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

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A study of the kinetics of the thermal dehydration of syngenite was carried out using the isothermal gravimetric method. Weight changes of the samples were followed by means of a Mettler Thermoanalyzer. The applicability of nine equations commonly used to describe the thermal decomposition of solids was investigated. The experimental results can be best represented, over the whole temperature range of the change, by the Avrami equation I

$$[-\ln(1-\alpha)]^{1/2} = Kt$$

where α = degree of decomposition, t = time, and K = rate constant. The activation energy deduced for the process is 51.8 ± 3.7 kcal · mole^{-1} and the log of the pre-exponential factor is 20.5 ± 0.1.

Our interest in the thermal decomposition of $K_2Ca(SO_4)_2 \cdot H_2O$ arose from the fact that in recent years work began in our country on the possibility of developing a suitable process for producing, on a commercial scale, mineral fertilizers from naturally-occurring polyhalite, $K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$. Syngenite is an intermediate in one of the possible methods of processing polyhalite, proposed by Conley and Partridge [1].

In the past twenty years two methods of thermal analysis, thermogravimetry (TG) and differential thermal analysis (DTA), have been extensively used to study the kinetics of reactions in the solid state (e.g. thermal dissociation).

Thermogravimetric analysis is used for measurements both under isothermal and under dynamic conditions. Isothermal methods have so far been preferred because it is commonly assumed that at constant temperature the shape of the curve representing the degree of decomposition as a function of time depends only on the mechanism of reaction. Under dynamic conditions it may depend on numerous physico-chemical factors and on the experimental conditions — attention has been drawn to this fact in a number of monographs [2—7] and in other publications. Of late, the popularity of combining isothermal and dynamic methods, or even using dynamic methods only, has been steadily growing.

In the present paper results on the kinetics of dehydration of syngenite under isothermal conditions are presented. The change of weight was followed as a function of time. Small samples were used, which made it possible to eliminate from consideration the factors of the rate of heat supply and of the rate of diffusion of the gaseous product away from the sample [8]. The results of parallel investigations carried out under dynamic conditions are being prepared for publication.

Experimental

Equipment and methods of measurement

Thermal analysis of syngenite was performed in the presence of static air, under isothermal conditions in the temperature range 230–280°. A Mettler Thermoanalyzer was used [9]. Temperatures were measured with Pt/Pt-Rh thermocouples. Around 20 mg samples of material were used; these were placed in a 0.1 cm^3 crucible (Pt Rh 10%). Simultaneous TG-DTG-DTA curves of $K_2Ca(SO_4)_2 \cdot H_2O$ are shown in Fig. 1.

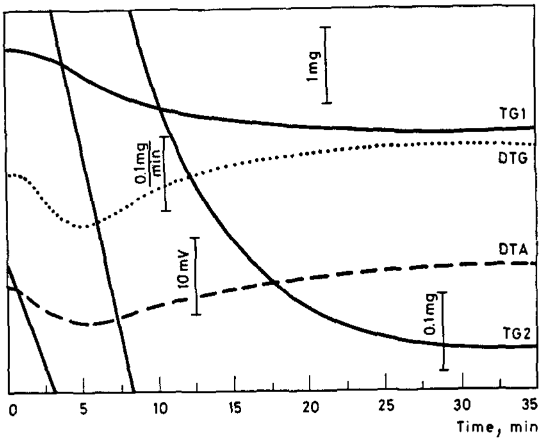

Fig. 1. Simultaneous TG–DTG–DTA curves for the dehydration of syngenite at 260 °

X-ray diffraction analysis was carried out with a TUR-M-61 apparatus.

Infrared spectra in the 3800–400 cm^{-1} range were recorded on a Zeiss UR-20 spectrophotometer using pellets in KBr.

Material used in the experiments

The syngenite $K_2Ca(SO_4)_2 \cdot H_2O$ was synthetized at 25°. It was crystallized, over 20 hours, from aqueous solutions of potassium (14 moles) and calcium (10 moles) sulphates per 1000 moles H_2O.

The precipitate was dried at 110° [10]. It was a finely-divided crystalline substance. The colourless crystals had the shape of elongated prisms with the ratio of length to width of 7 – 14 (this could be seen under 300x magnification) [11]. The results of chemical analysis were satisfactory. The *d*-spacing in the crystals (as obtained by X-ray diffraction) was, within experimental error, in agreement with the literature values for both the natural product [12] and the synthetized syngenite [13]. The IR spectrum was in agreement with literature data as to both the shape of the peaks and their wavenumbers [13, 14].

Results and discussion

Figure 2 shows curves illustrating the dependence of the degree of dehydration of syngenite, α, on time t, for six selected temperatures. The shape of these curves is typical for a solid-decomposition reaction. In order to determine the kinetic parameters, the relationship

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

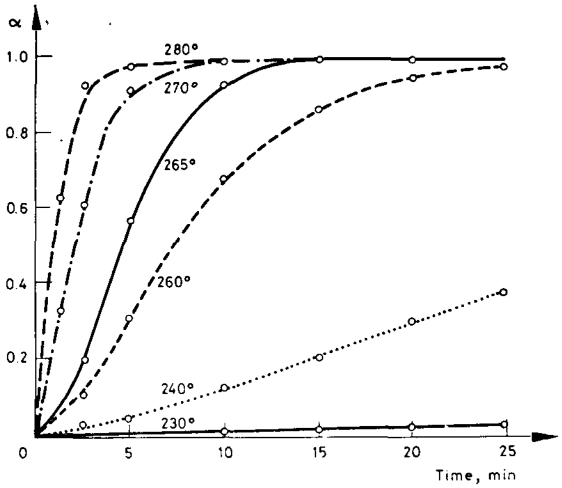

Fig. 2. The degree of the decomposition (α) *vs.* time (t) for the dehydration of syngenite in the temperature range 230—280 °

was used, where $f(\alpha)$ is a function of the mass loss. The form of $f(\alpha)$ depends on the mechanism of the reaction and $k(T)$ is the reaction rate constant. The dependence of $k(T)$ on temperature is described by the Arrhenius equation

$$k = Z \exp\left(-\frac{E}{RT}\right) \tag{2}$$

where E is the activation energy and Z the preexponential factor. R and T have their usual meanings.

After integration Eq. 1 takes the form

$$g(\alpha) = Kt \tag{3}$$

For a correctly-selected function $f(\alpha)$, a plot of $g(\alpha)$ against time should be a straight line. From its slope it should be possible to obtain the value of the rate constant at that temperature. The values of E and Z should be obtainable from an Arrhenius plot.

Table 1 shows the equations most frequently used in the literature to describe the kinetics of reactions in which one of the reactants is a solid. These equations assume various hypothetical rate-determining kinetics of dehydration of syngenite, $K_2Ca(SO_4)_2 \cdot H_2O$.

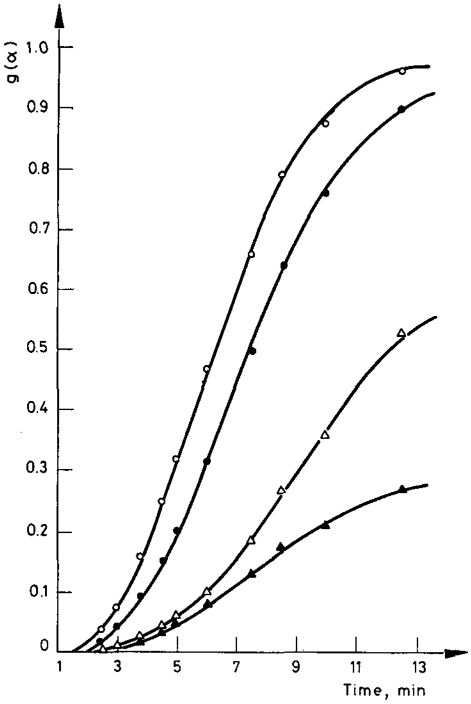

Fig. 3. Dependence of $g(\alpha)$ on time at 265° for equations $D_1 - D_4$ (see Table 1) D_1 ○, D_2 ●, D_3 △, D_4 ▲

The values of $g(\alpha)$ as a function of α were calculated with the help of the numerical data given by Sharp et al. [18]. Graphical analysis of all the nine equations demonstrated that the present experimental results (at 265°) can best be described by equation A_2 (Figs 3 and 4).

Figure 5 shows the time-dependence of the function A_2 in the range of temperatures where the dehydration of syngenite takes place. From the slopes of the plots the rate constants k have been obtained. They take the values: 0.0076, 0.0460, 0.1530, 0.3012 and 0.4942 min^{-1} at 230, 240, 260, 265 and 270°, respectively.

Table 1

Kinetic equation

Function $g(\alpha)$	Equation	Rate controlling process
D_1	$\alpha^2 = Kt$	Diffusion
D_2	$(1-\alpha)\ln(1-\alpha)+\alpha = Kt$	
D_3	$[1-(1-\alpha)^{1/3}]^2 = Kt$	
D_4	$(1-2/3\alpha)-(1-\alpha)^{2/3} = Kt$	
F_1	$-\ln(1-\alpha) = Kt$	Random nucleation
A_2	$[-\ln(1-\alpha)]^{1/2} = Kt$	Random nucleation Avrami equation I
A_3	$[-\ln(1-\alpha)]^{1/3} = Kt$	Random nucleation Avrami equation II
R_2	$1-(1-\alpha)^{1/2} = Kt$	Phase boundary reaction
R_3	$1-(1-\alpha)^{1/3} = Kt$	Phase boundary reaction

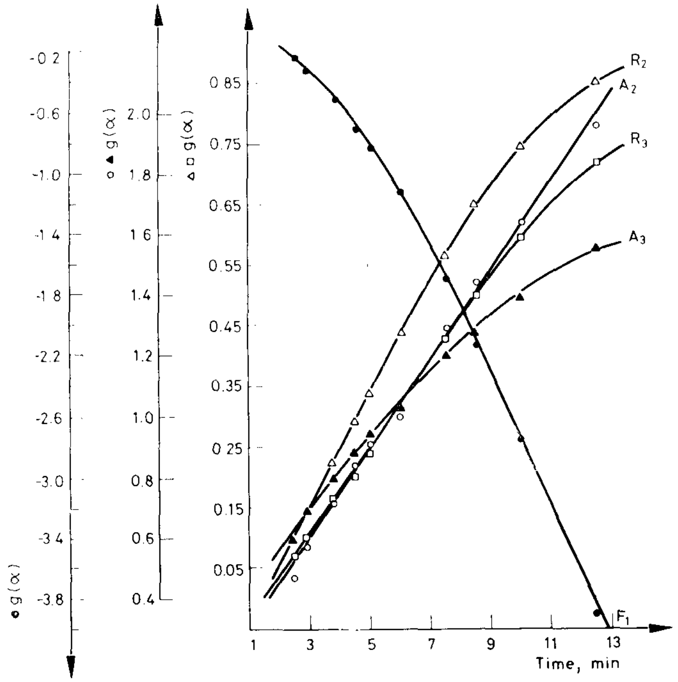

Fig. 4. Dependence of $g(\alpha)$ on time at 265 ° for equations F_1, R_2, R_3, A_2 and A_3 (see Table 1)

The activation energy obtained from the Arrhenius plot in Fig. 6 is 51.8 ± 3.7 kcal.mole^{-1} and log Z is 20.5 ± 0.1.

All straight lines in this Figure were plotted using the least squares method. The corresponding correlation coefficients were high. Appreciable deviations were

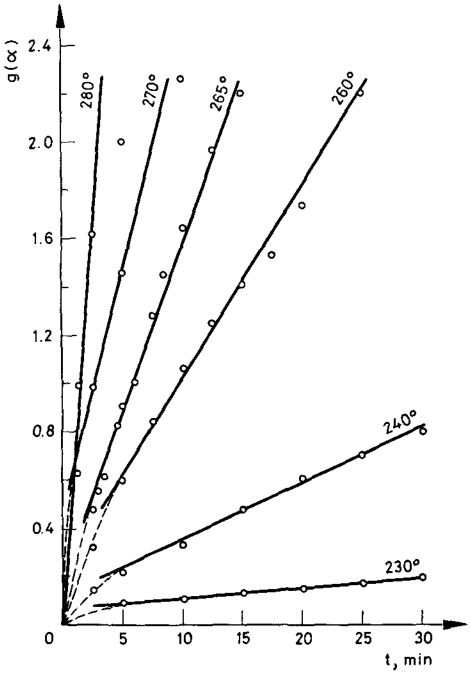

Fig. 5. Dependence of $[-\ln(1-\alpha)]^{1/2}$ on time in the temperature range 230−280°

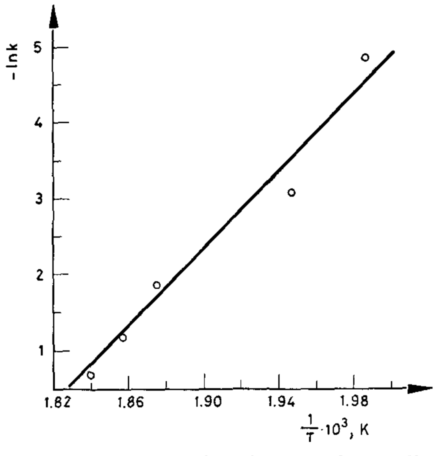

Fig. 6. Arrhenius plot for the dehydration of $K_2Ca(SO_4)_2 \cdot H_2O$

observed only for very low α and α close to one, where measurements are least accurate.

The fact that a good straight line is obtained over a large range of values of α indicates that the reaction has a single mechanism corresponding to the Avrami equation I (see Table 1).

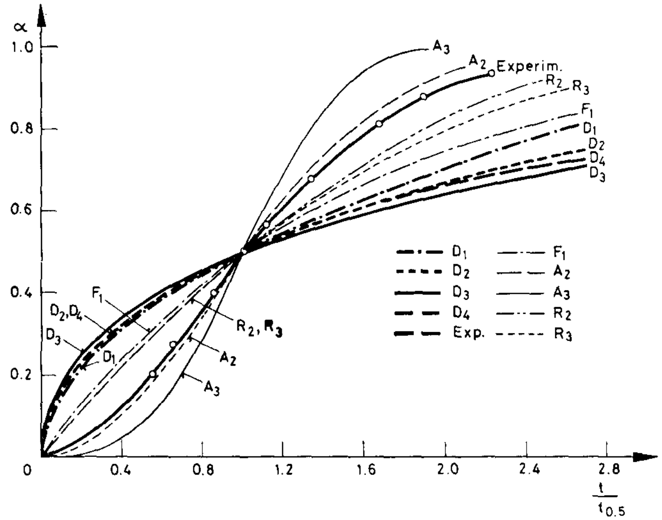

Fig. 7. Dependence of the degree of decomposition (α) on time ($t/t_{0.5}$) calculated for nine equations for solid state reaction (see Table 1) and the experimental curve for the dehydration of $K_2Ca(SO_4)_2 \cdot H_2O$

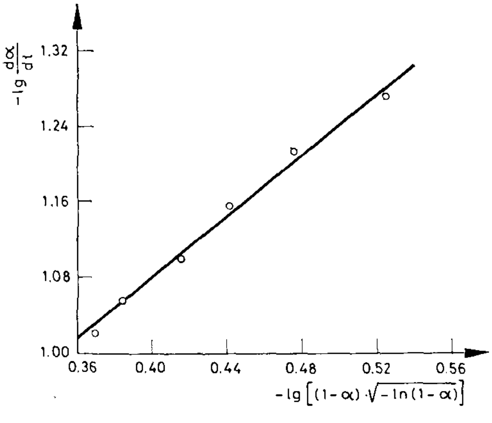

Fig. 8. Dependence of [$-\log d\alpha/dt$] on [$-\log f(\alpha)$] for function A_2 following Eq. (5) for the dehydration of syngenite at 260 °

Kinetic equation were also tested using the half-life of the reaction. Equation (3) can be written in the form

$$g(\alpha) = K'\left(\frac{t}{t_{0.5}}\right) \qquad (4)$$

where $t_{0.5}$ is the time for half-transformation and K' is a calculated constant dependent on the form of $g(\alpha)$. The experimental values of α have been plotted as a function of $t/t_{0.5}$ in Fig. 7.

The plot can be compared with the curves corresponding to the equations in Table 1. The curves were plotted with the help of the data given by Sharp et al. [18]. It can be seen that best agreement is obtained, as with the previous method, for function A_2.

The conclusions as to the applicability of equation A_2 were confirmed using the DTG curve. Equation (1) can be written in the logarithmic form

$$\log\frac{d\alpha}{dt} = \log k + \log f(\alpha)\,. \qquad (5)$$

A plot of log $d\alpha/dt$ against $\log f(\alpha)$ for function A_2 is, as expected, a straight line (Fig. 8.).

Conclusions

1. Thermal dehydration of syngenite in a static atmosphere of air occurs in the temperature range 230–280° and can be adequately described over the entire decomposition range by the Avrami equation I. This equation was selected using three different graphical approaches: integral, half-transformation and differential.
2. The activation energy E for the dehydration is 51.8 ± 3.7 kcal.mole^{-1} and log Z is 20.5 ± 0.1.
3. This paper demonstrates the usefulness of isothermal methods for determining the kinetic parameters; they are relatively simple and easy to interpret. The experimental work is, however, extremely time-consuming.

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RÉSUMÉ — On présente les résultats d'une étude cinétique de la déshydratation de la syngénite, effectuée en isotherme à l'aide du thermoanalyseur Mettler. On a testé neuf équations généralement appliquées pour décrire la cinétique de la décomposition thermique des solides. L'équation d'Avrami I:

$$[-\ln(1-\alpha)]^{1/2} = Kt$$

où α est le taux de transformation, t le temps, K la constante de vitesse, permet de rendre compte des résultats expérimentaux. La valeur de l'énergie d'activation E du processus est égale à 51.8 ± 3.7 kcal.mol^{-1} et celle du logarithme du facteur préexponentiel Z est de 20.5 ± 0.1.

ZUSAMMENFASSUNG — Eine Untersuchung der Kinetik der thermischen Entwässerung von Syngenit wurde unter Anwendung der isothermen gravimetrischen Methode durchgeführt. Der Gewichtsverlust der Proben wurde mit einem Mettler Thermoanalyser verfolgt. Die Anwendbarkeit von 9 für die thermische Zersetzung von Festkörpern gebräuchlichen Gleichungen wurde untersucht. Die experimentellen Ergebnisse können am besten über den gesamten Temperaturbereich der Änderung durch die Avrami-Gleichugn beschrieben werden

$$[-\ln(1-\alpha)]^{1/2} = Kt$$

mit α = Zersetzungsgrad, t = Zeit und K = Geschwindigkeitskonstante. Die für diesen Prozess abgeleitete Aktivierungsenergie E betrug 51.8 ± 3.7 (kcal·mol^{-1}) und der Logarithmus des Präexponentialfaktors Z 20.5 ± 0.1.

Резюме — Представлены результаты кинетических исследований дегидратации сингенита используя изометрические определение потери веса с помощью Термоанализатора фирмы “Меттлер”. Рассуждалось девять общих уравнений кинетики термического разложения твердых тел. Экспериментальные результаты во всей области степени превращения (α) описывает наилучшим образом уравнение Аврами I:

$$[-\ln(1-\alpha)]^{1/2}\,Kt$$

где: α — степень превращении, t — время, K — константа скорости реакции. Определены энергия активации этого процесса и лог предэкспоненциального фактора, которые, соответственно, равны 51.8 ± 3.7 ккал. моль$^{-1}$ и 20.5 ± 0.1.