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Regularities in the formation of orthotellurates in the three-component system $AgNO_3$–$K_2H_4TeO_6$–H_2O and properties of the compounds obtained

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Abstract

The system $AgNO_3$–$K_2H_4TeO_6$–H_2O has been studied and its solubility isotherm is drawn at 100°C. The composition of the phases in the system is determined by using the solubility isotherm and chemical, crystallo-optical and X-ray phase analyses after the phases are washed and dried.

Derivatograph analysis is carried out and a scheme of thermal decomposition is suggested.

INTRODUCTION

The data concerning orthotellurates of silver are very scarce and contradictory. In refs. 1–4, by mixing a 0.1 M solution of $K_2H_4TeO_6$ with a 0.6 M solution of $AgNO_3$, a precipitate was obtained and chemical analysis indicated $3Ag_2O \cdot 2TeO_2 \cdot 2H_2O$. This composition was assigned $Ag_3H_3TeO_6$. By treating that orthotellurate with hot water [1] or by treating $K_2H_4TeO_6$ with an excess of $AgNO_3$ for 12 h, upon heating [2] Ag_6TeO_6 was obtained. In ref. 4, $Ag_2H_4TeO_6$ was synthesized from stoichiometric amounts of H_6TeO_6 and $AgNO_3$ by adding a pH 4 buffer. However, no systematic studies of the conditions of synthesis have been made, nor have the properties of orthotellurates obtained been studied.

EXPERIMENTAL

The initial reagents were pure-for-analysis $AgNO_3$, and $K_2H_4TeO_6$ obtained by the present author from high-purity KOH and H_6TeO_6.

The initial solutions as well as the equilibrium solutions and the solid phases were analysed. Eleven samples were prepared by adding 50 ml of $K_2H_4TeO_6$ solution to 50 ml of $AgNO_3$ solution with concentration

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0.025 mol l^{-1}. The concentration of $K_2H_4TeO_6$ was such that the mol ratio TeO_6^{6-} : Ag^+ was 0–5. The samples were thermostated at 25°C for 24 h and then sealed in glass ampoules. The latter were thermostated in an air thermostat at 100 ± 0.5°C until equilibrium was obtained. This was established experimentally; then the liquid and the solid phases were separated at 100°C. The isotherm of the system was drawn from the residual concentration of Ag^+ and TeO_6^{6-}.

The chemical preparative analysis of the solid phases after separation and the chemical analysis of the washed and dried solid phases gave additional information concerning the processes taking place in the system under the experimental conditions.

The chemical analysis for Ag^+ was carried out by the Folhardt method [5], and for tellurite ions, iodometrically and gravimetrically by a technique described in ref. 6.

X-Ray and X-ray phase analyses were carried out on a DRON-2 apparatus at a copper anode, using Kα emission and a nickel filter for β emission.

An OD-12 derivatograph (MOM, Hungary) was used to study thermal decomposition.

RESULTS AND DISCUSSION

One normal and two acid salts were obtained in the system $AgNO_3$–$K_2H_4TeO_6$–H_2O (Fig. 1). When the ratio between the components $H_4TeO_6^{2-}$: Ag^+ was $n = 0$–0.17, normal silver orthotellurate Ag_6TeO_6 was synthesized. The acid salt, $Ag_3H_3TeO_6$, was obtained at $n = 0.33$, and at $n = 0.5$–5 the acid orthotellurate was $Ag_3H_4TeO_6$. Ag_6TeO_6 is an easily filterable, chocolate-brown compound, and $Ag_3H_3TeO_6$ is a brown crystalline product. Figure 2 shows the favourable pH interval for the

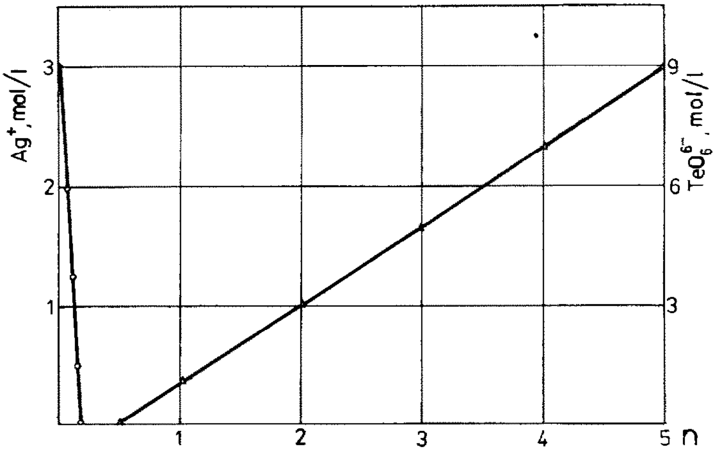

Fig. 1. Solubility of the $AgNO_3$–$K_2H_4TeO_6$–H_2O system at 100°C.

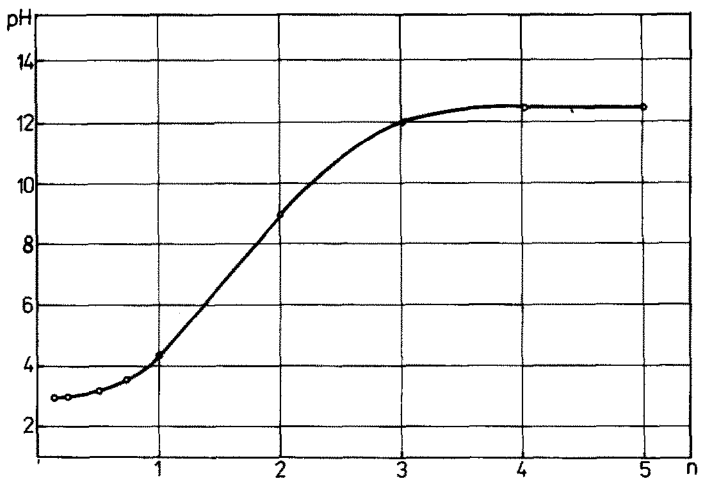

Fig. 2. pH dependence of the molar ratio $K_2H_4TeO_6:AgNO_3$.

TABLE 1

Chemical analysis of silver orthotellurates

Compound	Theoretical content (%)			Chemical analysis/data (%)		
	Ag_2O	TeO_3	H_2O	Ag_2O	TeO_4	H_2O
Ag_6TeO_6	79.84	20.16		79.89	20.13	
$Ag_3H_3TeO_6$	63.18	31.91	4.91	63.14	31.95	4.93
$Ag_2H_4TeO_6$	52.27	39.61	8.12	52.35	39.70	8.02

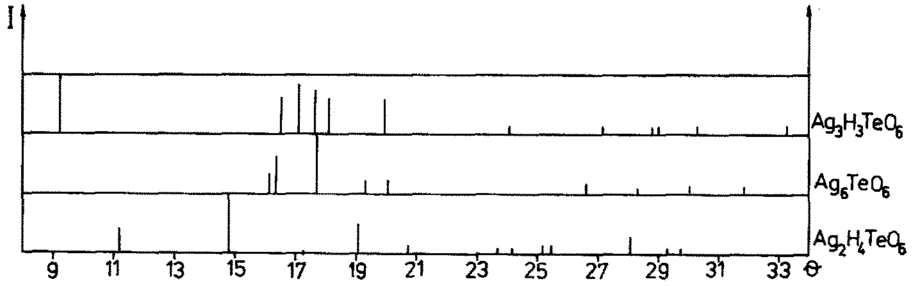

Fig. 3. X-Ray pattern of the solid phases of the system $AgNO_3$–$K_2H_4TeO_6$–H_2O at 100°C ($n = TeO_6^{6-}$ g ion l^{-1}):(Ag^+ g ion l^{-1}).

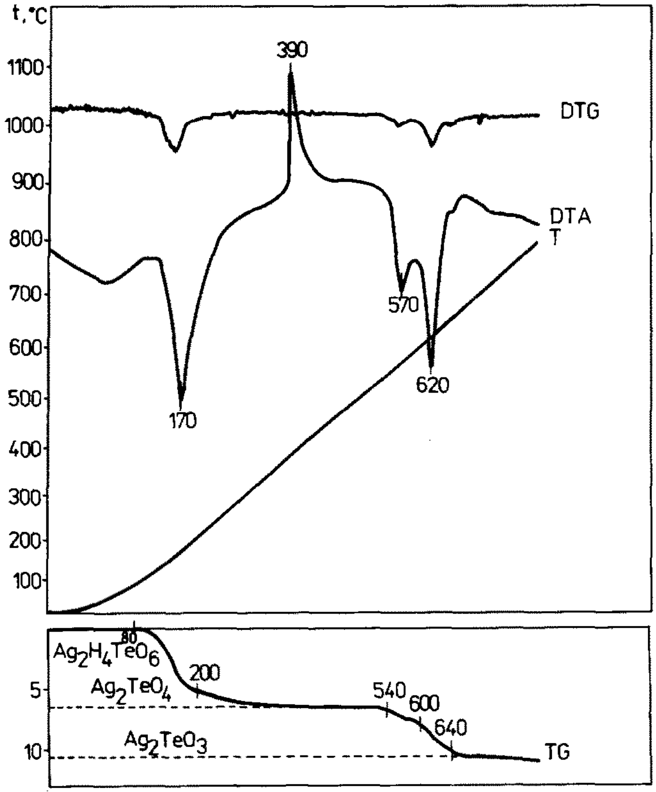

Fig. 4. Derivatogram of $Ag_2H_4TeO_6$.

synthesis of one or the other silver orthotellurate. Chemical analysis (Table 1) and hatched X-ray patterns (Fig. 3) prove that three compounds of the composition given above were synthesized in the system. The derivatogram of $Ag_2H_4TeO_6$ (Fig. 4) has an endothermal peak at 150–170°C corresponding to the removal of constituent water from silver hydrogen tellurate. The removal of traces of water was observed up to 390°C. The total mass loss due to removal of constituent water for 400 mg of the substance is 32.48 mg, which corresponds to the transition of acid orthotellurate into metatellurate. Chemical analysis gave the concentration of Ag_2O as 56.84% and that of TeO_3 as 43.23%, which exactly corresponds to the stoichiometry of Ag_2TeO_4. The metatellurate obtained at a temperature lower than 390°C is amorphous. This is shown by the X-ray pattern of the compound where no peaks are visible, as well as by its thermogram on which an exothermal peak can be seen at 390°C corresponding to the transition of the amorphous product into a crystalline compound. This conclusion is also supported by the fact that the product tempered at 390–450°C does not change its stoichiometric composition but the clear X-ray pattern obtained by X-ray phase analysis

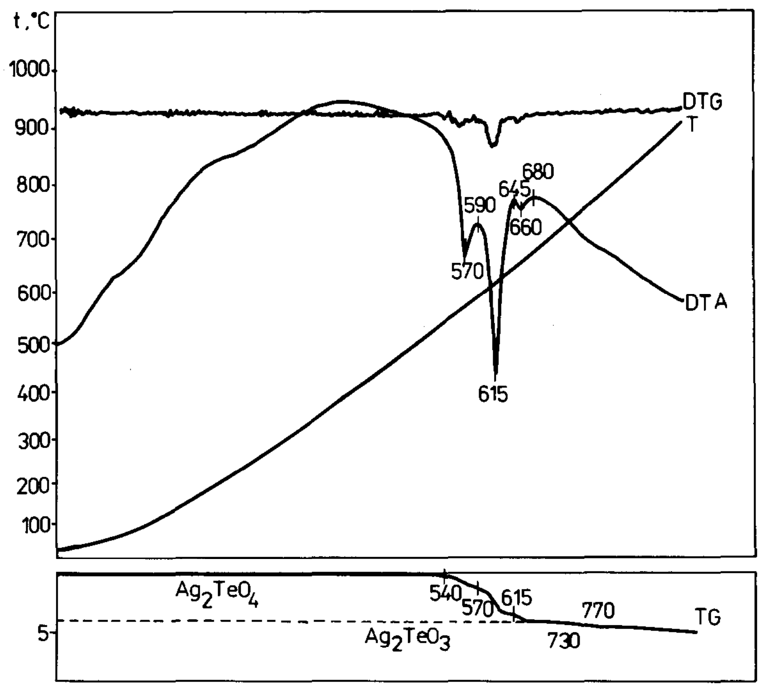

Fig. 5. Derivatogram of Ag_2TeO_4.

shows that it becomes a crystalline compound. In addition, when the product was tempered for 1 h at a temperature higher than 390°C but lower than that of the peak corresponding to the decomposition of metatellurate, there was no exothermal peak on the derivatogram.

Silver metatellurate is a black crystalline compound. It is insoluble in water and readily soluble in mineral acids.

Derivatograph analysis data (Fig. 5) show that silver metatellurate is thermostable at 540°C. The endothermal effect on the curve of heating with a minimum at 570°C indicates that half the silver metatellurate decomposes into Ag_2TeO_3. In addition, the solid phase obtained at 590°C is a separate compound of composition $Ag_2TeO_3 \cdot Ag_2TeO_4$ (Fig. 6). At

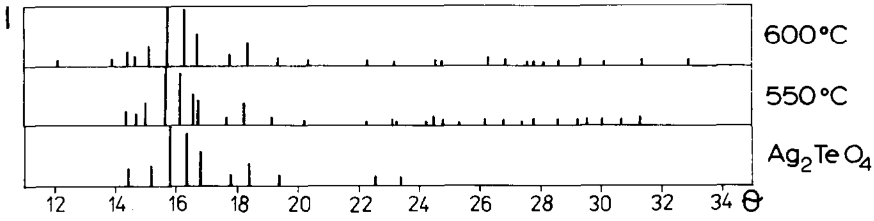

Fig. 6. Hatched X-ray patterns of the products of thermal decomposition of Ag_2TeO_4 at different temperatures.

650°C that phase melts incongruently. Complete decomposition takes place at 645–680°C. The silver tellurate obtained Ag_2TeO_3 is also thermally stable in the melted state. These results confirm the earlier results of the present author [7] that Ag_2TeO_3 is thermally stable at 920°C and disprove those reported by Hutchins [8] that silver tellurate does not exist above 200°C.

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