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REGULARITIES IN THE FORMATION OF SELENITES IN THE THREE-COMPONENT SYSTEM Al_2O_3–SeO_2–H_2O AND THEIR PROPERTIES

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ABSTRACT

The solubility isotherm of the system Al_2O_3–SeO_2–H_2O at 100 °C was drawn, and the thermal dissociation of the products obtained was studied. Thermal and X-ray analysis data are presented.

INTRODUCTION

The normal selenites of a number of metals may be turned into selenides of stoichiometric composition by reduction with hydrogen.

The crystals of some hydrogen selenites have seignettic and anti-seignettic properties. Therefore, the synthesis of selenites in the crystalline state and the study of their properties are of particular practical interest.

The data concerning aluminium selenites are rather contradictory. In ref. 1, the aluminium selenites obtained have 3 and 7 water molecules, while the aluminium selenite of ref. 2 is $Al_2(SeO_3)_3 \cdot 6H_2O$; in ref. 1 the composition of basic aluminium selenite is $Al_2O_3 \cdot 3Al_2(SeO_3)_3$, and in ref. 2 it is given as $2Al_2O_3 \cdot Al_2(SeO_3)_3$. There are also considerable discrepancies in the composition of the hydrogen selenites and pyroselenites obtained. The data in ref. 2 show that the composition of hydrogen selenite is $Al_2(SeO_3)_3 \cdot 3H_2SeO_3$, while according to ref. 1 three hydrogen selenites and two pyroselenites are possible.

EXPERIMENTAL

Reliable information concerning the composition of all the possible selenites of the system Al_2O_3–SeO_2–H_2O can be obtained by studying its solubility isotherm.

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TABLE 1

Solubility isotherm of the system Al_2O_3–SeO_2–H_2O at 100 °C

No.	Liquid phase		Solid phase		Composition of the solid phase
	Al_2O_3	SeO_2	Al_2O_3	SeO_2	
1	2.71×10^{-3}	1.58	14.97	49.03	$Al_2(SeO_3)_3\cdot6H_2O$
2	3.54×10^{-3}	1.77	16.25	15.08	
3	4.14×10^{-3}	8.14	15.60	51.75	
4	1.98×10^{-2}	9.13	14.50	64.16	$Al_2(SeO_3)_3\cdot H_2SeO_3$
5	4.45×10^{-2}	23.59	14.85	69.30	
6	4.90×10^{-2}	25.18	13.98	67.78	
7	5.80×10^{-2}	27.89	14.33	67.83	
8	5.94×10^{-2}	29.48	14.71	69.30	
9	4.81×10^{-2}	33.14	11.33	78.01	$Al_2(SeO_3)_3\cdot3H_2SeO_3$
10	3.70×10^{-2}	39.37	11.12	78.91	
11	3.65×10^{-2}	44.14	11.12	78.93	
12	3.35×10^{-2}	48.95	12.49	80.15	
13	2.38×10^{-2}	61.10	10.13	78.88	
14	7.29×10^{-3}	68.84	9.60	78.87	
15	5.38×10^{-3}	82.86	8.30	81.79	
16	3.18×10^{-3}	89.31	5.98	84.75	

The study was carried out by adding 2 g of $Al_2(SeO_3)_3$ (obtained by precipitation reaction) to an aqueous solution of selenious acid whose concentration varied over a wide range. For the sake of comparison, parallel samples with γ-Al_2O_3 and selenious acid were studied. The samples were thermostatted, stirred continuously for 24 hours and then sealed in glass ampoules. The latter were thermostated in an air thermostat at 100 ± 1 °C for 3 months and were periodically shaken. Then the ampoules were opened, the liquid and solid phases were separated by filtration at 100 °C and subjected to chemical analysis.

The chemical analysis for aluminium was made complexometrically [3], and for SeO_3^{2-}, iodometrically [4]. The results obtained for both sets of samples were identical.

RESULTS AND DISCUSSION

Table 1 and Fig. 1 show that three aluminium selenites, one normal and two acid salts, crystallise as equilibrium solid phases in the system Al_2O_3–SeO_2–H_2O. When SeO_2 in the liquid phase is 1.58–8.14 mass%, $Al_2(SeO_3)_3 \cdot 6H_2O$ crystallises. If the concentration of SeO_2 is 9.13–29.48 mass%, a field of equilibrium existence of $Al_2(SeO_3)_3 \cdot H_2SeO_3$ is formed. The third aluminium selenite exists in the concentration interval 33.14–89.31 mass% SeO_2 in the liquid phase; its composition is $Al_2(SeO_3)_3 \cdot 3H_2SeO_3$.

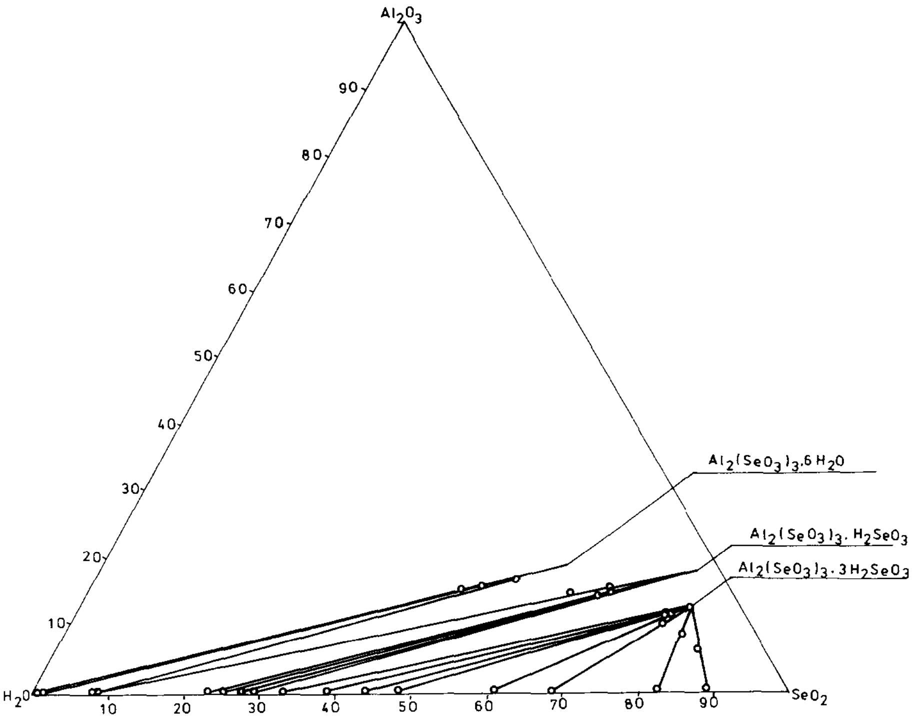

Fig. 1. Solubility isotherm of the system Al_2O_3-SeO_2-H_2O at 100 °C.

The solubility of $Al_2(SeO_3)_3 \cdot 6H_2O$ is negligible and it increases with increasing concentration of SeO_2 in the liquid phase. The solubility of the acid salt $Al_2(SeO_3)_3 \cdot H_2SeO_3$ is one order higher and it increases with increasing SeO_2 content in the liquid phase. The solubility of this salt at 33.14 mass% SeO_2 in the liquid phase, is $4.81 \times 10^{-2}\%$, while at 89.31 mass% SeO_2, it is $3.18 \times 10^{-3}\%$. A slight decreasing solubility trend was observed.

The eutonic point between $Al_2(SeO_3)_3 \cdot 6H_2O$ and $Al_2(SeO_3)_3 \cdot H_2SeO_3$ lies between 8.14 and 9.13 mass% SeO_2 in the liquid phase, and the point between $Al_2(SeO_3)_3 \cdot H_2SeO_3$ and $Al_2(SeO_3)_3 \cdot 3H_2SeO_3$ is between 29.48 and 33.14 mass% SeO_2 in the liquid phase.

The compounds obtained were identified by the Schreinemakers method, by chemical analysis of the well-washed and dried solid phases, by X-ray phase analysis (Table 2) and by thermal analysis.

Figure 1 shows that $Al_2(SeO_3)_3 \cdot 6H_2O$ and $Al_2(SeO_3)_3 \cdot 3H_2SeO_3$ are obtained at low and high concentrations of selenious acid. At an average concentration, the product obtained is a hydrogen selenite with composition $Al_2(SeO_3)_3 \cdot H_2SeO_3$, first obtained and characterised here by the present author.

TABLE 2

X-ray patterns of aluminium selenites

$Al_2(SeO_3)_3 \cdot 6H_2O$		$Al_2(SeO_3)_3 \cdot H_2SeO_3$		$Al_2(SeO_3)_3 \cdot 3H_2SeO_3$	
I/I_1	d (Å)	I/I_1	d (Å)	I/I_1	d (Å)
46	7.557	20	5.901	100	6.804
63	6.103	12	5.464	4	5.086
41	5.336	46	4.792	22	4.667
38	4.384	100	4.371	64	4.562
19	3.573	4	3.660	30	4.445
100	3.373	8	3.545	51	3.707
12	3.218	39	3.278	100	3.429
7	3.087	26	3.151	22	3.304
7	2.866	100	3.108	24	3.218
50	2.769	67	2.957	23	3.184
10	2.665	6	2.846	14	3.093
29	2.599	11	2.620	13	3.035
13	2.521	7	2.460	7	2.891
12	2.279	32	2.415	23	2.747
12	2.180	27	2.184	4	2.617
14	2.063	14	2.156	16	2.531
16	1.955	11	2.097	10	2.409
8	1.812	11	2.070	12	2.348
8	1.777	15	1.886	4	2.285
5	1.741	13	1.872	10	2.182
7	1.711	19	1.854	12	2.078
7	1.696	21	1.735	6	1.987
17	1.641	5	1.714	18	1.962
17	1.499	10	1.598	23	1.875
6	1.458	20	1.572	6	1.831
4	1.309	16	1.479	6	1.714
–	–	5	1.434	6	1.552
–	–	7	1.405	9	1.524
–	–	4	1.385	10	1.448
–	–	7	1.289	12	1.372

Thermal dissociation was studied using an apparatus described in ref. 5. To clarify the chemistry of the process corresponding to the thermal peaks in the thermograms, an additional thermogravimetric study was carried out. In addition, the initial selenite was heated under conditions modelling the conditions of thermal analysis. Also, the dissociation products were obtained by isothermal heating for their ensuing chemical and X-ray phase analysis.

In the thermogram of $Al_2(SeO_3)_3 \cdot 6H_2O$, five endothermal peaks are observed at 160, 255, 475, 562 and 715 °C (Fig. 2). The first peak corresponds to the partial dehydration of the crystal hydrate and the formation of

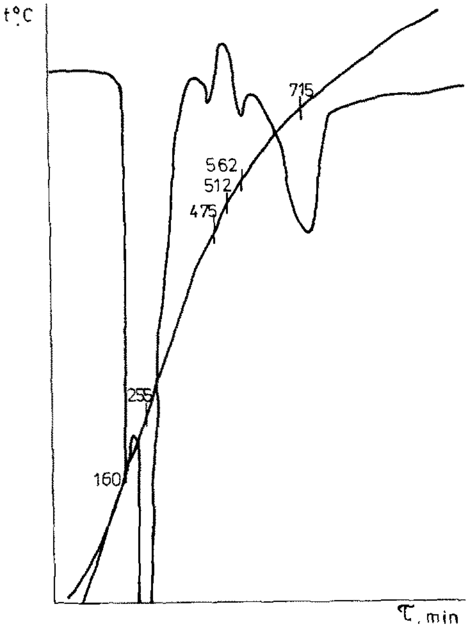

Fig. 2. Thermogram of $Al_2(SeO_3)_3 \cdot 6H_2O$.

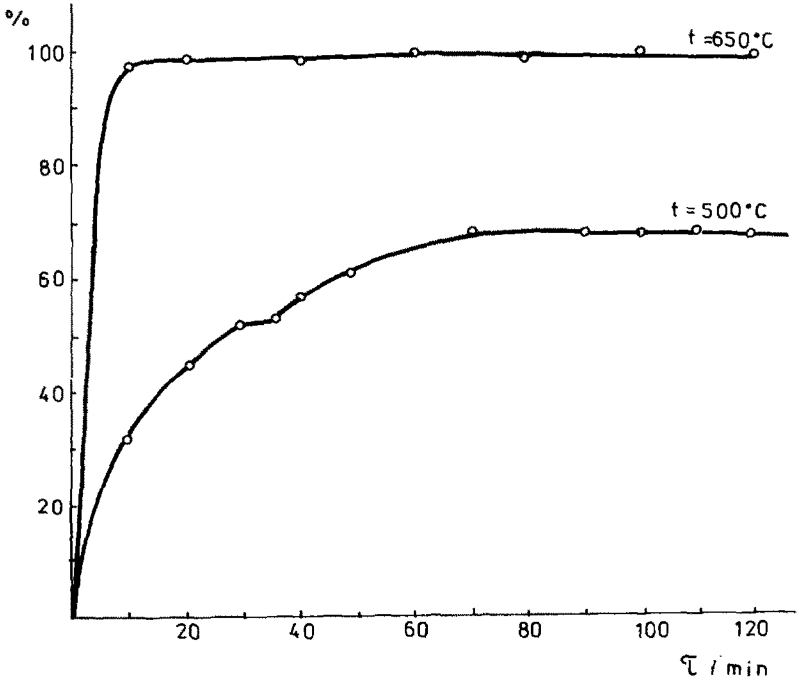

Fig. 3. Kinetic curves of the thermal dissociation of $Al_2(SeO_3)_3$; dependence of the degree of dissociation (α) on time (t).

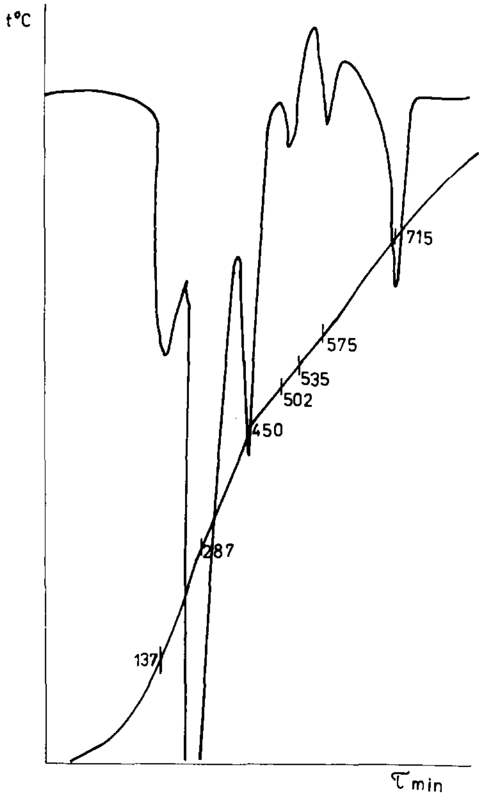

Fig. 4. Thermogram of $Al_2(SeO_3)_3 \cdot H_2SeO_3$.

$Al_2(SeO_3)_3 \cdot 2H_2O$. At 255 °C, gravimetric analysis indicated a mass loss of 19.89 mass%, while chemical analysis gave the concentration of Al_2O_3 as 23.44% and that of SeO_2 as 76.56%. Heating $Al_2(SeO_3)_3 \cdot 6H_2O$ at 255 °C gave a dehydrated product. X-ray phase analysis of dehydrated $Al_2(SeO_3)_3$ showed that its structure is amorphous. The third endothermal peak at 475 °C corresponds to the thermal transition of $Al_2(SeO_3)_3$ into $Al_2O_3 \cdot 2Al_2(SeO_3)_3$.

Chemical analysis at 500 °C showed that the concentration of Al_2O_3 and SeO_2 in the samples heated for 60–120 min is the same. The peaks obtained by X-ray phase analysis differ from those of Al_2O_3 and $Al_2(SeO_3)_3$, which proves that the product is basic aluminium selenite of composition $2Al_2O_3 \cdot Al_2(SeO_3)_3$ (Al_2O_3, 53.36%; and SeO_2, 46.64%). The phases $Al_2(SeO_3)_3$ and $2Al_2O_3 \cdot Al_2(SeO_3)_3$ can be identified following heating at this temperature for 10 min. The rate of dissociation increases with increasing temperature. The dissociation of $Al_2(SeO_3)_3$ is very intense at 650 °C, see Fig. 3. The degree of dissociation is as follows: 97% after 10 min, 99% after 40 min and

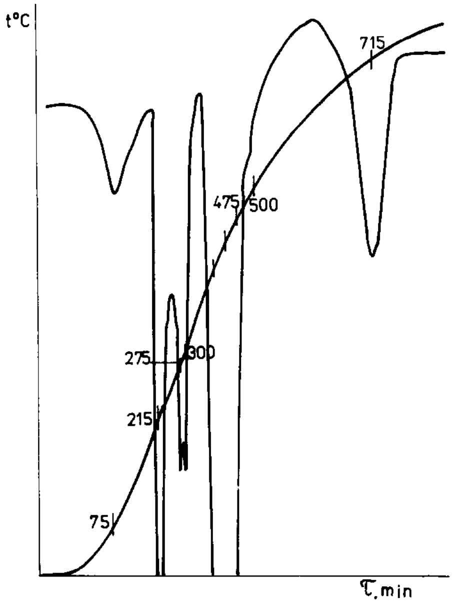

Fig. 5. Thermogram of $Al_2(SeO_3)_3 \cdot 3H_2SeO_3$.

100% after 60 min. Chemical and X-ray phase analyses indicated that the only product obtained after 100% dissociation is Al_2O_3.

On the basis of these explanations, the following scheme of thermal dissociation can be suggested

$$Al_2(SeO_3)_3 \cdot 6H_2O \overset{160\,°C}{\rightleftarrows} Al_2(SeO_3)_3 \cdot 2H_2O \xrightarrow{255\,°C} Al(SeO_3)_3(\text{amorph.})$$

$$\xrightarrow{475\,°C} Al_2O_3 \cdot 2Al_2(SeO_3)_3(\text{amorph.}) \xrightarrow{512\,°C} Al_2O_3 \cdot 2Al_2(SeO_3)_3(\text{cryst.})$$

$$\xrightarrow{562\,°C} 2Al_2O_3 \cdot Al_2(SeO_3)_3 \xrightarrow{715\,°C} Al_2O_3$$

Figures 4 and 5 show the thermograms of $Al_2(SeO_3)_3 \cdot H_2SeO_3$ and $Al_2(SeO_3)_3 \cdot 3H_2SeO_4$.

Using the above methods for identifying the dissociation products, the following scheme for the thermal dissociation of $Al_2(SeO_3)_3 \cdot H_2SeO_3$ can be suggested

$$Al_2(SeO_3)_3 \cdot H_2SeO_3 \xrightarrow{137\,°C} Al_2(SeO_3)_3 \cdot SeO_2 \xrightarrow{287\,°C} Al_2(SeO_3)_3(\text{amorph.})$$

$$\xrightarrow{450 \text{ and } 502\,°C} Al_2O_3 \cdot 2Al_2(SeO_3)_3(\text{amorph.})$$

$$\xrightarrow{535\,°C} Al_2O_3 \cdot 2Al_2(SeO_3)_3(\text{cryst.}) \xrightarrow{575\,°C} Al_2O_3 \cdot Al_2(SeO_3)_3$$

$$\xrightarrow{715\,°C} Al_2O_3$$

and for the thermal dissociation of $Al_2(SeO_3)_3 \cdot 3H_2SeO_3$

$$Al_2(SeO_3)_3 \cdot 3H_2SeO_3 \xrightarrow[-H_2O]{75^\circ C} Al_2(SeO_3)_3 \cdot 2H_2SeO_3 \cdot SeO_2$$

$$\xrightarrow{215^\circ C} Al_2(SeO_3)_3 \cdot 3SeO_3 \xrightarrow[-SeO_2]{275^\circ C} Al_2(SeO_3)_3 \cdot 2SeO_2$$

$$\xrightarrow{300^\circ C} Al_2(SeO_3)_3 \cdot SeO_2 \xrightarrow{420^\circ C} Al_2(SeO_3)_3 \xrightarrow{475^\circ C} Al_2O_3 \cdot 2Al_2(SeO_3)_3$$

$$\xrightarrow{500\text{-}575^\circ C} Al_2O_3 \cdot Al_2(SeO_3)_3 \xrightarrow{715^\circ C} Al_2O_3$$

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