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Note

PHASES OF THE SYSTEM Tl_2O_3–SeO_2–H_2O AND THEIR THERMAL STABILITY

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The data concerning the selenites of thallium are limited to a description of the synthesis of $Tl_2(SeO_3)_3$ and $Tl_2(SeO_3)_3 \cdot H_2SeO_3$ when newly-prepared thallium hydroxide reacts with an aqueous solution of selenious acid upon heating [1,2]. In ref. 2 the thermal dissociation of $Tl_2(SeO_3)_3 \cdot H_2SeO_3$ was studied. These publications, however, do not specify the conditions under which the compounds involved were obtained, neither do they answer the question as to the existence of any other thallium selenites.

This work presents the results of a study of the system Tl_2O_3–SeO_2–H_2O in a wide concentration range of selenious acid, as well as the thermal stability of the compounds obtained.

EXPERIMENTAL

The samples of the system Tl_2O_3–SeO_2–H_2O were prepared by mixing 2 g of $Tl_2O_3 \cdot H_2O$ and selenious oxide at varying concentrations. $Tl_2O_3 \cdot H_2O$ was obtained by the technique described in ref. 3, and SeO_2 was obtained using high-purity Se, class B-5, and HNO_3 (Merck) after being subjected to threefold sublimation [4].

The samples were thermostatted at 25°C for 24 h with continuous stirring, then placed into glass ampoules which were sealed. This was followed by further thermostatting of the ampoules for 3 months in an air thermostat at 100°C, that temperature being maintained with an accuracy of ± 1°C. At the end of this period, the ampoules were opened, the liquid phase was separated from the solid phase by filtration at 100°C and was subjected to chemical analysis complexometrically for Tl^{3+} [5] and iodometrically for SeO_3^{2-} [6].

RESULTS AND DISCUSSION

The results obtained are given in Table 1 and graphically presented by the method of Gibbs–Roozeboom in Fig. 1. As is seen from the data adduced, the solubility isotherm consists of two crystallization branches corresponding

TABLE 1

Solubility isotherm of the system Tl_2O_3–SeO_2–H_2O

No.	Liquid phase		Solid phase		Formula composition of solid phase
	Tl_2O_3	SeO_2	Tl_2O_3	SeO_2	
1	2.76×10^{-3}	0.21	44.81	32.13	$Tl_2(SeO_3)_3$
2	4.13×10^{-3}	1.24	56.50	40.70	$Tl_2(SeO_3)_3$
3	6.10×10^{-3}	3.37	55.63	40.94	$Tl_2(SeO_3)_3$
4	7.29×10^{-3}	4.21	53.42	39.50	$Tl_2(SeO_3)_3$
5	8.44×10^{-3}	8.11	56.55	41.78	$Tl_2(SeO_3)_3$
6	4.04×10^{-2}	10.38	56.68	41.93	$Tl_2(SeO_3)_3$
7	4.23×10^{-2}	12.29	57.02	41.74	$Tl_2(SeO_3)_3$
8	2.28×10^{-2}	14.17	50.92	42.78	$Tl_2(SeO_3)_3\cdot Tl_2(SeO_3)\cdot H_2SeO_3$
9	1.03×10^{-3}	16.50	43.36	44.07	$Tl_2(SeO_3)_3\cdot H_2SeO_3$
10	3.29×10^{-3}	16.72	27.11	34.55	$Tl_2(SeO_3)_3\cdot H_2SeO_3$
11	4.79×10^{-3}	20.07	29.76	38.20	$Tl_2(SeO_3)_3\cdot H_2SeO_3$
12	5.81×10^{-3}	31.62	40.47	44.49	$Tl_2(SeO_3)_3\cdot H_2SeO_3$
13	6.77×10^{-3}	39.99	31.63	44.85	$Tl_2(SeO_3)_3\cdot H_2SeO_3$
14	7.13×10^{-3}	41.46	47.70	48.39	$Tl_2(SeO_3)_3\cdot H_2SeO_3$
15	8.73×10^{-3}	48.16	31.87	48.25	$Tl_2(SeO_3)_3\cdot H_2SeO_3$
16	9.98×10^{-3}	53.05	26.22	50.48	$Tl_2(SeO_3)_3\cdot H_2SeO_3$
17	1.07×10^{-2}	58.18	48.68	48.05	$Tl_2(SeO_3)_3\cdot H_2SeO_3$
18	1.13×10^{-2}	62.96	47.84	48.62	$Tl_2(SeO_3)_3\cdot H_2SeO_3$
19	1.28×10^{-2}	67.60	40.49	51.75	$Tl_2(SeO_3)_3\cdot H_2SeO_3$
20	2.46×10^{-2}	76.56	38.28	54.12	$Tl_2(SeO_3)_3\cdot H_2SeO_3$
21	3.12×10^{-2}	78.84	35.62	56.84	$Tl_2(SeO_3)_3\cdot H_2SeO_3$

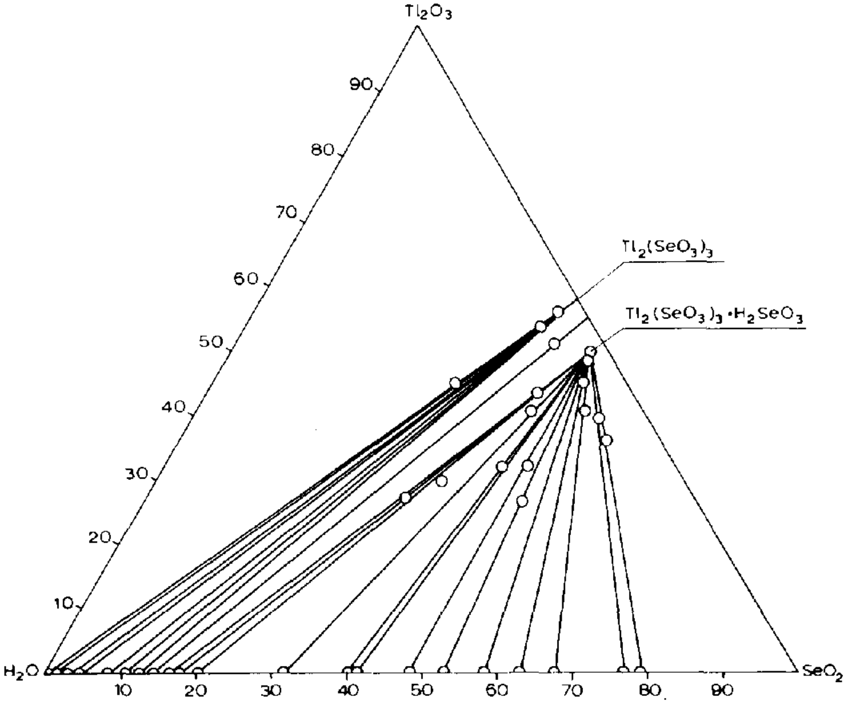

Fig. 1. Solubility isotherm of the system Tl_2O_3–SeO_2–H_2O at 100°C.

to the crystallization of two phases. For the first branch (from point 1 to point 7), the rays connecting the equilibrium saturated solutions and the solid "residue" meet at one point indicating the presence of a solid phase of anhydrous thallium selenite $Tl_2(SeO_3)_3$ (Tl_2O_3, 57.80 wt%; SeO_2, 42.20 wt%). The second branch (comprising points 9–31) is the biggest. Schreinemakers rays connecting the equilibrium liquid and solid phase meet at a point within the triangle. This indicates the formation of a chemical compound whose composition is $Tl_2(SeO_3)_3 \cdot H_2SeO_3$. It incongruently dissolves in water and contains 49.80 wt% Tl_2O_3, 48.22 wt% SeO_2 and 1.93 wt% H_2O. Point 8 is eutonic and its corresponding solid phase consists of a mixture of $Tl_2(SeO_3)$ and $Tl_2(SeO_3)_3 \cdot H_2SeO_3$. $Tl_2(SeO_3)_3$ is a crystalline lemon-coloured phase, and $Tl_2(SeO_3)_3 \cdot H_2SeO_3$ is a colourless crystal. Both compounds are very slightly soluble in their mother solution. Their solubility negligibly increases with increasing concentration of SeO_2 in the liquid phase.

The thermal stability of thallium selenites was studied using the apparatus for thermal analysis described in ref. 7.

In order to clarify the chemistry of the processes corresponding to the thermal peaks in the thermograms, additional thermogravimetric studies were carried out. The initial selenite was heated under conditions analogical

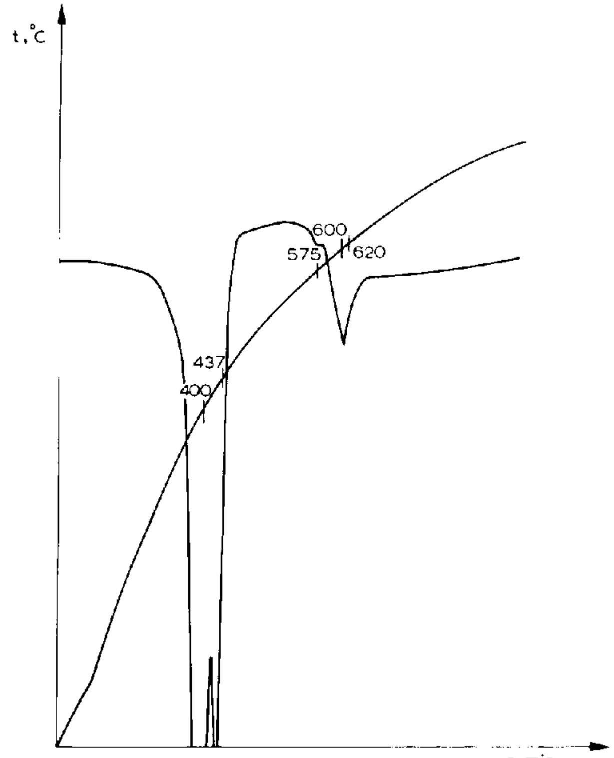

Fig. 2. Thermogram of $Tl_2(SeO_3)_3$.

to those of thermograph analysis, and the products needed for the ensuing thermal and X-ray phase analysis were obtained by the method of isothermal heating.

Figure 2 shows the thermogram of $Tl_2(SeO_3)_3$ which may be interpreted as follows: the first two thermal peaks (at 400 and 437°C) correspond to the stage liberation of SeO_2 and the formation of two intermediate products whose composition, according to the chemical analysis data, is $Tl_2O_3 \cdot 2\ Tl_2(SeO_3)_3$($Tl_2O_3$, 67.33 wt%; SeO_2, 32.66 wt%) and Tl_2O_3. $Tl_2(SeO_3)_3$ (Tl_2O_3, 73.19 wt%; SeO_2, 26.80 wt%). The identity of the compounds obtained was confirmed by X-ray analysis. The first compound is light-yellow, the second one has a bright lemon colour. The nature of the thermal transitions in the interval 575–600°C is rather complex. At that temperature the substance starts melting and quickly dissociates, forming a solid phase, i.e., incongruent melting of $Tl_2O_3 \cdot Tl_2(SeO_3)_3$ occurs and a colourless product is formed. The chemical analysis of the latter shows that it is a selenite of the univalent thallium, Tl_2SeO_4 (Tl_2O, 77.05 wt%; SeO_2, 23.00 wt%), i.e., intermolal reduction of trivalent thallium into univalent thallium and oxidation of tetravalent selenium to sixvalent selenium occurs according to the following equation

$$Tl_2O_3 \cdot Tl_2(SeO_3)_3 \rightarrow 2\ Tl_2SeO_4 + SeO_2 + O_2$$

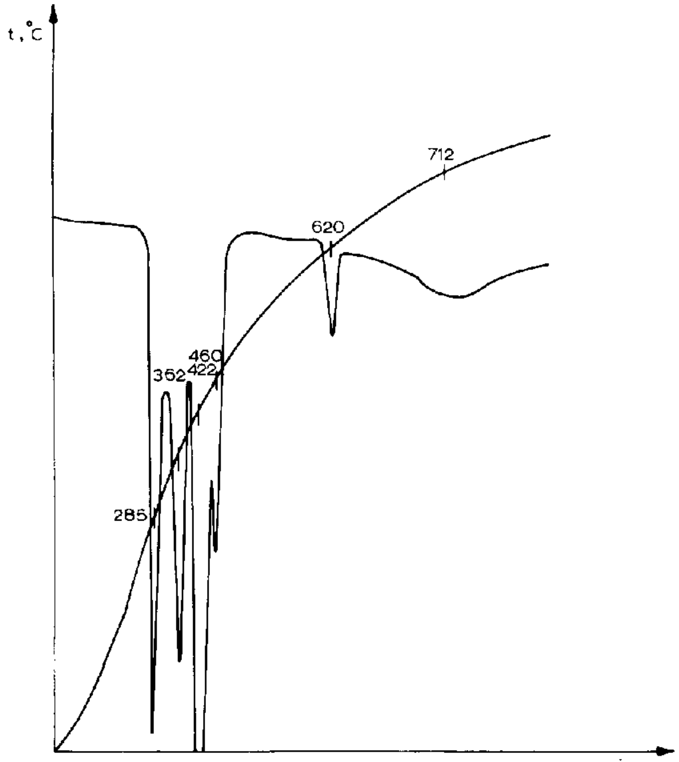

Fig. 3. Thermogram of $Tl_2(SeO_3)_3 \cdot H_2SeO_3$.

TABLE 2

X-ray patterns of thallium selenites

$Tl_2(SeO_3)_3$		$Tl_2(SeO_3)_3 \cdot H_2SeO_3$	
I/I_1	d(Å)	I/I_1	d(Å)
80	6.964	100	7.970
36	5.964	10	4.716
13	5.604	61	4.055
9	4.431	22	3.593
21	4.246	37	3.336
24	3.739	12	3.125
8	3.596	100	3.041
100	3.477	25	2.976
27	3.273	5	2.846
23	3.211	58	2.696
20	3.140	16	2.627
13	2.976	9	2.559
13	2.938	8	2.360
12	2.864	8	2.336
27	2.812	20	2.288
20	2.778	15	2.169
13	2.687	10	2.159
8	2.576	9	2.119
8	2.527	10	2.034
4	2.460	5	1.969
4	2.390	3	1.941
8	2.298	5	1.893
55	2.252	11	1.826
8	2.092	13	1.752
11	1.989	9	1.584
9	1.973	5	1.543
6	1.861	4	1.518
15	1.838	9	1.502
21	1.609	10	1.454
9	1.254	3	1.424

The product obtained dissolves readily in water. The solution is almost neutral, and no Tl^{3+} or SeO_3^{2-} can be detected. At 620°C Tl_2SeO_4 melts, and the further elevation of temperature results in weight loss which is conditioned by the gradual transition of Tl_2SeO_4 into Tl_2SeO_3. The latter sublimates without dissociation at the temperature mentioned above or at higher temperatures. Therefore, the thermal dissociation of $Tl_2(SeO_3)_3$ can be presented as follows

$$Tl_2(SeO_3)_3 \xrightarrow{400°C} Tl_2O_3 \cdot 2\,Tl_2(SeO_3)_3 \xrightarrow{437°C} Tl_2O_3 \cdot Tl_2(SeO_3)_3$$

$$\xrightarrow{575\text{–}600°C} Tl_2SeO_4 \xrightarrow{620°C} \text{melting} \xrightarrow{>620°C} Tl_2SeO_3 \text{ (sublimation)}$$

The thermogram of $Tl_2(SeO_3)_3 \cdot H_2SeO_3$ in Fig. 3 can be interpreted as follows: one mole of H_2O is liberated at 285°C and pyroselenite is obtained which liberates one mole of SeO_2 at 362°C and turns into $Tl_2(SeO_3)_3$. At higher temperatures, the scheme of the thermal dissociation of $Tl_2(SeO_3)_3$ is repeated

$$Tl_2(SeO_3)_3 \cdot H_2SeO_3 \xrightarrow{285^\circ C} Tl_2(SeO_3)_3 \cdot SeO_2 \xrightarrow{362^\circ C} Tl_2(SeO_3)_3$$

$$\xrightarrow{422^\circ C} Tl_2O_3 \cdot 2\,Tl_2SeO_3 \xrightarrow{460^\circ C} Tl_2O_3 \cdot Tl_2SeO_3 \xrightarrow{575\text{–}600^\circ C} Tl_2SeO_4 \xrightarrow{620^\circ C} \text{melting}$$

$$\xrightarrow{>620^\circ C} Tl_2SeO_3 \text{ (sublimation)}$$

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