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THERMAL AND THERMODYNAMIC PROPERTIES OF THE SELENITES OF THE ELEMENTS FROM GROUP IV IN THE PERIODIC TABLE

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ABSTRACT

The conditions necessary for the formation of basic lead selenites which result from the thermal dissociation of $PbSeO_3$ were investigated, as well as their thermodynamic properties.

INTRODUCTION

The data concerning the thermal and thermodynamic properties of the selenites of germanium, tin and lead are limited [1–9]. The mechanism of the thermal dissociation of the selenites of germanium and tin are well known; that of lead selenite is still unsolved. Indeed, previous works are contradictory; according to ref. 6, lead selenite dissolves to PbO, while according to refs. 8 and 9, the dissociation is quite complex and ends with the formation of two basic selenites $2PbO \cdot PbSeO_3$ and $4PbO \cdot PbSeO_3$ with an increasing thermal stability. The final residue is PbO.

With these facts in mind, it is rather interesting to investigate the conditions necessary for the formation of basic lead selenites i.e. $2PbO \cdot PbSeO_3$ and $4PbO \cdot PbSeO_3$ which result from the thermal dissociation of $PbSeO_3$. The present study is an investigation of the thermodynamic properties of the selenites of the elements from group IV of the periodic table. The melting temperatures of the compounds have not been thoroughly investigated [7] and there are no data concerning the specific heats.

EXPERIMENTAL

The selenites of germanium, tin and lead were obtained by their continued crystallization at 100 °C in aqueous solution of selenious acid, following the technique thoroughly described in refs. 1–3.

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TABLE 1

Chemical composition of the selenites of the elements from group IV of the periodic table

Compound	Theoretical Composition		Data from Chemical Composition	
	MeO_2 (MeO)	SeO_2	MeO_2 (MeO)	SeO_2
$Ge(SO_3)_2$	32.03	67.97	32.27, 32.10, 32.05	68.01, 67.95, 67.99
$Sn(SeO_3)_2$	40.44	59.56	40.57, 40.40, 40.45	59.58, 59.59, 59.60
$PbSeO_3$	66.79	33.21	66.77, 66.83, 66.80	33.25, 33.20, 33.28
$2PbO \cdot PbSeO_3$	85.78	14.22	85.85, 85.80, 85.77	14.23, 14.24, 14.21
$4PbO \cdot PbSeO_3$	90.96	9.04	91.01, 90.96, 90.98	9.10, 9.08, 9.14

Bearing in mind the fact that molten lead selenite dissolves quickly, the basic salts were obtained by heating well-ground homogeneous mixtures of lead oxide and lead selenite in vacuum-packed quartz ampoules. For the synthesis of the compounds by heating the mixtures, the composition corresponding to $2PbO \cdot PbSeO_3$ was heated to 560–570 ° C and for $4PbO \cdot PbSeO_3$, the mixture was heated to 630–640 ° C, both for 100 h.

Chemical, X-ray and thermographic analyses of the compounds obtained were carried out. The data from the chemical analysis are shown in Table 1 and indicate that compositionally the products correspond to the stoichiometry of the compounds $Ge(SeO_3)_2$, $Sn(SeO_3)_2$, $PbSeO_3$, $2PbO \cdot PbSeO_3$ and $4PbO \cdot PbSeO_3$. The X-ray and thermographic data, with those given in refs. 1–6 corroborate the data from the chemical analysis of the compounds obtained. We used a derivatograph made by the Hungarian firm MOM, type OD IO2, for investigating the thermal properties. The kinetics of the thermal dissociation were investigated using the methods described in ref. 1 [10].

We also used a differential scanning calorimeter type DSK-III (Seteram, France) to investigate the thermal and thermodynamic properties. The samples were put in hermetically sealed inert capsules. The temperature was increased at 10 ° C min^{-1} starting from room temperature and increasing to 820 ° C.

RESULTS AND DISCUSSION

Our research confirms the data in refs. 1–5 for one-phase dissociation of the selenites of germanium and tin, the residue being selenic dioxide. The oxides of germanium and tin are also obtained (Table 2). The thermal dissociation of lead selenite is much more complex. An endothermal effect, corresponding to the melting of the salt at 675 ° C, is marked on the derivatogram. From the thermogravimetric curve it can be seen that lead selenite begins to dissolve at 420–450 ° C. The maximum speed of dissociation corresponds to the temperature of melting.

TABLE 2

Temperatures and heats of the phase transition of dehydrated selenites of germanium, tin and lead

Phase transition	Our data		Reference data		References
	T of transition (°C)	Heat of transition ($-\Delta H$ (kcal mol^{-1}))	*T* of transition (°C)	Heat of transition ($-\Delta H$ (kcal mol^{-1}))	
$Ge(SeO_3)_2 \rightarrow GeO_2$	569	–	390-500	–	4
$Sn(SeO_3)_2 \rightarrow SnO_2$	600	–	480	–	5
$PbSeO_3 \rightarrow PbSeO_3$	680	8.67±0.03	675	9.0±1.8	6, 7
$2PbO \cdot PbSeO_3 \rightarrow 2PbO \cdot PbSeO_3$	760	–	755	–	6
$4PbO \cdot PbSeO_3 \rightarrow 4PbO \cdot PbSeO_3$	812	–	805	–	7

Both the speed and the process of dissociation itself are of interest. The kinetic curves drawn on Fig. 1 give the following information. At 600 °C, the speed of dissociation is obvious. At a melting temperature of 675 °C, lead selenite dissolves forming $2PbO \cdot PbSeO_3$. The process lasts 100 min and then that basic salt begins to dissociate. In the dissociation curve of $PbSeO_3$, a twist appears at 750 °C corresponding to the loss of SeO_2 (26.59%) and to the transition of $PbSeO_3$ into $4PbO \cdot PbSeO_3$. The thermal dissociation of this product to the basic salt is completed within 60 min and after that the process of melting begins, the final residue being PbO.

The results from the chemical analysis of the product heated at the same temperature and for the same time are very close to the theoretical estimate

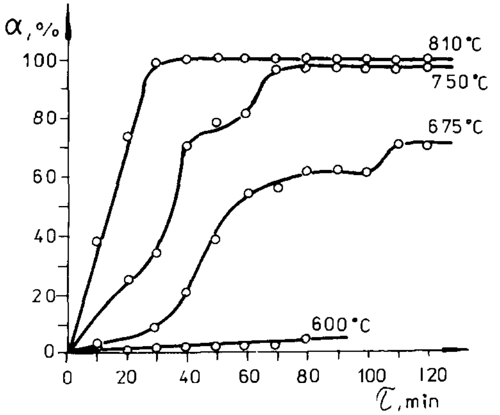

Fig. 1. Kinetic curves of the thermal dissociation of $PbSeO_3$ (dependence of the degree of dissociation (α) on time (τ)).

TABLE 3

Coefficients in the equation $C_p = a + bT + cT^2$, thermal dependence of the heat capacities of dehydrated selenites of germanium, tin and lead

Compounds	Coefficients of the equation $C_p = f(T)$			Temperature range of measurement (K)
	a	b	c	
$Ge(SeO_3)_2$	-5.37	19.38×10^{-2}	-3.95×10^{-5}	400–550
$Sn(SeO_3)_2$	48.79	6.08×10^{-3}	5.92×10^{-7}	400–550
$PbSeO_3$	122.94	-32.47×10^{-2}	6×10^{-4}	400–550
$2PbO \cdot PbSeO_3$	-4.0083	0.214084	-1.6911×10^{-4}	400–550
$4PbO \cdot PbSeO_3$	4.216	0.3456	-3.42189×10^{-4}	400–550

and prove the statement concerning the kinetic curves. The X-ray analysis of these products is identical to the X-ray analysis of $2PbO \cdot PbSeO_3$ and $4PbO \cdot PbSeO_3$ published in the literature. At 810 ° C, no twists are seen in the kinetic curves due to the considerable pressure exerted by the vapours of the basic salts.

Endothermal effects at 150 and 775 ° C, corresponding to the incongruous melting of the compound, are marked on the heating curve of the oxyselenite $2PbO \cdot PbSeO_3$. The oxyselenite $2PbO \cdot PbSeO_3$ begins to melt at 560–570 ° C and the speed of dissociation increases in the process. Heating the already molten $2PbO \cdot PbSeO_3$ at 750 ° C for 2 h leads to changes in its composition. Using X-ray analysis, in the compounds $4PbO \cdot PbSeO_3$ and PbO were discovered in the residue following the tempering. An effect at 810 ° C, corresponding to the melting of that salt, is fixed on the derivatogram of $4PbO \cdot PbSeO_3$. The oxysalt $4PbO \cdot PbSeO_3$ begins to melt at 640–660 ° C. Above 800 ° C, the speed of dissociation rapidly increases. The residue of the dissociation is PbO.

The specific heats of these selenites were defined, using a differential scanning calorimeter DSK-III, following the methods described in ref. 11, at a heating rate of 1 ° C min^{-1} in the temperature interval shown in Table 3. Al_2O_3 was used as the standard. The results from the specific heats obtained were analysed following the method of least-squares and the coefficients in the equation $C_p = a + bT + cT^2$ describe the dependence of C_p of the selenites on the temperature (Table 3).

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