

KINETICS OF THERMAL DEHYDRATION OF $\text{Ce}_2(\text{SO}_4)_2 \cdot n(\text{H}, \text{D})_2\text{O}$ ($n = 5, 8, 9$)

F. Martin, A. Gonzalez, J. Jimenez, J. Largo and J. A. De Saja*

LABORATORIO DE FISICA DEL ESTADO SOLIDO, FACULTAD DE CIENCIAS,
UNIVERSIDAD DE VALLADOLID, VALLADOLID, SPAIN

* DEPARTAMENTO DE TERMOLOGIA, COLEGIO UNIVERSITARIO DE ALAVA,
VITORIA, SPAIN

(Received October 17, 1983)

The thermal dehydration of $\text{Ce}_2(\text{SO}_4)_3 \cdot 5 \text{H}_2\text{O}$, $\text{Ce}_2(\text{SO}_4)_3 \cdot 8 \text{H}_2\text{O}$, $\text{Ce}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$ and their isomorphous deuterated compounds was studied by means of thermogravimetric measurements. A kinetic analysis of the TG curves obtained was carried out by computer. The thermal stability, Arrhenius parameters and mechanism of dehydration were investigated.

The thermal dehydration of hydrated rare-earth sulphates has been studied by a great number of authors [1-5], but in the case of cerium(III) series these investigations remain incomplete. The purpose of this paper is to present an analysis of the kinetic and microscopic mechanism associated with the dehydration stages of these latter compounds.

In these series of sulphates the only well defined crystalline salts are $\text{Ce}_2(\text{SO}_4)_3 \cdot 5 \text{H}_2\text{O}$, $\text{Ce}_2(\text{SO}_4)_3 \cdot 8 \text{H}_2\text{O}$ and $\text{Ce}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$. Our laboratory has long experience on their preparation and characterization, which has drawn our interest to the study of their thermal dehydration as a complementary part of a broader investigation related to the structural role of the water molecules in the stability and macroscopic properties of these crystals [6-11].

Experimental

Preparation of samples

Anhydrous cerium sulphate was obtained by dehydrating the hydrated compound, which was prepared by dissolving cerium oxide in dilute HCl and adding an equivalent amount of 0.1 N H_2SO_4 in order to yield a quantitative amount of sulphate; the resultant solute was precipitated by adding ethyl alcohol in excess. The crystals were filtered off, washed with water/alcohol and finally purified by successive recrystallizations.

Powdered samples of anhydrous cerium sulphate were obtained by dehydrating the above crystals under vacuum at 380°C. The hydrated crystals were prepared by dissolving the anhydrous salt in H₂O or D₂O, in conditions established in earlier investigations by this laboratory [6, 7, 8]. Elemental analysis of the hydrates agrees with theoretical chemical composition to better than 1 percent.

Thermal analysis

Kinetics of the thermal dehydration of the hydrated cerium(III) sulphates were studied by recording thermogravimetric measurements in a stream of nitrogen gas, using a commercial Perkin-Elmer TG-2 analyzer. The investigations were carried out at temperatures in the range from ambient temperature to 400° at a constant heating rate of 5 degree/min. No more than 10 mg samples of crystals, carefully ground with pestle and mortar, were used in each run.

Analytical method

Thermal dehydration reactions of solids are heterogeneous and topochemical processes, involving a solid → solid + gas transformation. The rate of this reaction usually follows the law expressed as

$$\frac{d\alpha}{dt} = Z \exp\left(-\frac{E}{RT}\right) f(\alpha)$$

and for non-isothermal process, changing the variables from time to temperature

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

where α is the fraction of solid reactant decomposed at time t (degree of conversion), Z and E are Arrhenius parameters, and the function $f(\alpha)$ reflects the nature of the kinetic mechanism and topochemistry of the reaction [12] at specified standard experimental conditions. These functions are based on the geometrical description of heterogeneous processes regardless of the physical hypothesis.

Obviously, the kinetic mechanism and their parameters will be performed by means of Eq. (1), in order to it, many methods of analyzing experimental data have been proposed. We will use two of these methods; one of them is an integral method described by Satava [13], the other is a differential method that is complementary to Satava's method, in the sense that it permits us to avoid the deficiencies arising from the integral method.

When the temperature of the sample increases at constant rate β , which constitutes a very useful experimental simplification, Eq. (1) can be integrated and becomes

$$\ln g(\alpha) - \ln p\left(\frac{E}{RT}\right) = \ln \frac{ZE}{R\beta} \quad (2)$$

in which $g(\alpha)$ is a functional form of α and $p(x) = \int x^{-2} \exp(-x) dx$ (where $x = E/RT$). Both $\ln g(\alpha)$ and $\ln p(x)$ functions are, as first approximation, linear functions of $1/T$, while the r. h. s. value of the Eq. (2) is independent of temperature. Ten algebraic expressions for the functions $f(\alpha)$ or $g(\alpha)$, corresponding to the kinetic mechanism more commonly used in the literature, were considered by us [12]. A plot of $\ln g(\alpha)$ versus $1/T$ for each $g(\alpha)$ function, calculated from the TG curves, allows us to find the most probable mechanism, which corresponds to the linear plot.

From the experimental data one can obtain the correct function $f(\alpha)$ to fit $\ln g(\alpha)$ to a straight line, and by operating on Eq. (2), one can obtain the kinetics parameters E and Z , which determine the kinetic mechanism.

This method presents some difficulties as the mathematical analysis sometimes leads to the same correlation factor for several different kinetic mechanisms $f(\alpha)$. In order to avoid this ambiguity we have used a differential method that is a useful tool when selecting an appropriate kinetic mechanism from the various possibilities considered when using Satava's method.

This differential method basically consists in rearranging Eq. (1) after transforming it to a logarithmic form, the new equation being the following

$$\ln \frac{\frac{d\alpha}{dT}}{f(\alpha)} = \ln \frac{Z}{\beta} - \frac{E}{R} \frac{1}{T} \quad (3)$$

This equation is then fitted to a straight line by the least squares method in order to obtain the most appropriate $f(\alpha)$ function. The kinetic parameters, E and Z can then be recalculated from Eq. (3).

Results

The experimental results corresponding to the dehydration of cerium(III) sulphate compounds are presented in Fig. 1 and Fig. 2, where n is the number of dehydration water molecules lost per molecular unity of the hydrated compound.

As can be seen from these curves, the dehydration involves several distinct steps that overlap, which makes the interpretation of the curves difficult. In order to solve this problem it is necessary to make the hypothesis that the superposition of the steps does not correspond to a strong interaction between the dehydration mechanism involved in each TG step. Raman and crystallographic results [6–11] were used as complementary data, which evidenced that there are water molecules with equivalent structural and dynamic behaviour; within this framework these molecules must be lost in the same dehydration step. This assumption allowed us to estimate the α -value corresponding to each dehydration step.

The numerical data obtained using the above hypothesis are summarized in Table 1. It is seen that the coherence of the results obtained for each step justifies our previous

hypothesis that there are no strong interactions between consecutive dehydration steps.

The activation energy of the process increases with the number of water molecules of hydration that the salts contain; thus, the greatest activation energies are obtained with the $\text{Ce}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$ sample. On the other hand the activation energies of the deuterated crystals are greater than those of the hydrated crystal; this result is in agreement with results obtained for the last compound using TSDC measurements (Thermally Stimulated Depolarization Currents [11]), whereby it is observed that bonding by deuterium atoms corresponds to higher energy than bonding by hydrogen atoms. It is also observed that the activation energies for the second and third steps are smaller than those for the first step.

The kinetic mechanisms of the dehydration process for the hydrated and deuterated Ce(III) sulphate series are also described in Table 1.

For the three hydrated salts, as well as for the three deuterated salts, the kinetic mechanism involved in the first dehydration step obeys the well known three-dimensional diffusion equation proposed by Jander [14], which corresponds to an interface motion described by a parabolic law and expressed by

$$g(\alpha) = [1 - (1 - \alpha)^{1/3}]^2 \quad (4)$$

For the other steps, the kinetic of dehydration can be described by a three-dimensional diffusion mechanism obeying the Ginstling equation [15], which does not

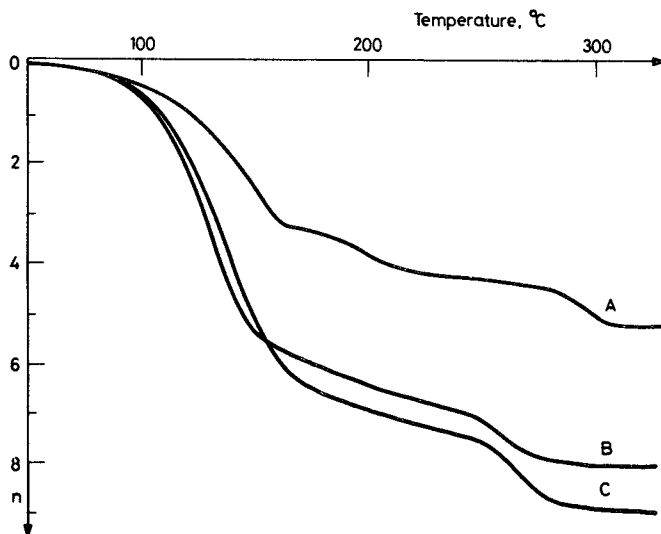


Fig. 1 Plot of n (number of water molecules lost per molecular unity of hydrated compounds) vs. T for the dehydration of: (A) $\text{Ce}_2(\text{SO}_4)_3 \cdot 5 \text{H}_2\text{O}$, (B) $\text{Ce}_2(\text{SO}_4)_3 \cdot 8 \text{H}_2\text{O}$, (C) $\text{Ce}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$

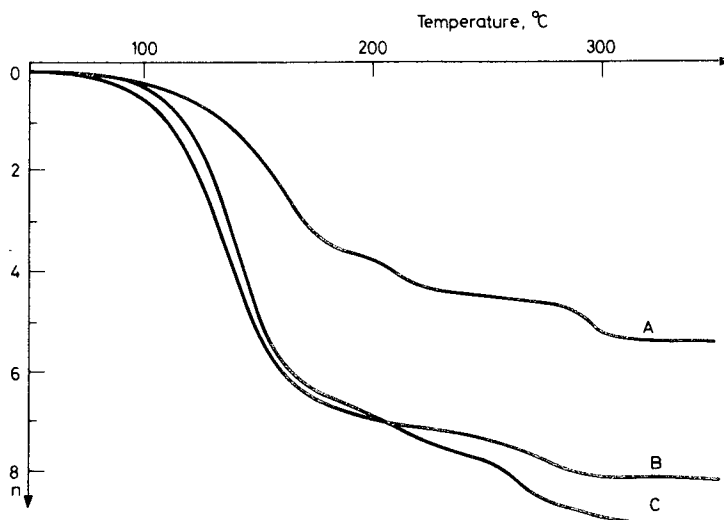


Fig. 2 Plot of n vs. T for the dehydration of: (A) $\text{Ce}_2(\text{SO}_4)_3 \cdot 5 \text{D}_2\text{O}$, (B) $\text{Ce}_2(\text{SO}_4)_3 \cdot 8 \text{D}_2\text{O}$, (C) $\text{Ce}_2(\text{SO}_4)_3 \cdot 9 \text{D}_2\text{O}$

correspond to a parabolic law, but rather to an equation that associates the increase of the product layer thickness (condensed water in our case) with the decrease in surface area of the interface. The Ginstling equation is expressed by

$$g(\alpha) = 1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3} \quad (5)$$

These two mechanisms, obtained from the experimental data, appear to be in agreement with the qualitative characteristics of the experimental curves. In fact the first mechanism (Jander) describes a free motion of the interface, while the second mechanism (Ginstling) implies a motion of the interface, which is dependent on the decrease of the interfacial area caused by the transformation of the crystal in the first dehydration step, and the consequent reduction in the free space of the system after this dehydration step has been accomplished.

Table 1 Kinetic mechanism and Arrhenius parameters of the hydrated and deuterated Ce(III) sulphate series

<i>First Step</i>					
	Kinetic	$T_i, ^\circ\text{C}$	$T_f, ^\circ\text{C}$	Parameters Arrhenius*	Number of water molecules
$\text{Ce}_2(\text{SO}_4)_3 \cdot 5 \text{H}_2\text{O}$	Eq. Jander	57	184	$E = 107.1$ $Z = 1.02 \text{ E}10$	3
$\text{Ce}_2(\text{SO}_4)_3 \cdot 5 \text{D}_2\text{O}$	Eq. Jander	60	192	$E = 113.5$ $Z = 2.82 \text{ E}10$	3
$\text{Ce}_2(\text{SO}_4)_3 \cdot 8 \text{H}_2\text{O}$	Eq. Jander	59	199	$E = 120.4$ $Z = 1.89 \text{ E}11$	6
$\text{Ce}_2(\text{SO}_4)_3 \cdot 8 \text{D}_2\text{O}$	Eq. Jander	58	174	$E = 127.5$ $Z = 5.81 \text{ E}12$	6
$\text{Ce}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$	Eq. Jander	61	175	$E = 134.7$ $Z = 6.10 \text{ E}13$	6
$\text{Ce}_2(\text{SO}_4)_3 \cdot 9 \text{D}_2\text{O}$	Eq. Jander	55	179	$E = 140.4$ $Z = 1.70 \text{ E}14$	6
<i>Second Step</i>					
	Kinetic	$T_i, ^\circ\text{C}$	$T_f, ^\circ\text{C}$	Parameters Arrhenius*	Number of water molecules
$\text{Ce}_2(\text{SO}_4)_3 \cdot 5 \text{H}_2\text{O}$	Eq. Ginstling	184	264	$E = 26.7$ $Z = 9.89 \text{ E}-2$	1
$\text{Ce}_2(\text{SO}_4)_3 \cdot 5 \text{D}_2\text{O}$	Eq. Ginstling	192	262	$E = 23.2$ $Z = 8.28 \text{ E}-2$	1
$\text{Ce}_2(\text{SO}_4)_3 \cdot 8 \text{H}_2\text{O}$	Eq. Ginstling	199	298	$E = 24.3$ $Z = 8.4 \text{ E}-2$	2
$\text{Ce}_2(\text{SO}_4)_3 \cdot 8 \text{D}_2\text{O}$	Eq. Ginstling	174	308	$E = 24.9$ $Z = 8.37 \text{ E}-2$	2
$\text{Ce}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$	Eq. Ginstling	175	301	$E = 2.51$ $Z = 1.85 \text{ E}-6$	3
$\text{Ce}_2(\text{SO}_4)_3 \cdot 9 \text{D}_2\text{O}$	Eq. Ginstling	179	338	$E = 2.37$ $Z = 1.33 \text{ E}-6$	3
<i>Third Step</i>					
	Kinetic	$T_i, ^\circ\text{C}$	$T_f, ^\circ\text{C}$	Parameters Arrhenius*	Number of water molecules
$\text{Ce}_2(\text{SO}_4)_3 \cdot 5 \text{H}_2\text{O}$	Eq. Ginstling	264	329	$E = 24.0$ $Z = 8.43 \text{ E}-2$	1
$\text{Ce}_2(\text{SO}_4)_3 \cdot 5 \text{D}_2\text{O}$	Eq. Ginstling	262	318	$E = 24.6$ $Z = 8.58 \text{ E}-2$	1

* E in kJ/mol and Z in s^{-1} .

References

- 1 G. R. Hall and T. L. Markin, *J. Inorg. Nucl. Chem.*, 4 (1957) 137.
- 2 F. H. Spedding and S. Jaffe, *J. Amer. Chem. Soc.*, 76 (1954) 882.
- 3 L. A. Alekseenko, A. F. Lemenkova and V. V. Serebrennikov, *Zh. Neorgan. Khim.*, 4 (1959) 1382.
- 4 W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, 7 (1958) 51.
- 5 W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, 19 (1961) 245.
- 6 A. De Saja, J. M. Pastor, F. Rull and J. A. De Saja, *Kristall u. Technik*, 13 (1978) 909.
- 7 A. De Saja, F. Rull, J. M. Pastor and J. A. De Saja, *Crystal Res. and Technol.*, 16 (1981) 3.
- 8 A. De Saja, J. M. Pastor, E. Hernandez, F. Rull and J. A. De Saja, *Crystal Res. and Technol.*, 16 (1981) 1389.
- 9 A. Torres, F. Rull and J. A. De Saja, *Spectrochim. Acta*, 36A (1980) 425.
- 10 F. Rull, U. Luu Dang and J. A. De Saja, *Spectrochim. Acta*, 38A (1982) 529.
- 11 A. Torres, J. Jimenez, V. Carbayo and J. A. De Saja, *Phys. Status Solidi*, 78 (1983) 671.
- 12 J. Sesták and G. Berggren, *Thermochim. Acta*, 3 (1971) 1.
- 13 V. Savata, *Thermochim. Acta*, 2 (1971) 423.
- 14 W. Jander, *Z. Anorg. Allgem. Chem.*, 163 (1927) 1.
- 15 A. M. Ginstling and B. I. Brounshtein, *Zh. Prikl. Khim.* 23 (1950) 1249.

Zusammenfassung – Die thermische Dehydratisierung von $\text{Ce}_2(\text{SO}_4)_3 \cdot 5 \text{H}_2\text{O}$, $\text{Ce}_2(\text{SO}_4)_3 \cdot 8 \text{H}_2\text{O}$ und $\text{Ce}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$ und die entsprechenden deuterierten Verbindungen wurden thermogravimetrisch untersucht. Die kinetische Analyse der erhaltenen TG-Kurven wurde mittels eines Computers ausgeführt. Die thermische Stabilität, die Arrhenius-Parameter und der Mechanismus der Dehydratisierung wurden untersucht.

Резюме – Методом ТГ изучена термическая дегидратация соединений $\text{Ce}_2(\text{SO}_4)_3 \cdot 5 \text{H}_2\text{O}$, $\text{Ce}_2(\text{SO}_4)_3 \cdot 8 \text{H}_2\text{O}$, $\text{Ce}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$ и их соответствующих дейтеропроизводных. Кинетический анализ полученных кривых ТГ был проведен с помощью ЭВМ. Были исследованы термостойчивость, аррениусовские параметры и механизм реакции дегидратации.