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PHYSICO-CHEMICAL INVESTIGATION OF THE SYSTEM $ZnO–SeO_2–H_2O$ AND SOME PROPERTIES OF THE COMPOUNDS OBTAINED

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ABSTRACT

The solubility isotherm of system $ZnO–SeO_2–H_2O$ at 100°C is determined. The mechanism of thermal dissociation of $ZnSeO_3$ and $ZnSeO_3 \cdot H_2SeO_3$ is studied.

INTRODUCTION

Data about the production and thermal stability of zinc selenites are a subject of considerable interest for a number of important practical problems. It is well-known that the reduction of $ZnSeO_3$ with H_2 produces ZnSe (widely used as luminophore). On the other hand, zinc selenite is one of the intermediate products formed during the calcination of selenium-containing zinc, lead and other concentrates. In order to understand the processes taking place during the oxidization it is necessary to study the thermal dissociation. Data about the production of zinc selenites are scarce [1], and those about their thermal dissociation contradictory [2–4]. According to data of ref. 2 zinc selenite melts and dissociates at 620 and 695–700°C, respectively. According to ref. 3 it is partially dissociated at 450°C and completely dissociated at 600°C. According to ref. 4 at 316°C polymorphic transition of α-$ZnSeO_3$ into β-$ZnSeO_3$ takes place which melts at 620–622°C and partially dissociates. The rate of dissociation greatly increases at 690–700°C.

The most accurate data regarding the type and the stability range of the possible zinc selenites can be obtained by studying the solubility isotherm of system $ZnO–SeO_2–H_2O$.

EXPERIMENTAL

The samples were prepared by adding 2 g of $Zn(OH)_2$ in 50 ml of selenious acid of different concentration. In order to achieve the best

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interaction, the samples were stirred with a magnet stirrer for 24 h. The samples were transferred to glass ampules and sealed. They were kept for 3 months in an air thermostat at 100°C, the maximum deviation from this temperature being ±1°C. In addition, conditions were being created for recrystallization of the initially formed selenites and the formation of purer selenites with larger crystals. The liquid phase was separated from the solid phase with a filter G4 and test samples were taken.

Chemical analysis of equilibrium liquid and solid phases was made complexometrically [5] for zinc and iodometrically [6] for selenium.

RESULTS AND DISCUSSION

The results in Table 1 and Fig. 1 show that the solubility isotherm of the system $ZnO-SeO_2-H_2O$ at 100°C consists of two branches corresponding to the crystallization of two compounds. In a concentration interval of SeO_2

TABLE 1

Solubility isotherm of the system $ZnO-SeO_2-H_2O$

No.	Liquid phase		Solid phase		Formula composition of solid phase
	ZnO	SeO_2	ZnO	SeO_2	
1	9.05×10^{-2}	1.19	42.00	56.25	$ZnSeO_3$
2	1.67×10^{-1}	3.18	42.19	57.53	$ZnSeO_3$
3	2.25×10^{-1}	5.63	42.08	57.19	$ZnSeO_3$
4	3.10×10^{-1}	8.92	39.35	54.92	$ZnSeO_3$
5	4.21×10^{-1}	16.42	37.40		$ZnSeO_3$
6	5.33×10^{-1}	24.37	32.79	49.18	$ZnSeO_3$
7	6.18×10^{-1}	27.16	34.88	52.51	$ZnSeO_3$
8	7.42×10^{-1}	30.79	38.09	54.51	$ZnSeO_3$
9	8.45×10^{-1}	33.26	36.35	54.57	$ZnSeO_3$
10	9.98×10^{-1}	34.65	29.62	51.76	$ZnSeO_3$
11	1.04	37.59	39.71	56.28	$ZnSeO_3$
12	1.12	41.61	37.03	56.62	$ZnSeO_3$
13	1.18	42.12	38.03	55.51	$ZnSeO_3$
14	1.45	45.87	37.42	56.22	$ZnSeO_3$
15	1.60	51.00	22.14	54.41	$ZnSeO_3$
16	1.88	59.71	37.47	58.37	$ZnSeO_3$ and $ZnSeO_3\cdot H_2SeO_3$
17	1.77	59.73	22.96	68.01	$ZnSeO_3\cdot H_2SeO_3$
18	1.15	66.20	14.75	68.25	$ZnSeO_3\cdot H_2SeO_3$
19	1.12	67.77	21.20	68.52	$ZnSeO_3\cdot H_2SeO_3$
20	1.03	68.81	12.84	69.02	$ZnSeO_3\cdot H_2SeO_3$
21	0.95	70.09	24.16	69.75	$ZnSeO_3\cdot H_2SeO_3$
22	0.56	74.52	21.76	70.32	$ZnSeO_3\cdot H_2SeO_3$
23	0.42	80.12	23.12	70.39	$ZnSeO_3\cdot H_2SeO_3$

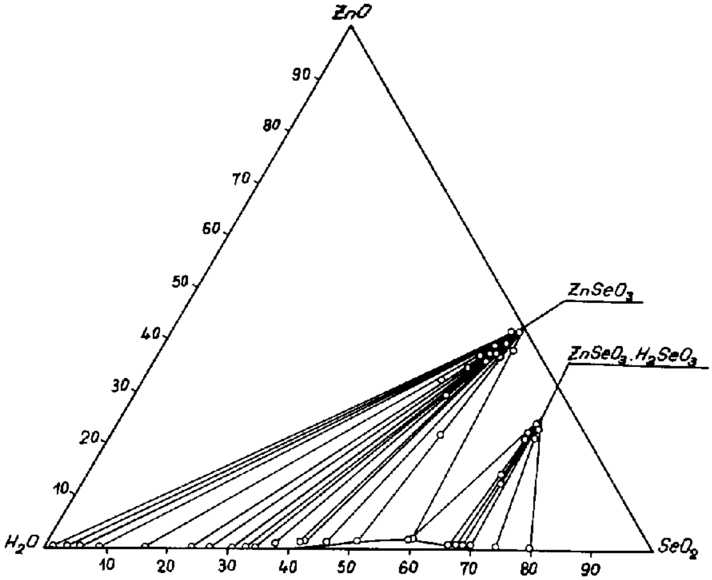

Fig. 1. Solubility isotherm of the system $ZnO-SeO_2-H_2O$ at 100°C.

from 1.19 to 59.79% the solubility of zinc selenite increases up to 1.88%. $ZnSeO_3$ is stable in this section of the diagram. A further increase in H_2SeO_3 concentration results in a decrease in solubility of the system, reaching 0.42% for ZnO when SeO_2 is 80.12%. The formation of a new compound in this section is indicated by the nodes which join at a point corresponding to the composition of the compound $ZnSeO_3 \cdot H_2SO_3$. The formation of the new phase can be easily recognized by the appearance of transparent colourless crystals. The eutonic point associated with the simultaneous existence of two phases corresponds to 1.88% of ZnO and 59.71% of SeO_2.

Zinc selenite and zinc hydroselenite are white crystal compounds slightly soluble in their mother solution. Both compounds are little soluble in water and spirit. At room temperature anhydrous zinc selenite is quite stable and does not change in air. In moist air, however, it adsorbs small amounts of moisture (up to 4–5%) which is easily liberated upon drying. Both selenites are soluble in acids, alkaline bases and ammonia.

The derivatogram of $ZnSeO_3$ exhibits three endothermic peaks (Fig. 2). Observations show that at 640°C $ZnSeO_3$ melts, its colour changing from white to grey-green. Dissociation begins at 450°C and at melting point its rate is quite high. At 720°C $ZnSeO_3$ dissociates intensively. The thermogravimetric curve at this temperature shows weight loss of the sample (28.85 wt%), while chemical analysis points to a composition similar to $ZnO \cdot ZnSeO_3$. According to X-ray analysis, however, the phase obtained is a mixture of ZnO and $ZnSeO_3$. We are in agreement with Muldagalieva et al. [7] who, having studied the system $ZnO-SeO_2$ thermographically, found out

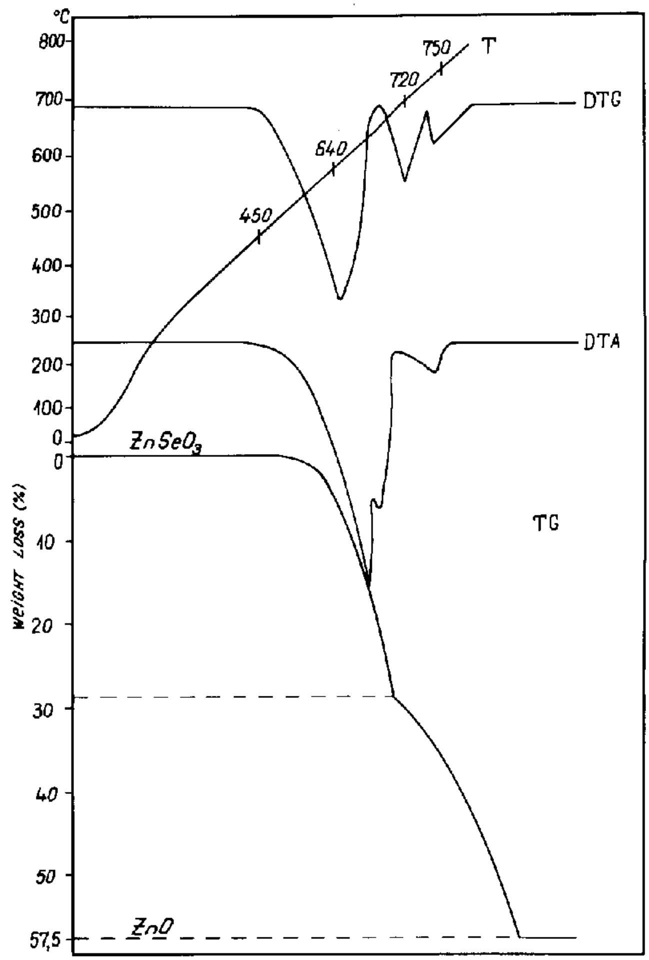

Fig. 2. Derivatogram of $ZnSeO_3$.

that basic selenites do not exist in it. The kinetic curves (Fig. 3) confirm the results of derivatograph analysis too. At 450°C $ZnSeO_3$ dissociates negligibly. At 620, 730 and 750°C the rate of dissociation is very high and in all cases the dissociation product is ZnO. The absence of bends in the dissociation curves also confirms the conclusion that basic zinc selenites are not formed. The fact that the dissociation peaks in the derivatogram of $ZnSeO_3$ split into two can be accounted for by mechanical changes in the dissociating sample. For example, visual observations show that, on heating to 730–750°C, the mixtures are dry and porous and fall apart, which probably determines the peaks in the derivatogram.

Figure 4 shows the derivatogram of $ZnSeO_3 \cdot H_2SeO_3$ with five endothermal peaks. The peak at 200–250°C corresponds to a weight loss of the sample (5.60 wt%), and chemical analysis of ZnO and SeO_2 indicates 26.83

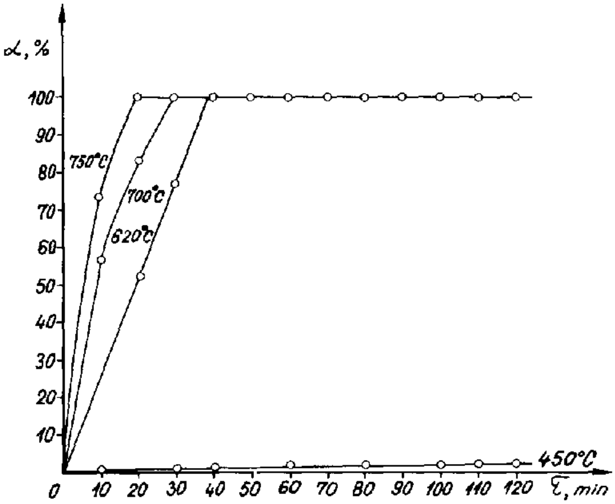

Fig. 3. Dependence of the degree of dissociation of $ZnSeO_3$ (α) on time (τ).

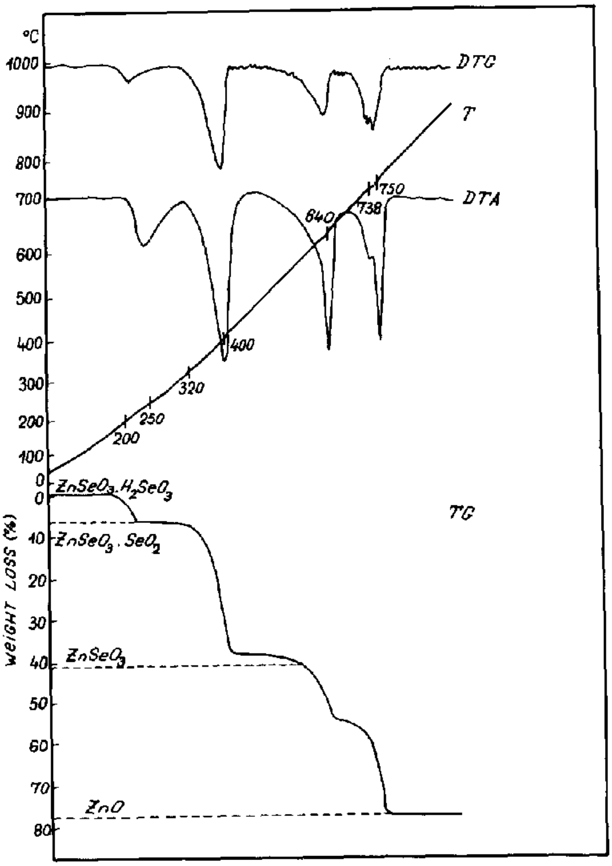

Fig. 4. Derivatogram of $ZnSeO_3 \cdot H_2SeO_3$.

and 73.17 wt% respectively, which corresponds to compounds with a formula composition $ZnSeO_3 \cdot SeO_2$. Therefore, at this temperature $ZnSeO_3 \cdot H_2SeO_3$ dissociates liberating 1 mol of water. The endothermic peak in the temperature range 320–400°C can be associated with the liberation of 1 mol of SeO_2 and the transformation of pyroselenite into β-$ZnSeO_3$ (ZnO, 42.30 wt%; SeO_2, 57.69 wt%). The further dissociation of β-$ZnSeO_3$ proceeds according to the scheme described above. Therefore, the scheme of thermal dissociation of $ZnSeO_3 \cdot H_2SeO_3$ is as follows

$$ZnSeO_3 \cdot H_2SeO_3 \xrightarrow{200-250^\circ C} ZnSeO_3 \cdot SeO_2 \xrightarrow{320-400^\circ C} \beta\text{-}ZnSeO_3$$

$$\xrightarrow{600^\circ C} \text{melt} \xrightarrow{738-750^\circ C} ZnO$$

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