdot\frac{1}{T} + \log Z + n\log(1-\alpha) \tag{10}$$

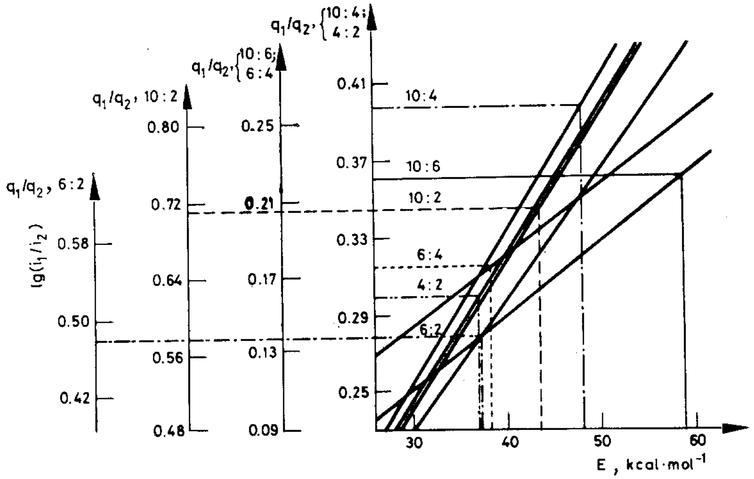

Fig. 5. An illustration of the procedure used by Gyulai et al. [17] for evaluating activation energies

where T is the temperature corresponding to the constant degree of decomposition α. Our data, plotted according to Eq. (10) are shown in Fig. 8, and the derived kinetic parameters are $E = 33$ kcal · mole^{-1}, $n = 6.80$ and $\log Z = 13.90$.

9. The final form of the equation proposed by Reich [22] for interpreting TG curves obtained at different heating rates is

$$\log\left(\frac{q}{T^2}\right) = -\frac{E}{2.303\,R}\cdot\frac{1}{T} \tag{11}$$

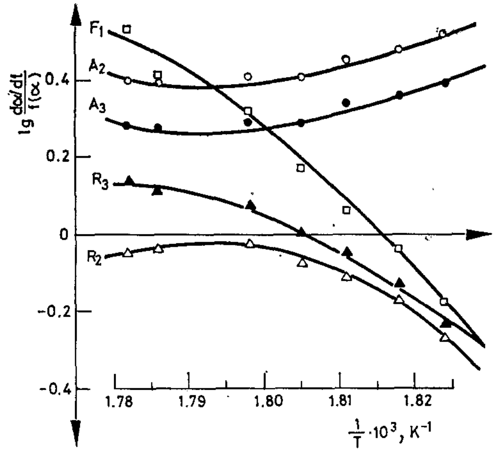

Fig. 6. Dependence of $\log\left[\frac{d\alpha}{dt}\cdot\frac{1}{f(\alpha)}\right]$ on $1/T$ according to Eq. (8)

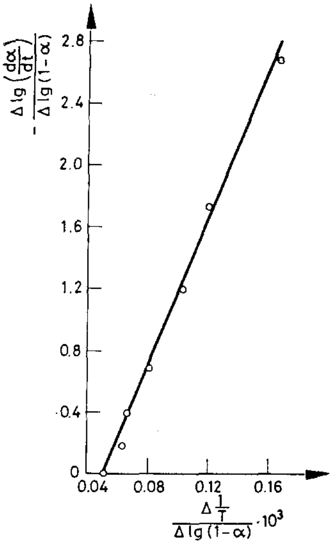

Fig. 7. Graphical representation of Eq. (9)

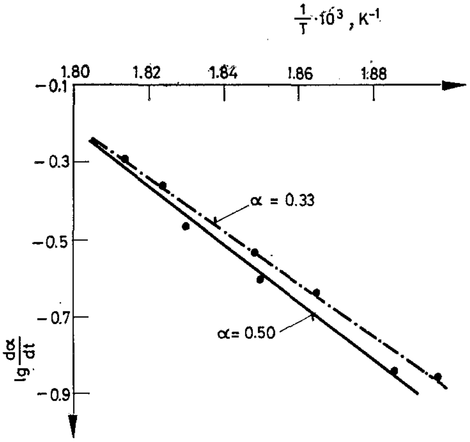

Fig. 8. Graphical representation of Eq. (10)

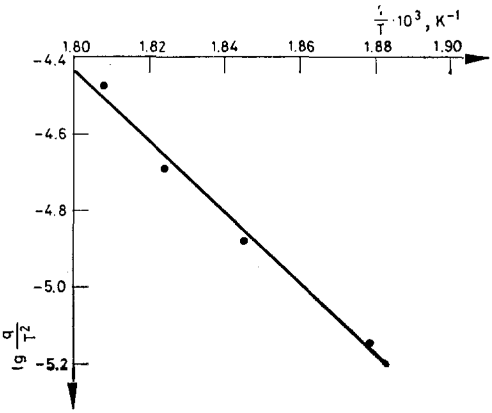

Fig. 9. Dependence of log (q/T^2) on 1/T according to Eq. (11)

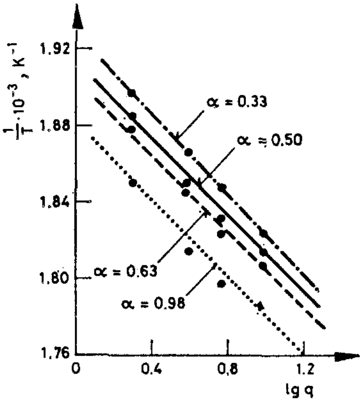

Fig. 10. Dependence of 1/T on log q according to Eqs (12) and (13)

T being defined as for Eq. [11]. Plots of $\log(q/T^2)$ against $1/T$ for four values of q are shown in Fig. 9. They gave $E = 42.0 \pm 2.8$ kcal · mole^{-1}

10. Figure 10 shows plots of $1/T$ against log q corresponding to the equations advocated by Berlin and Robinson [23] and Ozawa [24]:

$$\frac{1}{T} = -\frac{2.303\,R}{E}\log q + A \tag{12}$$

$$\text{where } A = \frac{2.303\,R}{E}\,[\log Z + n\log(1-\alpha) - \log \mathrm{d}\alpha/\mathrm{d}t]$$

$$\log q \cong \frac{0.4567E}{R}\cdot\frac{1}{T} \tag{13}$$

The slope leads to an E of about 42 kcal · mole^{-1}.

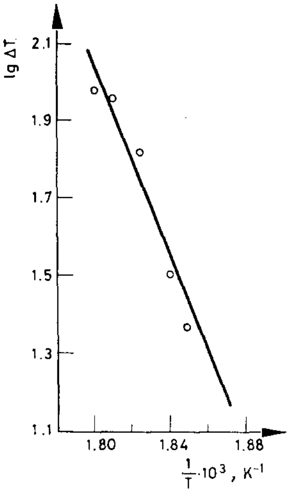

Fig. 11. Arrhenius plot for the method of Borchardt and Daniels [25]

11. For first-oder reactions in solution, Borchardt and Daniels [25] give the equation

$$k = \frac{\Delta T}{A - a} \tag{14}$$

where k is the reaction rate constant at the temperature T, ΔT is the height of the DTA peak at time t, A is the total area of the DTA peak and a is the area up to time t. The activation energy was obtained from a plot of $\log \frac{\Delta T}{A-a}$ against $1/T$ (shown in Fig. 11), assuming $n = 1$. The value of E obtained by this method was 78.8 ± 5.2 kcal · mole^{-1} and $\log Z = 30.27 \pm 0.07$.

12. Figure 12 shows a plot of $\dfrac{\Delta \log \left(\dfrac{\Delta T}{A}\right)}{\Delta \log \left(\dfrac{A}{(A-a)}\right)}$ against $\dfrac{\Delta \left(\dfrac{1}{T}\right)}{\Delta \log \left(\dfrac{A}{A-a}\right)}$. This is based on the equation of Fâtu [26]:

$$\frac{\Delta \log \left(\dfrac{\Delta T}{A}\right)}{\Delta \log \left(\dfrac{A}{A-a}\right)} = \frac{E}{2.303\,R} \cdot \frac{-\Delta \left(\dfrac{1}{T}\right)}{\Delta \log \left(\dfrac{A}{A-a}\right)} - n \tag{15}$$

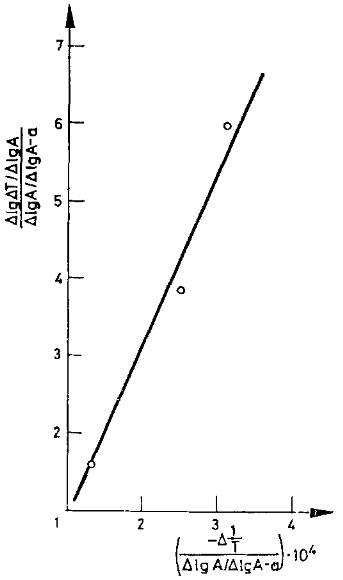

Fig. 12. Graphical representation of Eq. (15)

The kinetic constants obtained were $E = 101.8 \pm 53.2$ kcal · mole^{-1}, $\log Z = 40.21 \pm 20.39$ and $n = 1.53 \pm 1.60$ – a likely set of values.

13. The plot of $\log \Delta T$ versus $1/T$ presented in Fig. 13 was obtained using the equation recommended by Piloyan et al. [27]:

$$\log \Delta T \cong -\frac{E}{2.303\,R} \cdot \frac{1}{T} + C \tag{16}$$

where C is constant. It yields $E = 57.7 \pm 9.8$ kcal · mole^{-1}.

14. Kissinger's [28] equation relates the shift in the DTA peak temperature T_m to the heating rate:

$$\frac{d \log \left(\frac{q}{T_m^2}\right)}{d \left(\frac{1}{T_m}\right)} = - \frac{E}{2.303\,R} \tag{17}$$

The activation energy was obtained from a graph of log q/T_m^2 versus $1/T_m$ (Fig. 14). This method gave $E = 40.6 \pm 2.9$ kcal · mole^{-1} and $\log Z = 15.86 \pm 1.18$. The derived order of reaction [29] was 1.24 ± 0.03.

Some of the methods used to treat the experimental data for the dehydration of syngenite under dynamic conditions clearly do not give satisfactory results. This applies particularly to the methods which assume that the process can be described by Eq. [1], with the function $f(\alpha)$ taking the form $[1 - \alpha]^n$, where n is

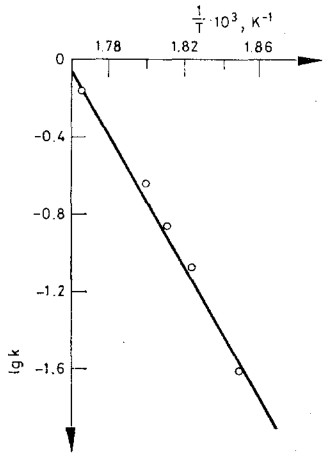

Fig. 13. Dependence of log ΔT on $1/T$ according to Eq. (16)

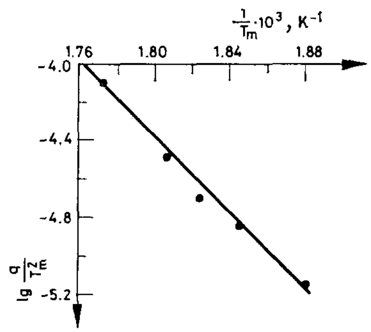

Fig. 14. Dependence of log (q/T_m^2) on $1/T$ according to Eq. (17)

the order of reaction. This assumption was made by Coats and Redfern [12], Horowitz and Metzger [14], Achar et al. [18], Freeman and Carroll [19] and Borchardt and Daniels [25]. It is known that for heterogeneous reactions the value of n cannot always be interpreted in simple physical terms. The second group of methods can be called "multi-curve" methods, because each of them uses several TG [17, 24], DTG [20–23] or DTA [28] curves obtained at different heating rates. The mechanism of reaction does not have to be assumed, but no nformation can be obtained as to the character of the euqation which might describe the process. The kinetic parameters obtained with the aid of these methods are mutually consistent. They lead to a mean value of the activation energy of about 40 kcal · mole^{-1}. The final choice of the kinetic equation and of the kinetic parameters which formed a self-consistent set and which could be reconciled with the results obtained under isothermal conditions [1] was made using the methods of Šatava and Škvára [16] and Zsakó [15]. Using the DTA curves, a similar value of the energy of activation can only be derived by employing the method of Piloyan et al. [27].

Conclusions

Results on the dehydration of syngenite under isothermal and non-isothermal conditions are comparable. It has been shown that the Avrami equation I,

$$[-\ln(1-\alpha)]^{1/2} = 3.46 \cdot 10^{21} \exp\left(-\frac{2.73 \cdot 10^4}{T}\right) t$$

describes the course of the reaction in a satisfactory manner with mean $E =$ $= 54$ kcal · mole^{-1} and $\log Z = 21.54$. This equation refers to the reaction taking place in air, under atmospheric pressure, in the temperature range 230–280°. It can be taken to indicate that the nucleation, and not the diffusion of water molecules or a reaction at the interphase boundary, is the rate determining step [7].

It has been demonstrated that in the investigation of reactions such as the thermal decomposition of solids, the integral graphical approach of Šatava and Škvára, applicable to TG results, is particularly advantageous in deriving the kinetic equation and the apparent kinetic parameters describing the process.

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RÉSUMÉ — Divers procédés de calcul appliqués aux courbes TG, TGD et ATD obtenues à l'aide d'un thermoanalyseur Mettler, avec une ou plusieurs vitesses de chauffage, conduisent à l'équation cinétique suivante pour exprimer le processus de déshydratation de la syngénite:

$$[-\ln(1-\alpha)]^{1/2} = 3.46 \cdot 10^{21} \exp\left(-\frac{2.73 \cdot 10^4}{T}\right) \cdot t$$

où α = degré de décomposition, T = température absolute, t = temps. La valeur moyenne de l'énergie d'activation est 54 kcal · mol^{-1}, en bon accord avec les résultats des études en conditions isothermes. La méthode de Šatava et Škvára, combinée avec les tables numériques de Zsakó, s'est révélée la plus efficace pour l'obtention de l'équations décrivant la cinétique de la décomposition thermique des corps solides.

ZUSAMMENFASSUNG — Mit verschiedenen Berechnungsmethoden wurde anhand der TG, DTG und DTA-Kurven, die bei einer und mehreren Aufheizgeschwindigkeiten der Probe im Thermoanalysator der Firma "Mettler" erhalten wurden bewiesen, daß die kinetische Gleichung zur Beschreibung des Dhydratisierungsprozesses des Syngenits folgende Gestalt hat:

$$[-\ln(1-\alpha)]^{1/2} = 3.46 \cdot 10^{21} \exp\left(-\frac{2.73 \cdot 10^4}{T}\right) \cdot t$$

(α-Zersetzungsgrad, T absolute Temperatur, t-Zeit) Der Mittelwert der Aktivierungsenergie beträgt: 54 kcal · mol^{-1}. Die Gleichung und die Werte der kinetischen Parameter stimmen gut mit den Ergebnissen der isothermen Experimente überein. Bei den Untersuchungen thermischer Reaktionen der Zersetzung von Festkörpern hat sich die Methode von Šatava und Škvára, ergänzt durch die numerische Tabelle von Zsakó als besonders geeignet erwiesen.

Резюме — С помощью термоанализатора фирмы «Меттлер» были измерены при одной какой-либо, а также при различных скоростях нагрева кривые ТГ, ДТГ и ДТА сингенита. Используя различные методы расчета, показано, что кинетика дегидратации сингенита может быть описана уравнением:

$$[-\ln(1-\alpha)]^{1/2} = 3.46 \cdot 10^{21} \exp -\left(\frac{2.73 \cdot 10^4}{T}\right) \cdot t$$

где α-степень превращения, T — абсолютная температура, t — время. Найдено, что среднее значение энергии активации равно 54 ккал.моль$^{-1}$. Как кинетическое уравнение, так и значение энергии активации хорошо согласуются с результатми изотермических данных. Установлено, что при исследовании реакций термического разложения твердых тел, наиболее удовлетворительные результаты могут быть получены применяя предложенные Жако значения-log $p(x)$ к методу Шатавы и Шквары.