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THERMAL BEHAVIOR OF DOUBLE SALT SCHOENITE

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Abstract

The thermal behavior of synthetic schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$) during heating has been studied by thermal methods. The temperatures of dehydration and decomposition of schoenite have also been determined by DTA, TG and DSC. The thermal reaction equations and the X-ray powder diffraction results of the products have been given and the corresponding kinetic parameters have also been obtained.

Keywords: kinetic, schoenite, thermal behavior, thermoanalysis

Introduction

Emons *et al.* 91 [1, 2] reviewed in detail the studies of thermoanalysis of carnallite, $MCl \cdot MgCl_2 \cdot 6H_2O$ ($M=NH_4$, Rb, Cs) including a few papers on the thermal analysis of kainite and leonite.

Chiudharl *et al.* [3] reported the X-ray diffraction and thermal behavior of kainite, and a brief description of the thermal behavior of schoenite at high-temperature was also given in the same paper. In this paper, the thermal behavior of synthesized schoenite has been studied in detail by DSC, and the thermal reaction kinetic parameters in different stages of non isothermal dehydration have been obtained.

The synthesis of schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$)

Point *E* according to the composition of K_2SO_4 14%, $MgSO_4$, 18%, H_2O 63%) was selected from the K_2SO_4–$MgSO_4$–H_2O ternary-system phase diagram at 25 and 75°C (Fig. 1). Given amounts of K_2SO_4 and $MgSO_4 \cdot 7H_2O$ reagents were dissolved completely in a calculated amount of water at 75°C. When the temperature dropped naturally to room temperature, the schoenite crystals would be crystallized, and then separated, and washed with 1:1 alcohol–acetone solution, and dried in air. The X-ray diffraction and IR-spectrograph (Fig. 2) of the schoenite sample were the same as those in literature. The chemical analysis of the sample (Table 1) was: K_2SO_4:$MgSO_4$:$6H_2O$ = 0.99:1:6.01. It was thus

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shown that the synthesized schoenite was of good quality for thermal analytical study.

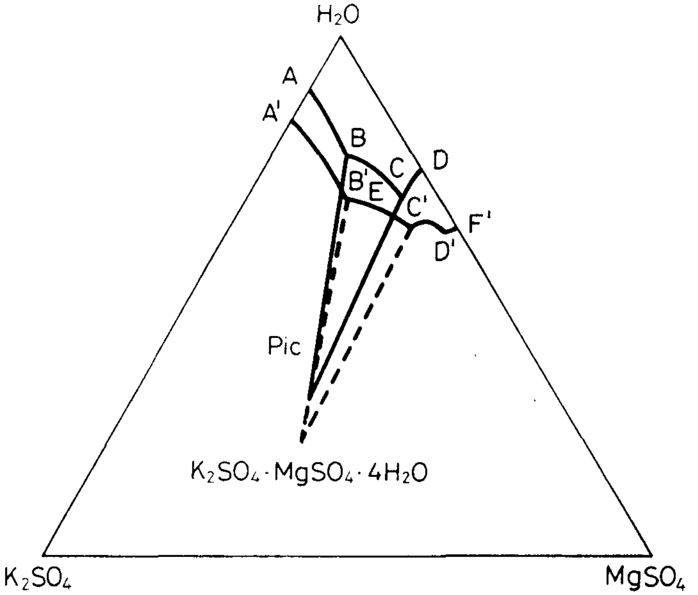

Fig. 1 The phase diagraphy of $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$

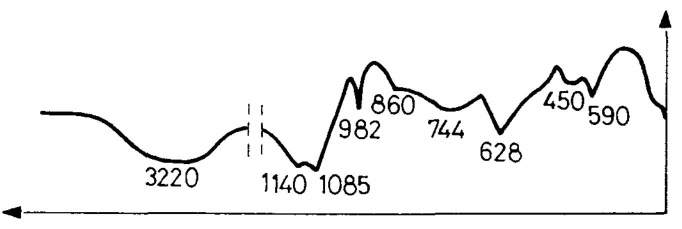

Fig. 2 The IR diagraphy of synthetical schoenite

Table 1 The analytical results of synthesized schoenite

Sample	Chemical analytical results /weight %						Molar ratio
	K^+	Mg^{2+}	SO_4^{2-}	K_2SO_4	$MgSO_4$	H_2O	K_2SO_4:$MgSO_4$:H_2O
Schoenite (S_1)	19.23	6.06	47.06	42.41	30.02	27.57	0.99:1:6.14
Schoenite (S_2)	19.31	6.10	47.20	43.03	30.21	26.76	0.98:1:5.92

Thermal behavior of schoenite

TG curve of schoenite was recorded by Setaram Tgrt A92 thermal analytical instrument, made in France. The weight of the sample was 68.85 mg and heating rate was 2 deg·min^{-1}, the gas flow rate of N_2 was 60 ml/min. DSC was also recorded by DSC-111, also made in France. The weight of schoenite sample was 58.10 mg, the flow rate of N_2 and the heating rate were the same as above.

TG

There are three stages of dehydration on the TG curve (Fig. 3): The first stage is from 23.4 to 129.4°C and the loss of weight is 9.34%, the second stage is from 129.4 to 181.4°C, the loss is 10.02% and the third stage is from 181.4 to 346.9°C and the loss is 8.76%. Each stage corresponds to a loss of two molecules of water (the theoretical loss of weight is 8.94%).

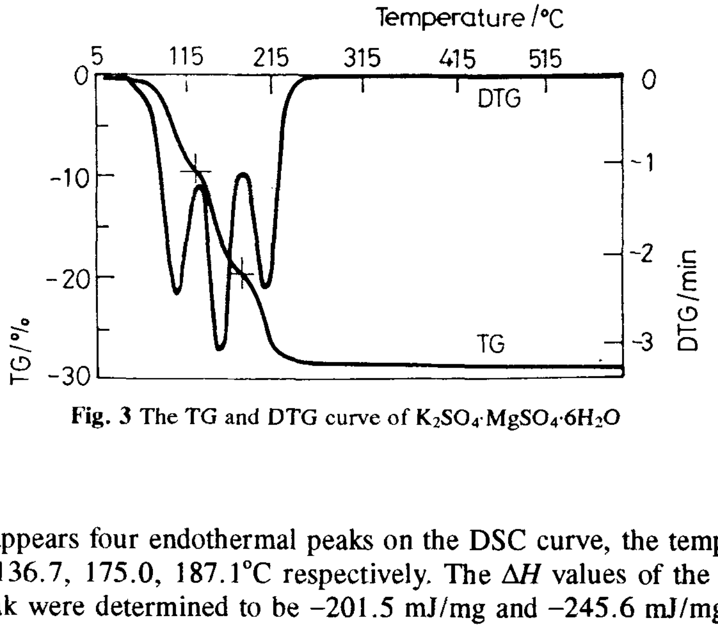

Fig. 3 The TG and DTG curve of $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$

DSC

There appears four endothermal peaks on the DSC curve, the temperatures are 81.3, 136.7, 175.0, 187.1°C respectively. The ΔH values of the first and second peak were determined to be −201.5 mJ/mg and −245.6 mJ/mg respectively. The third and the fourth peaks are so near and not clearly separated. The total enthalpy ΔH of dehydration of the third and the fourth stages was determined to be −229.8 mJ/mg.

Isothermal dehydration

A sample of schoenite (about 0.3 g) was heated isothermally in a thermostat and weighed at given intervals at 80, 110, 160 and 180°C respectively (Table 2). When the weights of the samples stayed constant during isothermal heating, phase analyses were done by X-ray diffraction.

Table 2 The results of iso-thermal dehydration of schoenite

Temp. / °C	Time / h	Sample weight /g	Weight of loss /%	Average loss of weight /%	Lost H_2O (molecular)	Solid phase
		0.2520	8.70			
80	10			8.67	1.94	$K_2SO_4{\cdot}MgSO_4{\cdot}4H_2O$
		0.4244	8.64			
		0.3140	10.60			$K_2SO_4{\cdot}MgSO_4{\cdot}4H_2O$ +
80	28			10.42	2.33	+ $K_2SO_4{\cdot}MgSO_4{\cdot}2H_2O$
		0.2919	10.33			
		0.2559	18.68			
110	1			18.62	4.03	
		0.2835	18.56			$K_2SO_4{\cdot}MgSO_4{\cdot}2H_2O$
	2	0.2729	18.60	18.60	4.02	
		0.5384	24.04			$K_2SO_4{\cdot}MgSO_4{\cdot}4H_2O$ +
160	1			24.07	5.38	+ $K_2SO_4{\cdot}MgSO_4$
		0.4416	24.09			
		0.3062	27.42			
180	1			27.36	6.1	$K_2SO_4{\cdot}2MgSO_4$ + K_2SO_4
		0.3458	27.30			

The samples were isothermally heated at 80°C for 10 h, and their average loss of weight is 8.67%, corresponding to a loss of $1.94H_2O$ and identified to be $K_2SO_4{\cdot}MgSO_4{\cdot}4H_2O$ by X-ray diffraction. Their samples were placed in a thermostat at the same temperature (80°C) for 26 h, average loss of weight is 10.42%, corresponding to a loss of $2.3H_2O$, and proved by X-ray diffraction to be a mixture of $K_2SO_4{\cdot}MgSO_4{\cdot}4H_2O$ and $K_2SO_4{\cdot}MgSO_4{\cdot}2H_2O$. The reaction equation might be:

$$K_2SO_4{\cdot}MgSO_4{\cdot}6H_2O_{(s)} \xrightarrow[10h]{80^{\circ}C} K_2SO_4{\cdot}MgSO_4{\cdot}4H_2O_{(s)} + 2H_2O_{(g)}$$

$$2K_2SO_4{\cdot}MgSO_4{\cdot}6H_2O_{(s)} \xrightarrow[26h]{80^{\circ}C}$$
$$K_2SO_4{\cdot}MgSO_4{\cdot}4H_2O_{(s)} + K_2SO_4{\cdot}MgSO_4{\cdot}2H_2O_{(s)} + 6H_2O_{(g)}$$

The samples were heated at 110°C for 1 h, and their average loss of weight was 18.62%, corresponding to a loss of $4.03H_2O$. The residue was confirmed to be $K_2SO_4{\cdot}MgSO_4{\cdot}2H_2O$ by X-ray diffraction. The reactions is:

$$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O_{(s)} \xrightarrow[1h]{110^\circ C} K_2SO_4 \cdot MgSO_4 \cdot 2H_2O_{(s)} + 4H_2O_{(g)}$$

The samples were heated at 160°C for 1 h and their average loss of weight was 24.07%, corresponding to a loss of $5.38H_2O$. The residue was identified to be a mixture of $K_2SO_4 \cdot MgSO_4 \cdot 2H_2O$ and $K_2SO_4 \cdot MgSO_4$. The reaction is:

$$2K_2SO_4 \cdot MgSO_4 \cdot 6H_2O_{(s)} \xrightarrow[1h]{160^\circ C} K_2SO_4 \cdot MgSO_4 \cdot 2H_2O_{(s)} + K_2SO_4 \cdot MgSO_4 + 10H_2O_{(g)}$$

The samples were heated at 180°C for 1 h and their average loss of weight was 27.36%, corresponding to a loss of $6.1H_2O$. The residue was proved to be a mixture of $K_2SO_4 \cdot 2MgSO_4$ and K_2SO_4. This is the same result as that of B. P. Choudharl *et al.* The reaction is:

$$2K_2SO_4 \cdot MgSO_4 \cdot 6H_2O_{(s)} \xrightarrow[1h]{180^\circ C} K_2SO_4 \cdot 2MgSO_{4\,(s)} + K_2SO_{4\,(s)} + 12H_2O_{(g)}$$

All the above results indicate that the thermal dehydration of schoenite can be continuously processed step by step, and it would be transformed to be leonite ($K_2SO_4 \cdot 2MgSO_4$) qickly.

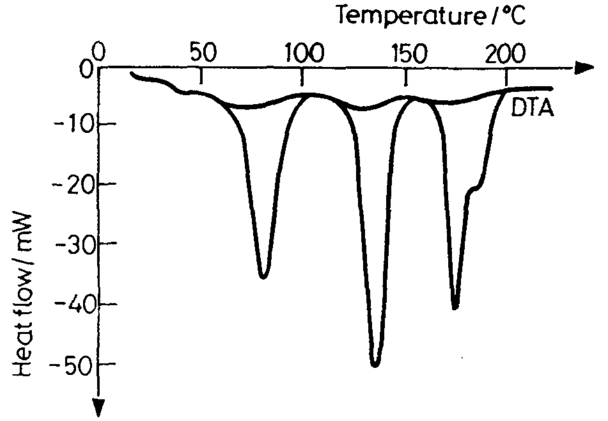

Fig. 4 The DSC curve of $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$

The kinetics of dehydration of Schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$)

The kinetic data of dehydration were obtained from the DSC curves of $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$. The Freeman and Carroll kinetic equation [4] and the DSC-111 programmes were used to calculate the kinetic parameters, $\log K_o$, activity energy E and reaction order n, in different stages of dehydration. The results are given in Table 3.

Table 3 The kinetic parameters of the thermal dehydration of $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$

Stages	Products	Temp./°C	$\log K_o$	n	E / kcal·mol^{-1}
First stage	$K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$	80.01– 89.23	43.26	0.93	34.70
Soond stage	$K_2SO_4 \cdot MgSO_4 \cdot 2H_2O$	136.90–144.74	32.58	0.44	31.44
Third and	$K_2SO_4 \cdot MgSO_4 + K_2SO_4$	178.40–188.33	61.03	1.78	59.78
Fourth stage	$+ K_2SO_4 \cdot 2MgSO_4$				

Discussion

Based on all the above results, the dehydration of schoenite is a step-by-step process and the reaction equations of dehydration might be written as follows:

The first step is:

$$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O\ (s) \xrightarrow{51.6-101.8^\circ C} K_2SO_4 \cdot MgSO_4 \cdot 4H_2O\ (s) + 2H_2O\ (g)$$

The second step is:

$$K_2SO_4 \cdot MgSO_4 \cdot 4H_2O\ (s) \xrightarrow{123.4-151.2^\circ C} K_2SO_4 \cdot MgSO_4 \cdot 2H_2O\ (s) + 2H_2O\ (g)$$

The third step is:

$$K_2SO_4 \cdot MgSO_4 \cdot 2H_2O\ (s) \xrightarrow{155.3-183.6^\circ C} K_2SO_4 \cdot MgSO_4\ (s) + 2H_2O\ (g)$$

The fourth step is:

$$K_2SO_4 \cdot MgSO_4\ (s) \xrightarrow{183.6-202.0^\circ C} K_2SO_4 \cdot 2MgSO_4\ (s) + K_2SO_4\ (s)$$

This is why there was no change of weight on the TG-curve in the fourth step.

References

1 H. H. Emons, J. Thermal Anal., 33 (1988) 113.
2 H. H. Emons and H. Voigt, Thermochim. Acta, (1987) 151.
3 B. P. Choudharl and D. S. Datar, Ind. J. Chem., 7 (1969) 1044.
4 E. S. Freeman and B. Carroll, J. Phys. Chem., 62 (1969) 394.

Zusammenfassung — Mittels thermischer Methoden wurde das thermische Verhalten von synthetischem Schoenit ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$) beim Erhitzen untersucht. Die Dehydratations- und Zersetzungstemperatur von Schoenit wurde auch mittels DTA, TG und DSC ermittelt. Die thermischen Reaktionsgleichungen und die Röntgen-Pulverdiffraktionsergebnisse der Produkte wurden gegeben und auch die dazugehörigen kinetischen Parameter erhalten.