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Note

Physico-chemical study of the equilibrium phases in the system $Pb(CH_3COO)_2$–$K_2H_4TeO_6$–H_2O at 100°C

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INTRODUCTION

Data concerning lead tellurites are rather scarce. Two compositions have been described: $Pb_2H_2TeO_6$, obtained by the interaction between H_6TeO_6 and $Pb(CH_3COO)_2$ [1], and $3PbO \cdot 2TeO_3 \cdot 2H_2O$, which was synthesized by the interaction between $Pb(NO_3)_2$ and $K_2H_4TeO_6$, the latter being dissolved in such a quantity of KOH that the product obtained was K_6TeO_6 [2-4].

In ref. 5, a lead tellurate of a different composition was synthesized: PbH_4TeO_6 was produced by mixing the reagents and using the technique in ref. 1. There are data concerning the synthesis of lead metatellurate $PbTeO_4$ by sintering PbO_2 with TeO_2 [6, 7]. Another lead tellurate was obtained by the interaction between PbTe and oxygen at $p = 50$ Torr and 400°C [8]. However, the problem of the composition of lead tellurites remains essentially open, and there are no data available concerning their properties. That problem can only be solved by studying the equilibrium solubility diagram of the system Pb salt–$K_2H_4TeO_6$–H_2O, and this is the aim of the present work.

EXPERIMENTAL, RESULTS AND DISCUSSION

The purity of the initial reagents $Pb(CH_3COO)_2$ and $K_2H_4TeO_6$ used to study the system was 99.995%. The system was prepared, the time for reaching equilibrium was determined, and analytical-preparative, chemical, X-ray phase, crystallo-optical and derivatographic analyses were performed by the technique described in ref. 9.

Figure 1 shows that the interaction in the system $Pb(CH_3COO)_2$–$K_2H_4TeO_6$–H_2O results in the synthesis of three compounds. The product

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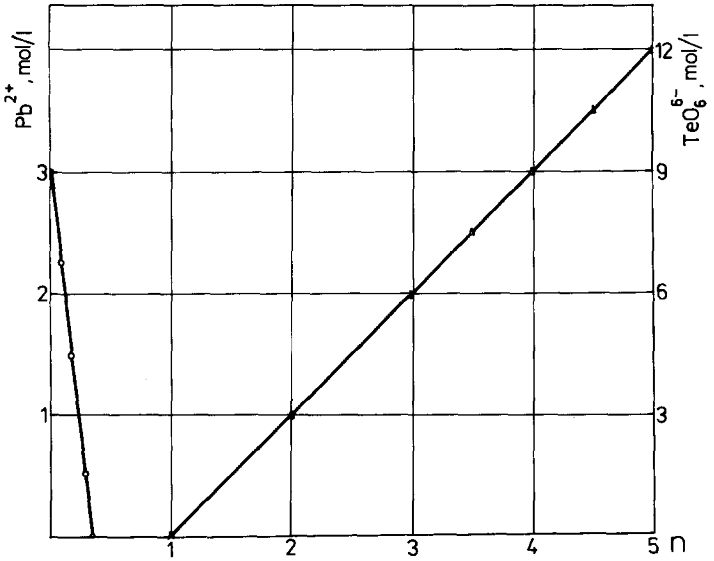

Fig. 1. Solubility diagram for the system $Pb(CH_3COO)_2$–$K_2H_4TeO_6$–H_2O at 100°C.

obtained at concentration $n = 0$–0.33 (where n is the mole ratio of the first two components) is Pb_3TeO_6. A confirmation of this is the fact that at $n = 0.33$ neither Pb^{2+} nor TeO_6^{6-} is present in the filtrate. In addition, the composition of the solid phases at $n = 0$–0.33 was determined by an analytical–preparative method. The identity of the solid phases in this concentration range is revealed by their hatched X-ray patterns (Fig. 2). At $n = 0.5$ there are no Pb^{2+} and TeO_6^{6-} ions in the filtrate which means that a new compound $Pb_2H_2TeO_6$ has been formed. The absence of tellurate and lead ions at $n = 1$ shows that a third phase PbH_4TeO_6 has been synthesized. Chemical analysis of all the solid phases at $n = 1$–5 reveals the same composition. The fact that the X-ray patterns of all solid phases in that concentration interval have no peaks means that the compounds obtained are amorphous. The pH curve in Fig. 3 shows that

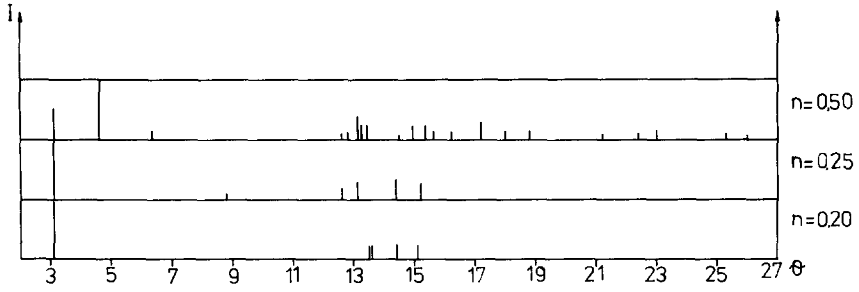

Fig. 2. X-ray pattern of the solid phases of the system $Pb(CH_3COO)_2$–$K_2H_4TeO_6$–H_2O at 100°C.

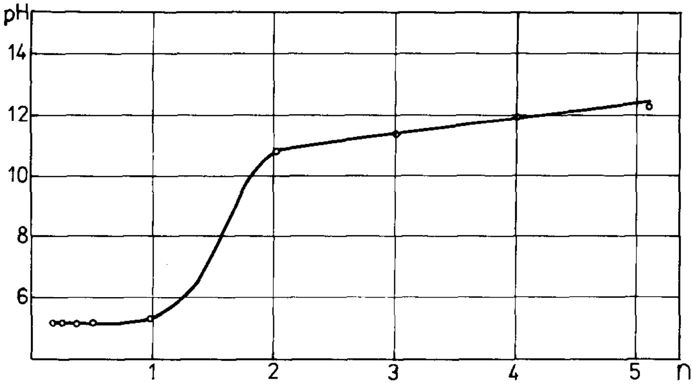

Fig. 3. pH dependence of the molar ratio $K_2H_4TeO_6:Pb(CH_3COO)_2$.

Pb_3TeO_6 is formed at low pH values, $Pb_2H_2TeO_6$ at average pH values, and PbH_4TeO_6 is produced at high pH values. Table 1 shows the results of direct determination of the composition of the solid phases obtained by the interaction between $Pb(CH_3COO)_2$ and $K_2H_4TeO_6$ at different mole ratios. For that purpose the solid phases were filtered off, washed, dried at room temperature and analysed.

The parameters of the elementary cell of Pb_3TeO_6 were calculated. The compound crystallizes in a monoclinic system with parameters of the elementary cell $a = 7.743$ Å, $b = 12.024$ Å, $c = 13.151$ Å, and $\theta = 125.83°$.

The thermal stability and the mechanism of thermal decomposition of PbH_4TeO_6 and $PbTeO_6$ were studied. Derivatographic analysis data (Fig. 4) show that the decomposition of lead hydrogen orthotellurate PbH_4TeO_6 begins at 100°C but its rate increases at 160°C. Complete liberation of water takes place at 500°C. Chemical analysis of the product after heating at 500°C gave the concentration of PbO as 55.89% and that of TeO_3 as 44.13%. These results are in good agreement with the stoichiometry of $PbTeO_4$. X-ray phase analysis shows that the compound $PbTeO_4$ is amorphous. The exothermic peak at 522°C, which is not connected with a mass loss of the sample, corresponds to the crystal-

TABLE 1

Results of chemical analysis

Compound	Calculated (%)			Found (%)		
	PbO	TeO_3	H_2O	PbO	TeO_3	H_2O
Pb_3TeO_6	79.22	20.78	–	79.30	20.71	–
$Pb_2H_2TeO_6$	69.75	27.44	2.81	69.69	27.46	2.79
PbH_4TeO_6	51.34	40.39	8.27	51.38	40.35	8.17

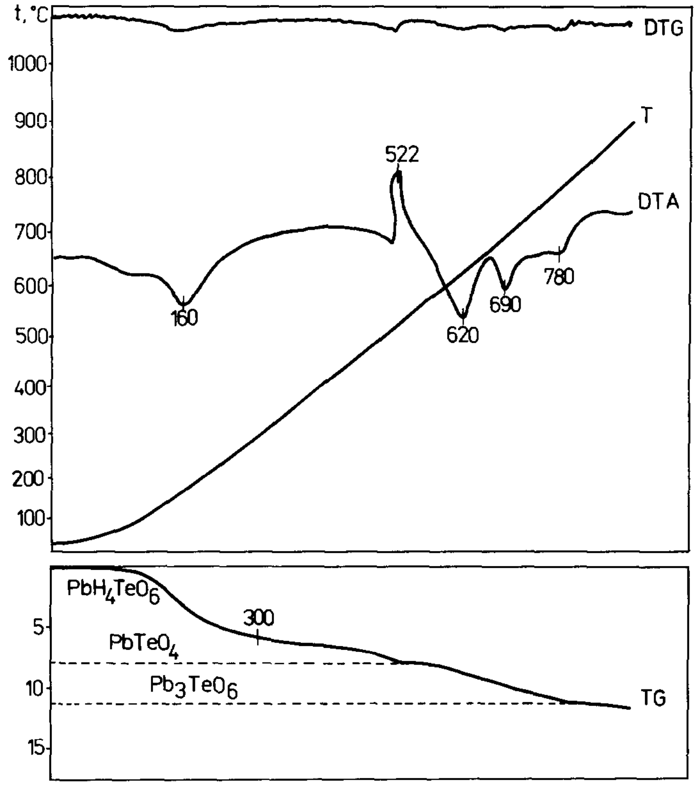

Fig. 4. Derivatogram of PbH_4TeO_6.

lization temperature of the amorphous metatellurate. In favour of this assertion is the fact that, one hour before reaching that temperature, the metatellurate tempered in a sealed evacuated ampoule gives a distinct X-ray pattern and there is no exothermic peak in its derivatogram (Fig. 5). The conclusion drawn in ref. 5, that metatellurate undergoes irreversible polymorphous change at 605°C, is unlikely. Both derivatograms show that thermal decomposition of metatellurate takes place at 590°C.

Lead metatellurate is a yellow crystalline substance. It crystallizes in a monoclinic system. Its space group is C2/m. The parameters of the elementary cell are $a = 5.413$ Å, $b = 4.947$ Å, $c = 6.018$ Å, $\theta = 99.596°$. The number of formula units is $Z = 2$. The experimental density determined in high purity toluene is 8.34 g cm^{-3}, and $d_{\text{X-ray}} = 8.29$ g cm^{-3}.

Lead metatellurate is thermally stable at 590°C (Fig. 5). The endothermic peak with a minimum at 635°C indicates that the decomposition of lead metatellurate takes place at 590–665°C and is accompanied by an insignificant weight loss. Chemical analysis data show that this decomposition results in an incomplete conversion of Te(VI) into Te(IV). Chemical analysis of the decomposition products in a flow system of an inert gas

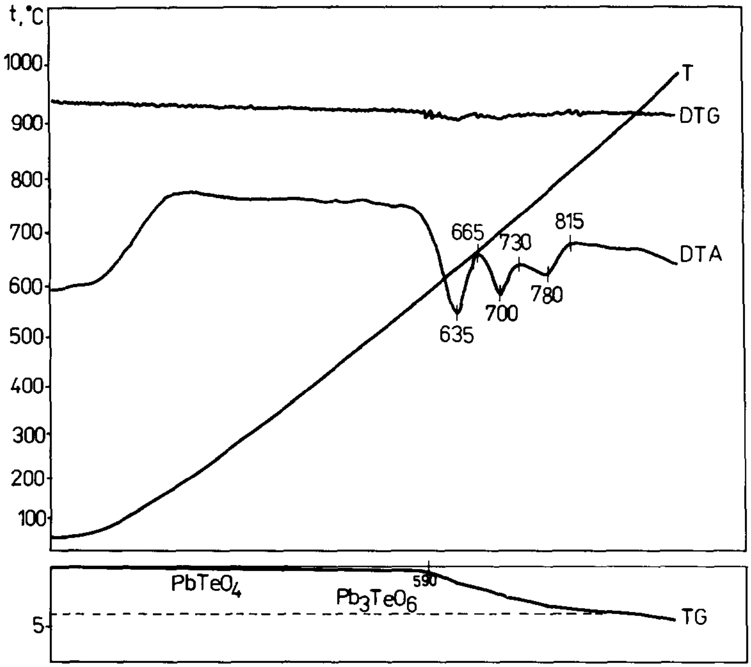

Fig. 5. Derivatogram of $PbTeO_4$.

(argon) indicated that decomposition is accompanied by liberation of oxygen. Having in mind the quantitative X-ray phase analysis data and chemical analysis data, the scheme of decomposition can be suggested as

$$3PbTeO_4 \rightarrow Pb_3TeO_6 + 2TeO_2 + O_2$$

It is also established that half of the metatellurate is changed into orthotellurate. X-ray phase analysis indicated that an intermediate phase $PbTeO_4 \cdot Pb_3TeO_6$ was formed between $PbTeO_4$ and Pb_3TeO_6. The endothermic peak on the derivatogram with a minimum at 700°C is assigned to the decomposition of that intermediate phase accompanied by liberation of oxygen. The third endothermic peak with a minimum at

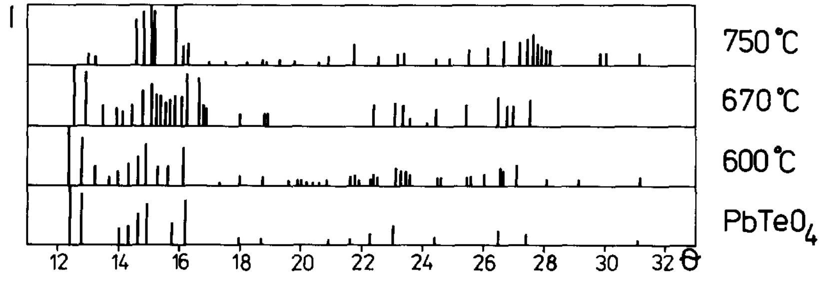

Fig. 6. Hatched X-ray patterns of the products of thermal decomposition of $PbTeO_4$ at various temperatures.

780°C corresponds to complete thermolysis and the formation of lead orthotellurate. Lead orthotellurate is very stable. The TG curve shows that, up to 1000°C, it undergoes only insignificant decomposition.

Figure 6 gives the hatched X-ray patterns of $PbTeO_4$ heated at various temperatures. These patterns also confirm the mechanism of decomposition of $PbTeO_4$ suggested above.

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