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THERMAL AND THERMODYNAMIC DATA CONCERNING THE SELENITES FROM GROUP IB IN THE PERIODIC TABLE

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ABSTRACT

The thermal dehydration of $CuSeO_3 \cdot 2\ H_2O$, and the thermal dissociation of $CuSeO_3$ and Ag_2SeO_3 are studied. The mechanism of these processes is suggested. The heats of phase transitions and the specific heats of the corresponding compounds are determined.

INTRODUCTION

The data concerning the temperatures of thermal dehydration and dissociation, and the mechanism of these processes regarding copper selenite are contradictory. Studying $CuSeO_3 \cdot 2\ H_2O$, Dolique [1] discovered that $CuSeO_3$ is an intermediate product of dissociation which becomes CuO at 380°C. Maier et al. [2] established that at 175°C $CuSeO_3 \cdot 2\ H_2O$ undergoes stepwise dehydration; at 200°C the product of heating has a similar composition to that of the crystal hydrate $CuSeO_3 \cdot 1/3\ H_2O$, and at 265°C complete dehydration of this salt takes place.

The thermal dissociation of $CuSeO_3$ proceeds according to the scheme

$$2\ CuSeO_3 \underset{-SeO_2}{\overset{565°C}{\rightarrow}} CuO \cdot CuSeO_3 \underset{-SeO_2}{\overset{660°C}{\rightarrow}} 2\ CuO$$

The thermogram adduced by Maier et al. [2] indicates that there are three dehydration peaks but they are not discussed in detail. The endothermic peaks of dissociation above 450°C which, as can be seen from refs. 2 and 3 are not two but three, are not discussed in detail either.

The processes of melting and thermal dissociation of Ag_2SeO_3 have been studied by a number of authors. Its melting point according to Bercelius [4] is about 455°C, while according to Buketov et al. [8] it is 530 ± 5°C. There are also differences in the temperatures of discernible thermal dissociation: at live coals [4]; 600°C [5]; 575°C (according to thermal analysis data) and 730°C according to thermogravimetric analysis data [6]; 640–840°C [7], and 800–900°C [8].

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As to the products of dissociation, some authors believe that dissociation results directly in Ag, SeO_2 and O_2 [6,8], while according to others [5] the dissociation scheme is

$$4\,Ag_2SeO_3 \rightarrow Ag_2Se + 3\,Ag_2SeO_4$$

$$Ag_2SeO_4 \rightarrow 2\,Ag + SeO_2 + O_2$$

$$Ag_2Se + O_2 \rightarrow 2\,Ag + SeO_2$$

EXPERIMENTAL

The required compounds, Ag_2SeO_3 and $CuSeO_3 \cdot 2\,H_2O$, were obtained by continued crystallization of the selenites of these metals by means of the technique described in detail in ref. 9. Anhydrous amorphous $CuSeO_3$ was obtained by dehydration of the crystal hydrate at 300°C, and $CuO \cdot CuSeO_3$ was obtained by heating $CuSeO_3 \cdot 2\,H_2O$ at 560°C, the sample being repeatedly weighed to a constant weight corresponding to the compound. The crystallization of the amorphous $CuSeO_3$ was accomplished by continued heating of the sample at 350°C.

Chemical and X-ray phase analysis of the compounds obtained was carried out. The chemical analysis for copper was made complexometrically [10], and for silver, with sulphocyanide, the indicator being ferriammonium sulphate [11]. Selenium was determined iodometrically [12]. The results are presented in Table 1.

X-Ray phase analysis was accomplished on a TURM-61 apparatus at CuK_α emission. On comparing with literature data, the X-ray patterns indicate that the synthesized compounds belong to the corresponding selenites.

The light microscopy studies of copper and silver selenites were carried out on a "Dokuwal"-type microscope (Karl Zeiss, Jena, D.D.R.). Figure 1 presents part of the light spectroscopy photographs obtained. $CuSeO_3 \cdot 2$

TABLE 1

Chemical analysis of copper and silver selenites [$MeO(Me_2O)$]

Compound	Theoretical composition·	Composition according to data from chemical analysis		
$CuSeO_3 \cdot 2\,H_2O$	35.12	48.99	35.20; 35.09; 35.10	48.87; 49.12; 49.01
$CuSeO_3 \cdot H_2O$	38.15	53.22	38.27; 38.11; 38.23	53.23; 53.18; 53.25
$CuSeO_3 \cdot 1/3\,H_2O$	40.48	56.47	40.45; 40.39; 40.50	56.19; 56.50; 56.49
$CuSeO_3$(amorphous)	41.76	58.24	41.72; 41.73; 41.75	58.30; 58.41; 58.20
$CuSeO_3$(crystalline)	41.76	58.24	41.59; 41.76; 41.70	58.37; 58.24; 58.31
$CuO \cdot 3\,CuSeO_3$	48.87	51.13	48.92; 48.85; 48.71	51.01; 51.20; 51.15
$CuO \cdot CuSeO_3$	58.91	41.09	59.02; 58.89; 58.90	41.12; 41.13; 41.05
Ag_2SeO_3	67.62	32.38	67.43; 67.70; 67.68	32.12; 32.43; 32.33

H_2O is in the form of blue, well-shaped, plate-like crystals with a size below 100 mkm (Fig. 1a), while the basic selenite $CuO \cdot 3\ CuSeO_3$ is a crystal powder with particle size from 1 to 10 mkm (Fig. 1b). Ag_2SeO_3 is a white

Fig. 1. Microphotographs of the crystals of copper and silver selenites: (A) $CuSeO_3 \cdot 2\ H_2O$ (×210); (B) $CuSeO_3$ heated at 450°C (×500).

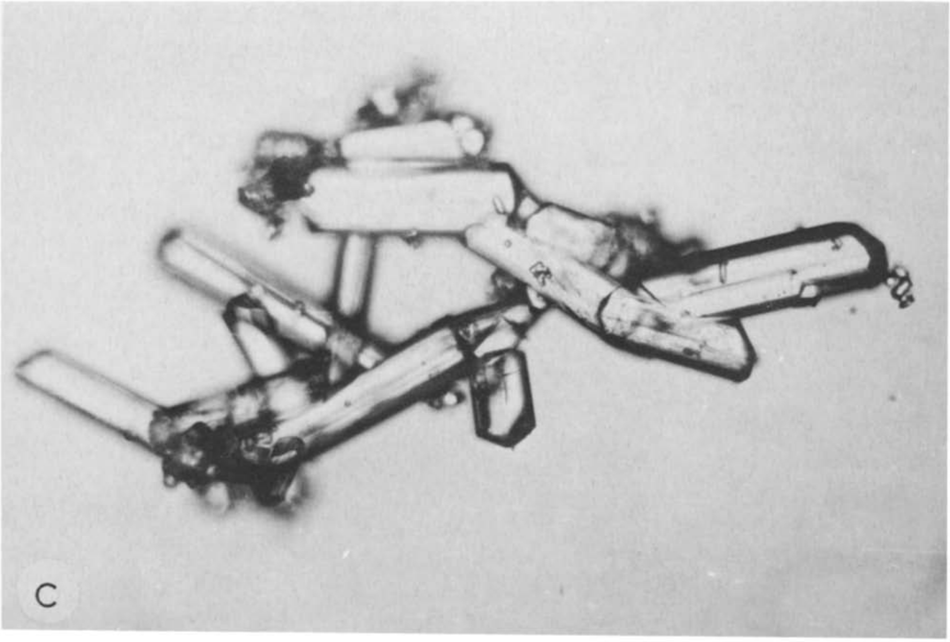

Fig. 1. (C) Ag_2SeO_3 (×210).

crystal compound. The light microscopy photographs in Fig. 1c show well-shaped, polyhedral, rod-like crystals about 200 mkm in length.

The derivatograph analysis was made with an OD-102-type derivatograph produced by MOM, Hungary.

The kinetic curves were drawn on the basis of the change of weight of the samples when the process was isothermal. The time of thermal dissociation was measured 50 s after the sample was introduced into the furnace. The interval of 50 s from placing the sample there to the beginning of measuring the time was necessary for the layer of the substance under study to be able to reach the experimental temperature. That period was preliminarily determined by using a second thermocouple previously placed directly in the crucible with the substance.

The heat of phase transition and the specific heat were determined with a DSC-III differential scanning calorimeter produced by Seteram, France.

RESULTS AND DISCUSSION

Figure 2 presents the DSC curve of $CuSeO_3 \cdot 2\ H_2O$. It shows that $CuSeO_3 \cdot 2\ H_2O$ is dehydrated in stages. In the temperature range 199–223°C $CuSeO_3 \cdot 2\ H_2O$ dissociates into $CuSeO_3 \cdot H_2O$. The weight loss of the sample for this transition according to the data obtained from the derivatograph analysis is 7.94 compared with the theoretical value of 7.95%. At

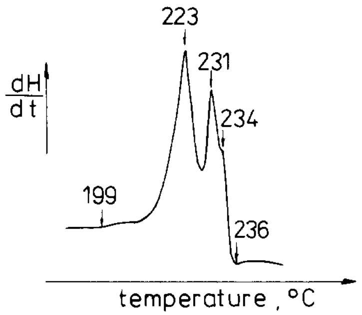

Fig. 2. DSC curve of $CuSeO_3 \cdot 2\ H_2O$.

231°C a total weight loss of 15.98% is visible which corresponds exactly to the transition of $CuSeO_3 \cdot 2\ H_2O \rightarrow CuSeO_3 \cdot 1/3\ H_2O$. The third transition at 234°C, according to thermogravimetric and chemical analyses, corresponds to the transition of $CuSeO_3 \cdot 1/3\ H_2O \rightarrow CuSeO_3$. A similar transition was observed by some authors [2] at 200°C, and, in refs. 13 and 14, on continued heating of $CuSeO_3 \cdot H_2O$ in a welded tube at 150°C.

Our study showed that the thermal dissociation of $CuSeO_3$ is a complex process. In the derivatogram and the DSC curve in the temperature range 450–546°C an endothermic peak was identified which could be related to neither of the known phases. In order to define more accurately the type and the number of phases, the kinetics of the thermal dissociation of $CuSeO_3$ were recorded at the temperatures of the corresponding peaks—450, 570 and

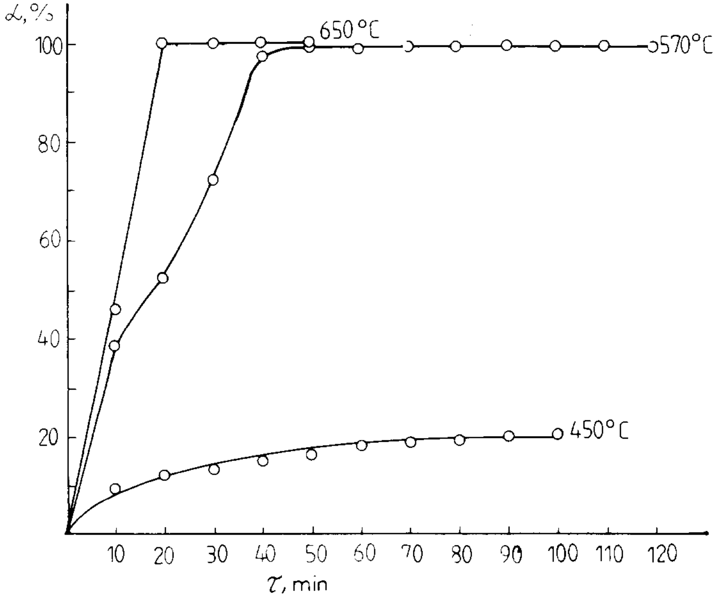

Fig. 3. Dependence of the degree of dissociation (α) of $CuSeO_3$ on the time of heating (τ).

650°C (Fig. 3). $CuSeO_3$ dissociates considerably at 450°C and forms basic copper selenite $CuO \cdot 3\ CuSeO_3$. At 570°C $CuSeO_3$ dissociates into the second basic salt, $CuO \cdot CuSeO_3$. At this temperature the process lasts about 20 min. The last stage of the thermal dissociation of $CuSeO_3$ results in CuO. The scheme of the thermal dissociation is

$$CuSeO_3 \xrightarrow{450-546°C} CuO \cdot 3\ CuSeO_3 \xrightarrow{570-582°C} CuO \cdot CuSeO_3 \xrightarrow{620-650°C} CuO$$

Endothermic peaks were identified in the thermogram of Ag_2SeO_3: one with a minimum at 537°C, and another double endothermic peak with a minimum at 700 and 830°C. Observation of the process of heating showed that silver selenite gradually changes its colour upon heating: it turns greenish and then yellow-brown. At 537°C it melts. The rate of dissociation of the substance near its melting point is still slow since the melted and immediately cooled selenite has a composition (Ag_2O 67.59 mass% and SeO_2 32.24 mass%) practically the same as the initial composition.

In order to explain the nature of the peaks above 537°C we studied the kinetic curves of dissociation at 550, 700, 750 and 800°C (Fig. 4). As these curves show, at 550°C the dissociation of silver selenite is negligible. The degree of dissociation of the product heated for 2 h at this temperature is 3.9% due to the obtained SeO_2 and O_2. Ag_2SeO_3 dissociates intensively at 700°C. The degree of dissociation of Ag_2SeO_3 heated for 2 h at this temperature is 49.6%. At 750°C the dissociation after heating for 2 h

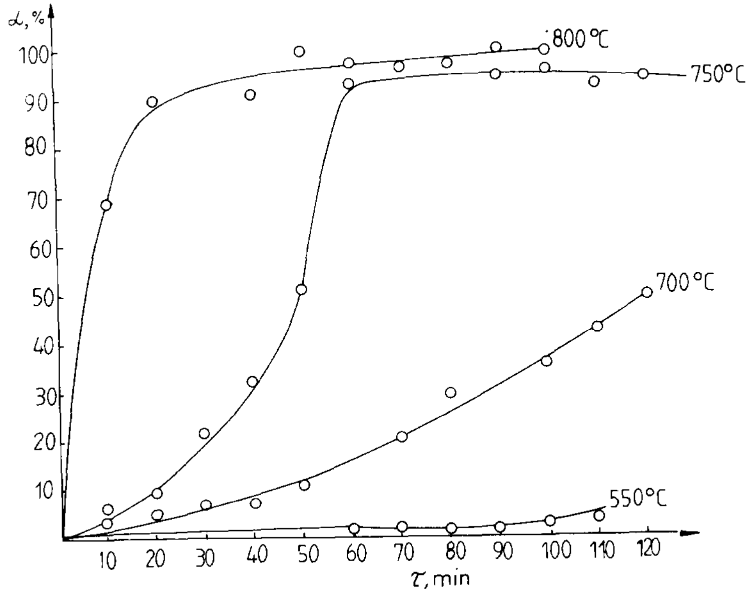

Fig. 4. Dependence of the degree of dissociation (α) of Ag_2SeO_3 on the time of heating (τ).

TABLE 2

Temperatures and heats of phase transitions of the selenites of the elements from group IB of the periodic system

Phase transition	Transition temp. (°C)	Transition heat (kcal mol^{-1})	
$CuSeO_3 \cdot 2\ H_2O \rightarrow CuSeO_3 \cdot H_2O$	223	13.35	20.60
$CuSeO_3 \cdot H_2O \rightarrow CuSeO_3 \cdot 1/3\ H_2O$	231	7.26	
$CuSeO_3 \cdot 1/3\ H_2O \rightarrow CuSeO_3$	234		3.84
$CuSeO_3$(amorph.) → $CuSeO_3$(cryst.)	339		
$CuSeO_3$(cryst.) → $CuO \cdot 3\ CuSeO_3$	546	8.63	
$CuSeO_3$(cryst.) → $CuO \cdot CuSeO_3$	582		
$CuO \cdot CuSeO_3 \rightarrow CuO$	655		
Ag_2SeO_3(solid) → Ag_2SeO_3(melt)	537	9.25	

TABLE 3

Coefficients for the temperature-dependence of heat capacity in the equation $c_p = a + bT + cT^2$

Compound	Coefficients in the equation $c_p = f(T)$			Temp. range (°C)
	a	b	c	
$CuSeO_3$(cryst)	0.29	7.31×10^{-2}	4.29×10^{-6}	320–400
$CuO \cdot CuSeO_3$	35.47	-6.36×10^{-3}	4.25×10^{-5}	320–400
Ag_2SeO_3	17.61	7.45×10^{-2}	-6.88×10^{-5}	320–400

constitutes 94.1%. Complete dissociation occurs at 800°C. The residue of this dissociation is metallic silver. The scheme of dissociation of Ag_2SeO_3 which we suggest—$Ag_2SeO_3 \rightarrow 2\ Ag + SeO_2 + 1/2\ O_2$—is analogous to that reported in ref. 8.

Table 2 presents the values of the temperatures and heats of phase transitions. The heats of phase transitions were first determined by us. The melting point of Ag_2SeO_3 is nearly the same as that reported in ref. 8.

The heat capacities of the selenites from group IB were determined using a technique described in ref. 15. The results were obtained using the method of least squares and were expressed by the equation

$$C_p = a + bT + cT^2$$

Table 3 shows the coefficients in this equation for the various selenites and the temperature range of the measurement.

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